Topics in
STEREOCHEMISTRY

N. L. Allinger & E. L. Eliel

EDITORS

Volume 9

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STEREOCHEMISTRY

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To the 1975 Nobel Laureates in Chemistry

John W. Cornforth

and

Vladimir Prelog

INTRODUCTION TO THE SERIES

During the last decade several texts in the areas of stereochemistry and conformational analysis have been published, including *Stereochemistry of Carbon Compounds* (Eliel, McGraw-Hill, 1962) and *Conformational Analysis* (Eliel, Allinger, Angyal, and Morrison, Interscience, 1965). While the writing of these books was stimulated by the high level of research activity in the area of stereochemistry, it has, in turn, spurred further activity. As a result, many of the details found in these texts are already inadequate or out of date, although the student of stereochemistry and conformational analysis may still learn the basic concepts of the subject from them.

For both human and economic reasons, standard textbooks can be revised only at infrequent intervals. Yet the spate of periodical publications in the field of stereochemistry is such that it is an almost hopeless task for anyone to update himself by reading all the original literature. The present series is designed to bridge the resulting gap.

If that were its only purpose, this series would have been called "Advances (or "Recent Advances") in Stereochemistry," It must be remembered, however, that the above-mentioned texts were themselves not treatises and did not aim at an exhaustive treatement of the field. Thus the present series has a second purpose, namely to deal in greater detail with some of the topics summarized in the standard texts. It is for this reason that we have selected the title *Topics in Stereochemistry*.

The series is intended for the advanced student, the teacher, and the active researcher. A background of the basic knowledge in the field of stereochemistry is assumed. Each chapter is written by an expert in the field and, hopefully, covers its subject in depth. We have tried to choose topics of fundamental inport aimed primarily at an audience of organic chemists but involved frequently with fundamental principles of physical chemistry and molecular physics, and dealing also with certain stereochemical aspects of inorganic chemistry and biochemistry.

It is our intention to bring out future volumes at intervals of one to two years. The Editors will welcome suggestions as to suitable topics.

We are fortunate in having been able to secure the help of an international board of Editorial Advisors who have been of great assistance by suggesting topics and authors for several articles and by helping us avoid duplication of

topics appearing in other, related monograph series. We are grateful to the Editorial Advisors for this assistance, but the Editors and Authors alone must assume the responsibility for any shortcomings of *Topics in Stereochemistry.*

N. L. Allinger
E. L. Eliel

February 1976

PREFACE

Volume IX of *Topics in Stereochemistry* begins with a chapter, written as a postscript to the 1974 Le Bel-van't Hoff centennial, entitled "The Foundations of Classical Stereochemistry." In it, S. F. Mason gives a brief history of chemical thinking leading to the famous work by van't Hoff and Le Bel as well as Werner.

When *Conformational Analysis* was published in 1965, it was possible to discuss the relationship between mass spectrometry and the stereochemistry of organic molecules in one paragraph. It was suggested then that "mass spectrometry may be of very considerable future use in conformational analysis." The second chapter, by Mark M. Green, outlines some of that "future use" which has, in fact, taken place in the intervening ten years. There is no question now but that a number of kinds of sterochemical problems are susceptible to attack by means of mass spectrometry.

The single experimental technique which has contributed the most to stereochemical knowledge in the last 15 years or so has, without question, been nmr spectroscopy. Not only are the number and types of systems studied constantly being increased, but also the development of new and expanded nmr techniques for such studies continues unabated. In Chapter 3, Otmar Hofer discusses the "Lanthanide Induced Shift Technique in Conformational Analysis." This is a technique which has given a whole new dimension to proton magnetic resonance through the spreading out of the chemical shift range available. In addition, it appears to have a very powerful quantitative potential for the determination of structure in solution. One might well ask if this technique can play the role for structural chemistry in solution that X-ray crystallography has played in the crystalline state.

Macrocyclic rings have long presented an intriguing puzzle to the stereochemist. The variety of conformations available to rings containing more than six members, and the pathways by which one conformation is converted to another, form the subject matter for the chapter by Johannes Dale. Although the situation in medium and large rings is complex, the conformational transformations can be broken down into stepwise changes that are reasonable and understandable. Nmr has been the key experimental tool in this area.

The final chapter is concerned with the crystal structures of steroids. With X-ray data becoming easily and abundantly available, they play an increasingly important role in the understanding of stereochemistry. There are now some 150 X-ray structures of steroids known; here, W. L. Duax presents a detailed

and systematic summary of this large body of information. Interpretation of how the variation in structural parameters is related to the overall nature of a number of steroid molecules becomes possible as a result of such systematization.

The editors are delighted that the second Nobel Prize in chemistry during the span of existence of this series has been awarded for work centered on stereochemistry, and we respectfully dedicate this volume to J. W. Conrforth and V. Prelog, the 1975 Nobel Laureates in chemistry.

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January 1976
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CONTENTS

THE FOUNDATIONS OF CLASSICAL STEREOCHEMISTRY

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I. INTRODUCTION

According to the providential view of history, in which
events are the outcome of 'the contingent and the unforeseen'
(1), the progress of science depends upon the casual chance of
genius which appears adventitiously, like Gargantua from
Gargamelle's ear (2), to solve the problems of each period.
As the historical heirs of the alchemists, who saw all-perva-
sive analogies between the macrocosm and the microcosm (3),
chemists well appreciate the ubiquity of a macroscopic, as
well as the microscopic, uncertainty principle, but nonethe-
less know from experience that some scientific innovations
are 'in the air,' and that their discovery in broad outline,
if not in detail, is attended by a near-certain inevitability,
while other innovations are doomed to delay and even frustra-
tion by the principle of unripe time (4).

Historically the innovations that are 'in the air' are
often characterized by multiple discovery and by wide accept-
ance from the outset or after only minor delays. Both of the
main stages in the development of classical stereochemistry
are characterized by these criteria. The work of van't Hoff
and Le Bel, whose seminal papers appeared 100 years ago, was
independent and simultaneous, as was that of Kekulé and Scott
Couper in 1858 (5). Both van't Hoff and Kekulé had a keen
appreciation of ripe and unripe time. Refering to his 1858 work,

Kekule observed in 1890 (6), "As a young Privatdozent at
Heidelberg I put these ideas down on paper and showed this
work to two of my closest friends. Both of them shook their
heads doubtfully. I thought that either my theory was not yet
ripe, or the time not yet ripe for it, and put my manuscript
away in a drawer." For his Utrecht doctorate van't Hoff submit-
ted in 1874 a straightforward exercise in normal science (7),
"a routine dissertation on cyanacetic and malonic acids" (8),
and wisely withheld his theoretical pamphlet on chemistry in
space. His younger contemporary, Arrhenius, was less fortunate
and, floating the idea of the incomplete dissociation of elec-
trolytes in his Uppsala doctoral dissertation, he was awarded a
fourth class Ph.D, in 1884. But for the then-commanding in-
fluence of Ostwald, Arrhenius would have been precluded from an
academic career (9)

Where patronage is absent a notable innovation due to an
isolated worker may appear so egregious that it remains inef-
fective for an extended period and even may await rediscovery,
like the *berthollides* and the concept of mass action of Claude
Berthollet (1748-1822). Avogadro's hypothesis (1811), which
underpinned the atomic valencies and molecular weights required
for the structural theory of the 1860s, was largely neglected
for half a century. Similarly, Pasteur's concept of molecular
dissymmetry, based on his work with the tartrates (1848-1860),
made only a minor contribution in 1874 to the stereochemical
theory of van't Hoff, although it influenced Le Bel more
profoundly.

Towards the end of the nineteenth century, when organic
stereochemical theory was well established, the earlier work
of Pasteur became more generally known and appreciated. From
that time dates the hagiographal tradition that Pasteur was the
'founder of stereochemistry,' as Crum Brown put it in 1897 (10)
and Robert Robinson (1886-1975), on the occasion of the van't
Hoff - Le Bel centenary, in 1974 (11). Pasteur might have been
the founder of stereochemistry had he continued to work in the
chemical field after 1860 and to support one or more of the
main thrusts of chemical thinking. But he did not as, among
other things, the following reconstruction of the development
of classical stereochemistry endeavours to show.

II.   INORGANIC PRINCIPLES AND PROCEDURES

In its early formative period each branch of the chemical
sciences has experienced the domination of an inaugural man-
darin who gives the subject an identity and an autonomy by
bringing together, and intergrating to a degree, previously
separated, or only loosely associated, principles and practices.
Jöns Jacob Berzelius (1779-1848) endeavored to lay down the form
and organize the content of mineral chemistry for some 40 years

through the six volumes of his Handbook, published from 1808, by way of his students, and above all through his annual reports on the progress of chemistry and mineralogy (1822-1848), in which he described and commented upon, favorably or otherwise, the chemical studies of the past year. The inaugurating pontiffs of organic and of physical chemistry, Justus Liebig (1803-1873) and Wilhelm Ostwald (1853-1923), respectively, exercised a similar, though lesser, command over their individual fields, again by way of their students and control of a periodical publication, Leibig through his *Annalen* from 1832 and Ostwald through the *Zeitschrift für physikalische Chemie* from its foundation in 1887.

The influence of Liebig and, more particularly, that of Ostwald was inevitably less substantial than that of Berzelius on account of the sheer growth and proliferation of chemical science over the years that separated their respective ascendancies. Liebig never completely assimilated the organic chemistry of his French contemporaries, and he turned increasingly to agricultural and physiological chemistry from about 1840. Ostwald similarly failed to come to terms with developments in statistical mechanics and, founding his *Annalen der Naturphilosophie* in 1901, turned to the consolations of philosophy. Of the three inaugural mandarins only Berzelius remained steadfastly a chemist to the end of his days, attempting in his later years to assimilate the new developments in organic chemistry into the inorganic model he had constructed in his youth and prime.

Berzelius based his conception of a research program for the chemical sciences on the developments in pneumatic chemistry, mineral analysis, and electrolysis, which culminated in the new gas laws, stoichiometry, electrochemical concepts, and Daltonian atomic theory of the first decade of the nineteenth century. The field of chemical studies was defined by the law of constant proportions. Berthollet lost the extended dispute of 1800-1808 with Joseph Proust (1754-1826) on the question of constancy of composition, and the *berthollide* substances were banished from chemical science for the following century. Only the *daltonides* with constant composition were recognized as distinct compounds whose elementary composition and interconversions were eligible for chemical investigation.

Initially doubts were expressed whether any organic materials lay within the province of chemistry, but in 1814 Berzelius showed by combustion analysis that a number of simple organic substances satisfied the demarcation criterion of constant elementary proportions (12). A sharp distinction was drawn, however, between *organic* substances, which satisfied the criterion, and *organized* matter, like the proteins, glutens, and gums, which apparently did not (13). The organic substances admitted to the chemical fold exemplified to a more marked and varied degree than inorganic compounds the law of multiple proportions proposed by John Dalton (1766-1828) in 1804. Multi-

ple proportions gave Dalton's atomic theory of 1808 its ration-
ale, and the compounds exemplifying the law raised for the
first time the problem of molecular structure. Dalton himself
drew schematic structural formulae of the simple hydrides and
oxides (14) and even of such complex substances as albumen and
gelatin which he depicted as isomers of C_2H_2NO (15) (Fig. 1).
For some 30 years Dalton employed ball-and-pin atomic models
for teaching purposes (15). However, these formulae and models
led to no new practicable expectations during Dalton's lifetime,
and many workers preferred to use equivalents rather than atomic
weights in the 1820-1860 period.

Binary

21   22   23   24   25

Ternary

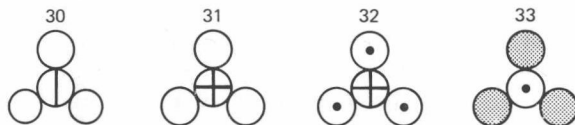26   27   28   29

Quaternary

30   31   32   33

Quinquenary and Sertenary

34   35

Septenary

36   37

21.   An atom of water or steam, composed of 1 of
        oxygen and 1 of hydrogen retained in phys-
        ical contact by a strong affinity, and
        supposed to be surrounded by a common atmos-

	phere of heat; its relative weight=	8
22.	An atom of ammonia, composed of 1 of azote and 1 of hydrogen	6
23.	An atom of nitrous gas, composed of 1 of azote and 1 of oxygen	12
24.	An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen	6
25.	An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen	12
26.	An atom of nitrous oxide, 2 azote + 1 oxygen	17
27.	An atom of nitric acid, 1 azote + 2 oxygen	19
28.	An atom of carbonic acid, 1 carbone + 2 oxygen	19
29.	An atom of carburetted hydrogen, 1 carbone + 2 hydrogen	7
30.	An atom of oxynitric acid, 1 azote + 3 oxygen	26
31.	An atom of sulphuric acid, 1 sulphur + 3 oxygen	34
32.	An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen	16
33.	An atom of alcohol, 3 carbone + 1 hydrogen	16
34.	An atom of nitrous acid, 1 nitric acid + 1 nitrous gas	31
35.	An atom of acetous acid, 2 carbone + 2 water	26
36.	An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water	33
37.	An atom of sugar, 1 alcohol + 1 carbonic acid	35

Fig. 1. The formulation of molecular structure by John Dalton, *A New System of Chemical Philosophy*, (1808).

William Wollaston (1766-1828) was initially an enthusiastic supporter of Dalton's atomic theory, and in 1808 he accounted in structural terms for the multiple proportions he had found in the oxalate, binoxalate, and quadroxalate of potash, proposing that the second and the third of these were made up, respectively, of a symmetrical linear and tetrahedral array of oxalate around the potash (16). The corresponding trisoxalate, he felt, could not exist, owing to an inherent instability of an equatorial triangle of oxalates around the potash without polar groups to sustain the structure (16). By 1814 Wollaston had become disenchanted with the atomic theory on the ground that there appeared to be no criterion for distinguishing the multiple proportion of AB and AB_2 from that of A_2B and AB (17).