MTP International Review of Science

Volume 1

Structure Determination in Organic Chemistry

Edited by **W. D. Ollis, F.R.S.**
University of Sheffield

MTP International Review of Science

Structure Determination in Organic Chemistry

THE BUTTERWORTH GROUP

ENGLAND
Butterworth & Co (Publishers) Ltd
London: 88 Kingsway, WC2B 6AB

AUSTRALIA
Butterworths Pty Ltd
Sydney: 586 Pacific Highway 2067
Melbourne: 343 Little Collins Street, 3000
Brisbane: 240 Queen Street, 4000

NEW ZEALAND
Butterworths of New Zealand Ltd
Wellington: 26–28 Waring Taylor Street, 1

SOUTH AFRICA
Butterworth & Co (South Africa) (Pty) Ltd
Durban: 152–154 Gale Street

ISBN 0 408 70275 3

UNIVERSITY PARK PRESS

U.S.A. and CANADA
University Park Press
Chamber of Commerce Building
Baltimore, Maryland, 21202

Library of Congress Cataloging in Publication Data

Ollis, William David
Structure determination in organic chemistry.

(Organic chemistry, series one, v. 1) (MTP international review of science)
1. Chemistry, Organic. 2. Chemistry, Analytic.
I. Title.
QD251.2.074 vol. 1 [QD271] 547'.1'22
ISBN 0–8391–1029–4 72–13072

First Published 1973 and © 1973
MTP MEDICAL AND TECHNICAL PUBLISHING CO. LTD.
St. Leonard's House,
St. Leonard's Gate,
Lancaster, Lancs.
and
BUTTERWORTH & CO. (PUBLISHERS) LTD.

Filmset by Photoprint Plates Ltd., Rayleigh, Essex
Printed in England by Redwood Press Ltd., Trowbridge, Wilts
and bound by R. J. Acford Ltd., Chichester, Sussex

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Publisher's Note

The MTP International Review of Science is an important new venture in scientific publishing, which we present in association with MTP Medical and Technical Publishing Co. Ltd. and University Park Press, Baltimore. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. We are starting with chemistry because the problems of literature survey are probably more acute in this subject than in any other. As a matter of policy, the authorship of the MTP Review of Chemistry is international and distinguished; the subject coverage is extensive, systematic and critical; and most important of all, new issues of the Review will be published every two years.

In the MTP Review of Chemistry (Series One), Inorganic, Physical and Organic Chemistry are comprehensively reviewed in 33 text volumes and 3 index volumes, details of which are shown opposite. In general, the reviews cover the period 1967 to 1971. In 1974, it is planned to issue the MTP Review of Chemistry (Series Two), consisting of a similar set of volumes covering the period 1971 to 1973. Series Three is planned for 1976, and so on.

The MTP Review of Chemistry has been conceived within a carefully organised editorial framework. The over-all plan was drawn up, and the volume editors were appointed, by three consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence, the 300 or so contributions to the MTP Review of Chemistry come from many countries of the world and provide an authoritative account of progress in chemistry.

To facilitate rapid production, individual volumes do not have an index. Instead, each chapter has been prefaced with a detailed list of contents, and an index to the 10 volumes of the MTP Review of Organic Chemistry (Series One) will appear, as a separate volume, after publication of the final volume. Similar arrangements will apply to the MTP Review of subsequent series.

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Structure Determination in Organic Chemistry

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Consultant Editor's Note

The subject of Organic Chemistry is in a rapidly changing state. At the one extreme it is becoming more and more closely involved with biology and living processes and at the other it is deriving a new impetus from the extending implications of modern theoretical developments. At the same time the study of the subject at the practical level is being subjected to the introduction of new techniques and advancements in instrumentation at an unprecedented level. One consequence of these changes is an enormous increase in the rate of accumulation of new knowledge. The need for authoritative documentation at regular intervals on a world-wide basis is therefore self-evident.

The ten volumes in Organic Chemistry in this First Series of biennial reviews in the MTP International Review of Science attempt to place on record the published achievements of the years 1970 and 1971 together with some earlier material found desirable to assist the initiation of the new venture. In order to do this on an international basis, Volume Editors and Authors have been drawn from many parts of the world.

There are many alternative ways in which the subject of Organic Chemistry can be subdivided into areas for more or less self-contained reviews. No single system can avoid some overlapping and many such systems can leave gaps unfilled. In the present series the subject matter in eight volumes is defined mainly on a structural basis on conventional lines. In addition, one volume has been specially devoted to methods of structure determination, which include developments in new techniques and instrumental methods. A further separate volume has been devoted to Free Radical Reactions, which is justified by the rapidly expanding interest in this field. If there prove to be any major omissions it is hoped that these can be remedied in the Second Series.

It is my pleasure to thank the Volume Editors who have made the publication of these volumes possible.

London

D. H. Hey

Preface

The topics for this volume were fairly easily determined by considering the general importance of certain areas of research in modern organic chemistry. These considerations, covering molecules from methane to natural biopolymers, were made in relation to the term structure, which includes constitution, configuration, conformation, and chirality.

Recently there have been important developments in the nomenclature of stereochemistry. This is clearly relevant not only to chemistry, but also to the understanding of biological processes at the molecular level. Another major influence in structural elucidation has been the availability of modern physical methods including mass spectrometry, ultraviolet and visible spectroscopy, optical rotatory dispersion, circular dichroism, nuclear magnetic resonance spectroscopy, and x-ray crystallography. Chapters devoted to these topics are complementary to the large number of excellent monographs which are available describing these physical techniques. These chapters are not intended to provide comprehensive introductions, but their content has been particularly directed towards recent developments and applications of general interest. The decision not to include a chapter on infrared spectroscopy was deliberate: this and other physical methods will be covered in a future volume.

Chemists would not normally expect a chapter on 'Structure and Reaction Intermediates' in a book with this title. However, this subject does provide some particularly elegant illustrations of the power of modern methods for the investigation of the static and dynamic behaviour of molecules, reaction intermediates, and transition states. Furthermore, there will be considerable interest in the promise that the imbalance between our present understanding of photochemical reactions as compared with ground state processes is likely to be redressed in the near future.

The determination of the structures of natural products has always played a dominant role in the development of organic chemistry. Now the emphasis is shifting and this is evident in the Chapters 8, 9, and 10. Again, these chapters should not be regarded as comprehensive surveys of recent developments, but as essays illustrating the power and achievement of modern methods of structural elucidation which, in the case of natural products, must include an understanding of their biological function as well as the processes associated with their formation.

Sheffield

W. D. Ollis

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Sheffield W. D. Ollis

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1
Stereochemistry

J. F. STODDART
University of Sheffield

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1.1 INTRODUCTION

In recent years conceptual advances in stereochemistry have not only heralded the growth of a new language but have also been the signal for a re-appraisal of much of the older terminology which has been employed by chemists in the past. Such is the importance of these new developments in stereochemical nomenclature that any review devoted to a discussion of stereochemistry at this point in time must necessarily pay some allegiance at the outset to matters of nomenclature.

Since the emergence of conformational analysis from the original principles expounded by Barton and Hassel in the early 1950s, numerous reviews[1–11], textbooks[12–14], and monographs[15–17] have been published, and the conformational aspects of stereochemistry have received a lot of attention in the original literature and in review organs such as *Progress in Stereochemistry* and *Topics in Stereochemistry*. None the less, the development of the discipline has tended to be empirically based and predictive approaches have been of a semi-quantitative nature. However, with the advent of high-speed electronic computers, the long-standing ambition of chemists to be able to calculate the geometry and energy of a molecule with some degree of accuracy and reliability is finally beginning to be realised. It would therefore seem to be appropriate to review this new and developing field of theoretical conformational analysis in the second part of this article.

1.2 NOMENCLATURE

1.2.1 Symmetry and chirality

The symmetry properties of a particular molecular conformation may be defined in terms of its symmetry elements which in turn may be recognised[13,14,17,18] by certain symmetry operations (Table 1.1). Molecules which have either a plane ($\sigma \equiv S_1$) or centre of symmetry ($i \equiv S_2$), or any other rotation–reflection axis (S_n with $n > 2$) of symmetry have *reflection symmetry* and are said to be *achiral*. Molecules without reflection symmetry are said to be *chiral*[13,17,19,20] and those devoid of all symmetry elements apart from the identity element are said to be *asymmetric*. It should be noted that chiral molecules can have an axis of symmetry [(+)-tartaric acid, for example, has a C_2 axis associated with its Fischer projection] and hence not all chiral molecules need be asymmetric, although all asymmetric molecules are necessarily chiral[18]. It is for this reason that the term *centre of chirality* (sometimes abbreviated to the less precise term *chiral centre*) has superseded[21] the older term asymmetric centre. The word chiral (Greek *cheir* ≡ hand) was first employed by Lord Kelvin in 1884 to describe geometrical figures or groups of points which exhibited 'handedness' or what he preferred to call *chirality*. This terminology was subsequently introduced into the stereochemical literature by Cahn, Ingold, and Prelog[19] in 1966 at the suggestion of Professor K. Mislow.

Table 1.1 Symmetry elements and symmetry operations

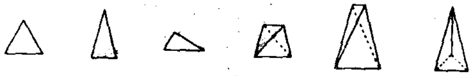
Symmetry elements	*Symmetry operations*
C_n* (axis of symmetry)	Rotation about an axis through 360°/n
σ† (plane of symmetry)	Reflection in a plane
i‡ (centre of symmetry)	Inversion through a centre
S_n (rotation reflection) (axis of symmetry)	Rotation about an axis through 360°/n followed by reflection in a plane perpendicular to the axis

*All molecules have trivial C_1 axes which are referred to as the identity elements, E.
†A plane of symmetry corresponds to the special case where S_n has $n = 1$.
‡A centre of symmetry corresponds to the special case where S_n has $n = 2$

1.2.2 Chemical topology

Chemical topology is concerned with the geometrical properties of molecules as represented by molecular models. As far as molecules are concerned, chirality may be exhibited in either two- or three-dimensional space.

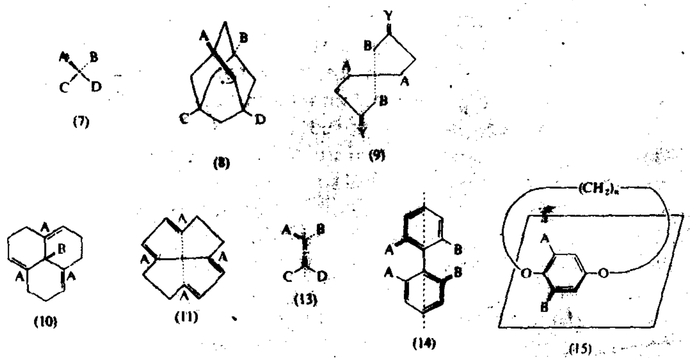
Prelog[22, 23] has found it convenient to discuss chirality in terms of simplices – specifically, triangles (1), (2) and (3) to represent two-dimensional space and tetrahedra (4), (5) and (6) for three-dimensional space as shown in Figure 1.1. Planar molecules such as acetaldehyde, and pyruvic, maleic and fumaric acids, may be represented by the C_1 simplex (3) and are therefore chiral in two-dimensional space, a fact which enzymes can most convincingly demonstrate. For geometrical figures occupying three-dimensional space, the symmetry properties of the tetrahedra (4), (5) and (6) in Figure 1.1 define the element of chirality as being either a centre (T_d), an axis (D_{2d}), or a plane (C_s). These simplices are also the geometrical reference figures for elements of prochirality and pseudo-asymmetry which are discussed later on.



(1) (2) (3) (4) (5) (6)

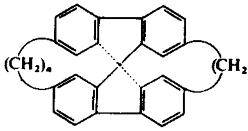
Figure 1.1 The symmetry properties of the simplices used to describe molecular geometry

Molecules with centres of chirality fall into different classes as shown in Figure 1.2 depending upon the chiral point-group to which they belong. The C_1 class includes compounds with a chiral centre as in XABCD (7) and also certain adamantoid derivatives (8). De-symmetrisation of a centre, thereby converting an achiral molecule into a chiral one, can also be achieved by associating the ligands with rings. Thus, spiro compounds XAABB (9), of which spiro[4,4]nonane-1,6-dione (Y = O) is an example[24], belong to the class C_2 and the hexahydrotriphenalene XAAA$\bar{B}$ (10) provides an illustration



(7) (8) (9) (10) (11) (13) (14) (15)

Figure 1.2 Examples of molecular types with centres of chirality (7)–(11), axes of chirality (13) and (14), and planes of chirality (15). An axis of chirality is based on the elongated D_{2d} tetrahedron (5) whereas a plane of chirality is based on the C_s tetrahedron (6) of class C_3 type compounds. The demonstration of chirality in compounds of the type XAAAA (11) which belong to class D_2 was achieved only recently when a number of compounds called vespirenes (12) were synthesised[25]. The absolute configurations of all the compounds prepared were determined from their chiroptical properties in several different ways and the (−)-vespirenes were all shown to have the (*R*)-configuration.



n = 6, 7 or 8

(12)

In appropriately substituted allenes (13) and biphenyls (14), the element of chirality is an axis (see Figure 1.2). On the other hand, a chiral plane is evident in molecules such as the chiral paracyclophane (15) shown in Figure 1.2. The helicity which is characteristic of the helicenes and of the secondary structures of many proteins, polysaccharides and nucleic acids may be considered[19] as a special case of chirality.

1.2.3 Isomerism

Stereochemistry is concerned primarily with the chemistry of isomers which may be related constitutionally, configurationally, or conformationally. This statement immediately raises the question of what is meant by the terms constitution, configuration, and conformation. The definition of these terms has been the subject of some debate recently and the general consensus of opinion at present is summarised in the IUPAC Tentative Rules for Fundamental Stereochemistry[20]. Here, it is sufficient to state that *constitution* refers to the nature and sequence of the bonding between atoms in molecules, *configuration* to the particular spatial arrangement of atoms in molecules without regard to those arrangements which differ only on torsion about single bonds, and *conformation* to the different spatial arrangements of atoms in molecules obtained on torsion about one or more single bonds. When bonds with partial and formal π bond character have to be considered, the distinction between configuration and conformation is not so clear-cut. For discussion of this problem, the reader is referred elsewhere[13, 14, 20]. Only when the constitution, configuration, and conformation are all known, is the *structure* of a molecule defined.

With reference to polymers the term *primary structure* relates to the constitution of the polymer and to the configuration of all the chiral centres along the chain or in the side chains. When the conformation of the chain is defined, the *secondary structure* is known. The term *tertiary structure* is employed to describe how two or more chains in the same or separate molecules interact intramolecularly and intermolecularly (e.g. to form double and triple helices).

Acceptance of the above definitions leads to a distinction between constitutional, configurational, and conformational isomerism which can be further clarified by assuming that only molecules in their ground states qualify to be called isomers. None the less, completely arbitrary distinctions based upon the height of the energy barrier to interconversion tend to be drawn. For example, tautomerism is often used to describe a class of readily interconvertible constitutional isomers, while at the other end of the scale some authors prefer to refer to those conformational isomers which are stable enough to be isolated as exhibiting *atropisomerism*.

Isomers of the configurational and conformational type may be referred to collectively as *stereoisomers*, which in turn, may be *enantiomers* or *diastereoisomers*. This dichotomous subdivision, which was first suggested by Wheland[18] and has now gained general acceptance[13,20,21,26], is based on the simple premise that stereoisomers which are not enantiomers are diastereoisomers. This means that not only stereoisomers such as (+)-tartaric acid and *meso*-tartaric acid, or *cis*- and *trans*-1,3-dimethylcyclohexane, which contain chiral centres are classified as being diastereoisomers but so are stereoisomers such as *cis*- and *trans*-1,4-dimethylcyclohexane, or *cis*- and *trans*-but-2-ene, which are devoid of centres of chirality. Although the term *cis–trans isomerism* has been retained[20,21] to describe special cases of diastereoisomerism, terms such as optical and geometrical isomerism should soon fall into disuse.

In some instances, special nomenclature is justified by novelty as in the case of some cyclopeptides which have been called[27,28] *cyclostereoisomers*. Those which are related as object is to mirror image may be considered to exist as enantiomers depending on the direction, clockwise or anticlockwise, in which the peptide bonds are oriented. Another type of stereoisomerism is exhibited by cyclic molecules like catenanes, which form interlocking rings. This has been termed[14,29,30] *topological isomerism*.

The *RS* nomenclature system for specifying absolute configuration[31,32] has undergone[19–21] some important revisions recently. For example, the complementation procedure associated with the formalistic treatment of multiple linkages as multiple single bonds has received some modifications as have the rules governing the specification of axial chirality in systems such as biphenyls. In addition, a new pair of configurational descriptors, *Z* (*Zusammen*) to replace *cis* (*seqcis*), and *E* (*Entgegen*) to replace *trans* (*seqtrans*) has been introduced[20,21,33] to specify configuration in substituted olefins, with the advantage that they may be readily incorporated into the systematic names of such compounds. Finally, with regard to configurational descriptors, the Beilstein *r* system for naming diastereomeric polysubstituted cyclanes has been adopted[20,21].

With the aid of the sequence rule[19], conformations are described[20,34] as being *synperiplanar* (*sp*), *synclinal* (*sc*), *anticlinal* (*ac*) or *antiperiplanar* (*ap*) according as the torsion angle is within 30 degrees of 0, ±60, ±120, or ±180 degrees, respectively.

1.2.4 Topism

One of the most recent conceptual advances in stereochemistry has been the recognition[13,14,17,21,26,34] that pairs of ligands in molecules may be defined in terms of their intramolecular relationships (Figure 1.3). Thus, if ligands are in constitutionally different environments, they are said[21,34,35] to be *constitutionally heterotopic* (Greek *topos* = place), whereas ligands in stereoisomerically different environments are said[21,34,35] to be *stereoheterotopic*. More specifically, stereoheterotopic ligands are[21,26,34,35] *enantiotopic*, if their consecutive replacement by some test ligand leads to a pair of enantiomers, and *diastereotopic*, if diastereoisomers result from such a substitution procedure. Finally, ligands which are in constitutionally identical environments, and which on applying the above substitution criterion result in a single compound, are said to be *equivalent*[26] or *homotopic*[21,34]. These different kinds of intramolecular relationships are illustrated in Figure 1.3 and it should be noted that while homotopic ligands may be exchanged by a C_n symmetry operation, and enantiotopic ligands by an S_n symmetry

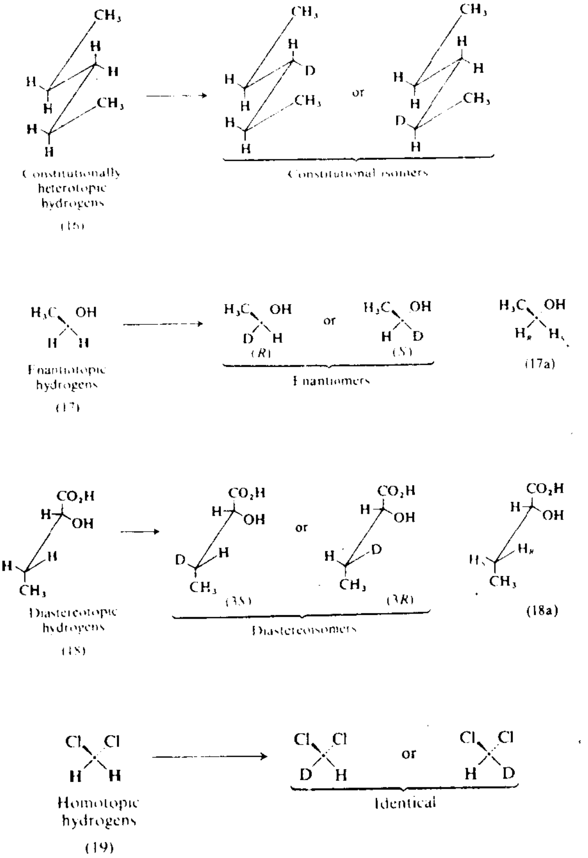


Figure 1.3 Topic relationships between ligands in molecules

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