Spectroscopy of Organic Compounds: P. S. Kalsi. Wiley Eastern Limited, New Delhi. Price: 125. pp. 444

Status of the subject

Gone are the days when the structure of a simple organic molecule had to be determined by extensive chemical degradation followed by a rational synthesis. The analytical methods are not only time-consuming but also require large amount of material. Many important natural products and many bioactive compounds such as animal and plant hormones are often available in too small a quantity to be investigated by these methods and their complex structures may defy synthesis. Chemists, therefore, are more and more dependent on the use of physical methods, especially spectroscopic techniques such as electronic (UV and visible), vibrational and rotational (IR and Raman), and nuclear magnetic resonance (NMR) spectroscopy and also high resolution mass spectrometry. X-ray diffraction (now computer-aided) is possibly the single most powerful tool of determination of structure; but it cannot be routinely used and only applies to molecules giving 'good' crystals. The above-mentioned methods are relatively simple and can supply data within a few minutes which not only help in assigning structure of a molecule but also provide valuable information regarding the stereochemistry (most of the compounds possess one or more chiral and stereogenic centres).

UV and visible spectroscopy is the first of these techniques to be used by organic chemists routinely since the early thirties. It shows absorption bands due to electronic transitions and helps to identify or confirm some 'gross' structural units present in a molecule such as an aromatic ring, a diene or a polyene, an unsaturated carbonyl moiety, and a few other functionalities, irrespective of the size of the molecule. Later when the concept of conformation was introduced, it is used to give more sophisticated information such as restricted rotation around a bond (as in biphenyls) and axial-equatorial nature of certain substituents in cyclohexanone system.

Before the introduction of NMR technique, the IR spectroscopy has served as the single most widely used routine tool for structural assignment of organic compounds. The IR spectra arise due to low energy transitions between various vibrational and rotational levels and often show very complex patterns the interpretation of which can give a plethora of structural information such as the exact nature of of the functional group(s), the presence of specific substituent(s), and even the percentage composition of a mixture. An IR spectrum is unique for a compound (like the fingerprint of an individual) and can, therefore, unequivocally establish the identity or nonidentity of two compounds obtained from different sources (synthetic and natural, for example). The spectra are profitably used in monitoring kinetic and thermodynamic processes and also in conformational analysis where more than one molecular species exist each contributing their individual spectrum to be observed. Proper mathematical treatment of IR spectral data can even provide information regarding bond lengths, bond strengths, and thermodynamic properties in many cases. The recent introduction of FT-IR technique has broadened its scope.

The introduction of ^{1}H–NMR spectroscopy in the mid-fifties has brought out a revolution in structure determination of organic compounds. Its success lies in the fact that the NMR spectrum of a moderately complex molecule can be fully interpreted and related to the structure (unlike an IR spectrum). It was soon followed by ^{13}C-NMR (made possible by computer-aided Fourier-transform techniques) and these two combinedly can provide practically all the relevant structural information of an organic molecule such as the nature and type of H and C atoms, their relative abundance (in H-NMR), and their steric relationship with their neighbours. Further ramifications of NMR such as variable temperature NMR (dynamic NMR), double irradiation technique (Nuclear Overhauser Effect), two-dimensional (also multidimensional) spectra which show internuclear correlation through bonds and space, use of shift reagents, computer-simulation of spectra, and so on have made the method extremely versatile. NMR techniques have proved unrivalled in solving many intricate stereochemical problems which include assignment of configuration, determination of enantiomeric purity of a chiral compound, estimation of free energies of activation in conformational changes, and many others.

The mass spectrometry constitutes another most powerful weapon in the arsenal of an analytical chemist. It provides accurate molecular weights and fragmentation patterns, correct interpretation of which helps to determine the structure. The high resolution mass spectrometry, now almost routinely used, can give even the elemental composition of the molecule and its fragments from the highly accurate molecular weights (taking account of the natural abundance of the elements in isotopic forms). A large number of mass spectra of different groups of organic molecules are now stored (in computer memory) and the spectrum of any compound of a group can be readily compared and its structure determined.

The book under review

The above discussion, necessarily brief and inadequate, shows the importance of spectroscopic methods in organic structure determination. A knowledge of these techniques is, therefore, imperative to any aspirant young student of chemistry, preferably starting from the undergraduate level. The purpose of the book is exactly the same: to familarize the beginners with the principles and applications of the four important spectroscopic techniques at a 'modest level of sophistication and expertise'. It starts with an introductory chapter providing the basics of absorption spectroscopy (an idea of emission spectroscopy would have been welcome). The subsequent chapters deal with UV and visible, IR, NMR, and mass spectrometry in that order. The inclusion of four important spectroscopic methods in a single volume, though not unprecedented, is very welcome since it would offer simultaneous use of different spectroscopic data to solve the problems set in the book rather abundantly.

The merit of the book lies in the reproduction of numerous spectra from literature which will provide the students with visual assistance before they actually handle the instruments. Of the four methods of spectroscopy, that of IR has been more thorough and written with a great deal of expertise. Notable lacunae are the omission of FT-IR technique and Raman spectroscopy (and possibly perhaps micro wave). Considering the greater importance, discussion on NMR should have been a little more elaborate, for example, the use of variable temperature NMR (both proton and carbon) determin-

ing energy barrier in conformational changes should have been illustrated with equations and data. The concept of delta parameter is not clarified enough and the readers may be left with confusion. High resolution mass spectrometry has not been mentioned as also its impact on structure elucidation.

The language is, in general, simple although occasionally marred with too many repetitions, apart from some typographical errors (unnecessary capitalizations, incorrect use of articles, and indiscriminate use of 'e.g.'). Some statements are incorrect and may lead to confusion to the beginners. Thus in the beginning of Chapter 4, 'spin state of a nuclear magnetic moment' should better be 'spin state of a nuclear magnet'; in p. 170, 'tiny bar magnets' be replaced by 'tiny *spinning* bar magnets'.

On the whole the book is very informative and largely fulfils the requirements for the undergraduate students for whom it has been clearly meant. The price is affordable and the printing is good.

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Annual Review of Biochemistry 1993. Charles C. Richardson, John N. Abelhson, Alton Meister and Christopher T. Walsh eds. Annual Reviews Inc., El Camino Way, Palo Alto, California, 94306, USA. 1993, vol. 62, 1039 pp. Price: USA $46, elsewhere $52.

The autobiographical article in this volume is by Esmond E. Snell, who did pioneering work on mechanisms of action of pyridoxal phosphate requiring enzymes. This prefatory chapter gives a personal glimpse of motivations for research and this account has added much to our understanding of how the research area on vitamins and coenzymes itself developed in the last 50 years.

There are six interesting articles covering various aspects of protein structure, function, folding and stability. Advances in spectroscopy, protein engineering and peptide synthesis have had a dramatic impact on our understanding of the structures and stabilities of transient folding intermediates. An article of great interest to biochemists is on 'Pathways of protein foldings' by C. Robert Mathews. This review discerns both the general and the specific features that characterize folding mechanisms. Representative examples of those approaches and findings that have led to an improved understanding of the foldings process are highlighted. Molecular chaperones which function in protein folding, oligomerization have emerged over recent years as an important topic in biological studies. The review article on 'Molecular chaperone functions of heat-shock proteins' by J. P. Hendrick and F. Hartl summarizes the major lines of evidence which suggest that these proteins are involved in a multitude of processes. While tyrosine phosphorylation was being avidly pursued as a central theme of many cellular processes in the early eighties, studies into tyrosine dephosphorylation seemed relegated to a 'back seat'. However in the last 5 years protein tyrosine phosphatases began to attract wider attention and to date there are almost 30 different protein tyrosine phosphatases that have been isolated and characterized. K. M. Walton and J. E. Dixon's article on protein tyrosine phosphatases gives an indepth view on these enzymes and their roles in different cellular pathways. In the past couple of years there has been a virtual explosion of new X-ray crystal structures aimed at characterization of precise interactions between inhibitors and their target enzymes. The review 'Structure-based inhibitors of HIV–1 protease' by A. Wlodawer and J. W. Erickson discusses the current state of structural investigations of HIV-protease inhibitor complexes and highlights the general features important for drug design. Since the last review on aminoacyl-tRNA synthetases appeared, new sequences and at least 3 new X-ray crystal structures have been reported. 'Cognition, mechanism, and evolutionary relationships in aminoacyl-tRNA synthetases' by C. W. Carter describes the exhaustive work on these biomolecules which have substantially altered many perceptions about these enzymes. Considerable progress has been made in quantitating the interactions that determine and stabilize protein structures in the last few years. An encouraging development in the last few years has been the freedom with which amino acid replacements can be introduced in a protein of interest. Brian-Mathews' review on 'Structural and genetic analysis of protein stability' highlights studies on new insights into hydrophobic and electrostatic interactions that have been provided by studies of mutant proteins with emphasis on those studies for which high-resolution structural information is available.

Although two excellent reviews describing eucaryotic DNA replication/polymerases and on fidelity of DNA replication were published in this series, the two articles on this topic in this volume focus on the significant advances made in the last two years in our understanding of the mechanistic basis of DNA polymerase fidelity. The article on 'Eucaryotic DNA replication' by M. L. DePamphilis highlights the origins of replication in metazoan genomes. To determine how a polymerase can achieve such extraordinary fidelity, one must understand the mechanistic basis of DNA polymerase fidelity. The article 'Conformational coupling in DNA polymerase fidelity' by K. A. Johnson summarizes our current understanding of the structural, kinetic and thermodynamic basis of two distinct reactions, viz. the polymerization reaction per se, and the proof-reading exonuclease reaction.

It is now becoming clear that cells might regulate DNA replication by linking it to gene expression. This series has 3 articles on regulation of gene expression at the transcription level. Roeder and his colleagues prepared and fractionated transcriptionally active extracts and demonstrated that initiation by RNA polymerase II requires the action of multiple initiation factors. In the last couple of years many laboratories in the world have identified, purified and characterized general initiation factors from yeast, Neurospora, silkworm, Drosophila, chicken, mouse, rat and human cells. The review 'General initiation factors for RNA polymerase II' focusses on our understanding of the mechanism by which RNA polymerase II binds selectively to and initiates transcription. This article also discusses the work on the C-terminal domain (CTD) of RNA polymerase II and its role in transcription initiation.

Fifty years ago Monod extensively studied the 'glucose effect'. Cells when grown in the presence of a pair of sugars show a 2-step diauxic growth. It is now clearly established that cAMP and its receptor protein CRP have a role in the