

**MTP International  
Review of Science**

---

**Alicyclic Compounds**

---

**Organic Chemistry  
Series One  
Volume 5**

---

**Consultant Editor  
D H Hey FRS  
Volume Editor  
W Parker**

**Butterworths  
University Park Press**

068/  
S26.1  
V.5

068  
V.1/5

7962444  
5

MTP International Review of Science

**Volume 5**

## **Alicyclic Compounds**

Edited by **W. Parker**  
University of Stirling



**E7952444**

**Butterworths**      **London**  
**University Park Press**      **Baltimore**

## 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 70279 6

## 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

Parker, William, 1932-

Alicyclic compounds.

(Organic chemistry, series one, v. 5) (MTP international review of science)

1. Alicyclic compounds. I. Title.

[DNLM: 1. Chemistry, Organic. 2. Fats. QD301 A398 1973]

QD251.2.074 vol. 5 [QD305.H9] 547'.008s [547'.5]

ISBN 0-8391-1033-2 73-7911

First Published 1973 and © 1973

MTP MEDICAL AND TECHNICAL PUBLISHING CO. LTD.

St. Leonard's House

St. Leonardgate

Lancaster, Lincs.

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

MTP International Review of Science

## **Alicyclic Compounds**

## MTP International Review of Science

### 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.

## Organic Chemistry

### Series One

Consultant Editor

D. H. Hey, F.R.S.

*Department of Chemistry*

*King's College, University of London*

### Volume titles and Editors

#### 1 STRUCTURE DETERMINATION IN ORGANIC CHEMISTRY

Professor W. D. Ollis, F.R.S.,

*University of Sheffield*

#### 2 ALIPHATIC COMPOUNDS

Professor N. B. Chapman,

*Hull University*

#### 3 AROMATIC COMPOUNDS

Professor H. Zollinger, *Swiss Federal*

*Institute of Technology*

#### 4 HETEROCYCLIC COMPOUNDS

Dr. K. Schofield, *University of Exeter*

#### 5 ALICYCLIC COMPOUNDS

Professor W. Parker, *University of*

*Stirling*

#### 6 AMINO ACIDS, PEPTIDES AND RELATED COMPOUNDS

Professor D. H. Hey, F.R.S. and

Dr. D. I. John,

*King's College, University of London*

#### 7 CARBOHYDRATES

Professor G. O. Aspinall, *Trent University,*

*Ontario*

#### 8 STEROIDS

Dr. W. F. Johns, *G. D. Searle & Co.,*

*Chicago*

#### 9 ALKALOIDS

Professor K. Wiesner, F.R.S.,

*University of New Brunswick*

#### 10 FREE RADICAL REACTIONS

Professor W. A. Waters, F.R.S.,

*University of Oxford*

### INDEX VOLUME

## **Physical Chemistry**

### **Series One**

Consultant Editor

A. D. Buckingham

*Department of Chemistry*

*University of Cambridge*

*Volume titles and Editors*

#### **1 THEORETICAL CHEMISTRY**

Professor W. Byers Brown, *University of Manchester*

#### **2 MOLECULAR STRUCTURE AND PROPERTIES**

Professor G. Allen, *University of Manchester*

#### **3 SPECTROSCOPY**

Dr. D. A. Ramsay, F.R.S.C.,  
*National Research Council of Canada*

#### **4 MAGNETIC RESONANCE**

Professor C. A. McDowell, F.R.S.C.,  
*University of British Columbia*

#### **5 MASS SPECTROMETRY**

Professor A. Maccoll, *University College, University of London*

#### **6 ELECTROCHEMISTRY**

Professor J. O'M. Bockris, *University of Pennsylvania*

#### **7 SURFACE CHEMISTRY AND COLLOIDS**

Professor M. Kerker, *Clarkson College of Technology, New York*

#### **8 MACROMOLECULAR SCIENCE**

Professor C. E. H. Bawn, F.R.S.,  
*University of Liverpool*

#### **9 CHEMICAL KINETICS**

Professor J. C. Polanyi, F.R.S.,  
*University of Toronto*

#### **10 THERMOCHEMISTRY AND THERMODYNAMICS**

Dr. H. A. Skinner, *University of Manchester*

#### **11 CHEMICAL CRYSTALLOGRAPHY**

Professor J. Monteath Robertson, F.R.S.,  
*University of Glasgow*

#### **12 ANALYTICAL CHEMISTRY—PART 1**

Professor T. S. West, *Imperial College, University of London*

#### **13 ANALYTICAL CHEMISTRY—PART 2**

Professor T. S. West, *Imperial College, University of London*

**INDEX VOLUME**

## **Inorganic Chemistry**

### **Series One**

Consultant Editor

H. J. Emeléus, F.R.S.

*Department of Chemistry*

*University of Cambridge*

*Volume titles and Editors*

#### **1 MAIN GROUP ELEMENTS—HYDROGEN AND GROUPS I–IV**

Professor M. F. Lappert, *University of Sussex*

#### **2 MAIN GROUP ELEMENTS—GROUPS V AND VI**

Professor C. C. Addison, F.R.S. and  
Dr. D. B. Sowerby, *University of Nottingham*

#### **3 MAIN GROUP ELEMENTS—GROUP VII AND NOBLE GASES**

Professor Viktor Gutmann, *Technical University of Vienna*

#### **4 ORGANOMETALLIC DERIVATIVES OF THE MAIN GROUP ELEMENTS**

Dr. B. J. Aylett, *Westfield College, University of London*

#### **5 TRANSITION METALS—PART 1**

Professor D. W. A. Sharp, *University of Glasgow*

#### **6 TRANSITION METALS—PART 2**

Dr. M. J. Mays, *University of Cambridge*

#### **7 LANTHANIDES AND ACTINIDES**

Professor K. W. Bagnall, *University of Manchester*

#### **8 RADIOCHEMISTRY**

Dr. A. G. Maddock, *University of Cambridge*

#### **9 REACTION MECHANISMS IN INORGANIC CHEMISTRY**

Professor M. L. Tobe, *University College, University of London*

#### **10 SOLID STATE CHEMISTRY**

Dr. L. E. J. Roberts, *Atomic Energy Research Establishment, Harwell*

**INDEX VOLUME**

# **Organic Chemistry**

## **Series One**

Consultant Editor  
**D. H. Hey, F.R.S.**



## 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

Several thousand papers devoted to the chemistry of alicyclic compounds were published during the period (January 1970–December 1971) covered by this volume. Obviously it is impossible to survey comprehensively this output in a book of 300 pages, so those areas were selected in which major developments have taken place.

The advent of more sophisticated instrumental techniques, particularly  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy, has aided greatly in the structural elucidation of alicyclic compounds and equally impressive has been the success enjoyed by various calculation methods (*ab. initio*, MINDO, etc.) for determining structure and the associated thermodynamic parameters.

Conformational factors which affect chemical reactivity have received considerable attention in the past two years.

The chapters devoted to photochemistry, metal-catalysed reactions of strained ring systems and thermolyses, survey three of the most active fields in the whole of organic chemistry at the present time. The intensity of the effort in these fields has undoubtedly been brought about to a large extent by the enunciation of the Woodward–Hoffmann rules for the conservation of orbital symmetry in concerted processes.

Medium-sized ring chemistry has been particularly active in the development of new synthetic methodology, the application of advanced spectroscopic techniques (e.g. Nuclear Overhauser Effect) to the study of preferred conformations and the chemistry of cyclic allenes, acetylenes and *trans*-olefins.

The chapter on adamantane and related systems reviews an area of alicyclic chemistry which stretches from medicinal chemistry (antiviral activity) at one extreme to the correlation of strain energy calculations with bridgehead reactivity at the other.

Unfortunately, chapters on Synthesis and Structure/Reactivity relationship have had to be omitted from this volume but these areas will be dealt with in the second series.

# Contents



<b>Structure of alicyclic compounds</b>	1
N. M. D. Brown and D. J. Cowley, <i>New University of Ulster</i>	
<b>Conformational analysis of alicyclic compounds</b>	45
B. T. Golding, <i>University of Warwick</i>	
<b>Alicyclic photochemistry</b>	87
R. Bishop, <i>University of Stirling</i>	
<b>Metal-catalysed reactions in strained ring systems</b>	127
L. A. Paquette, <i>Ohio State University</i>	
<b>Thermolysis of alicyclic compounds</b>	159
J. M. Brown, <i>University of Warwick</i>	
<b>Aspects of the chemistry of seven- to eleven-membered rings</b>	205
M. S. Baird, <i>University of Newcastle upon Tyne</i>	
<b>Adamantane and its relatives</b>	239
E. M. Engler and P. v. R. Schleyer, <i>Princeton University</i>	



# 1

## Structure of Alicyclic Compounds

N. M. D. BROWN and D. J. COWLEY

New University of Ulster

1.1	INTRODUCTION	2
1.1.1	<i>General reviews</i>	3
1.2	DIRECT DETERMINATION OF MOLECULAR STRUCTURE	4
1.2.1	<i>Microwave spectroscopy</i>	4
1.2.1.1	<i>Three-membered rings</i>	4
1.2.1.2	<i>Four- and five-membered rings</i>	4
1.2.1.3	<i>Six-membered rings</i>	5
1.2.1.4	<i>Bicyclic systems</i>	5
1.2.2	<i>Gas-phase electron diffraction</i>	5
1.2.2.1	<i>Three-membered rings</i>	5
1.2.2.2	<i>Four- and five-membered rings</i>	6
1.2.2.3	<i>Six- and eight-membered rings</i>	6
1.2.2.4	<i>Bicyclic and other systems</i>	7
1.2.3	<i>X-Ray crystallography</i>	8
1.2.3.1	<i>Three-membered rings</i>	8
1.2.3.2	<i>Four- and five-membered rings</i>	8
1.2.3.3	<i>Six- and seven-membered rings</i>	9
1.2.3.4	<i>Eight-membered and larger rings</i>	10
1.2.3.5	<i>Bicyclic and other systems</i>	12
1.3	ELECTRONIC STRUCTURE AND THEORETICAL CALCULATIONS	14
1.3.1	<i>Electronic structure</i>	14
1.3.1.1	<i>General</i>	14
1.3.1.2	<i>Three-membered rings</i>	14
1.3.1.3	<i>Four-membered rings</i>	15
1.3.1.4	<i>Five-membered rings</i>	16
1.3.1.5	<i>Bicyclic and other systems</i>	16
1.3.2	<i>Theoretical calculation of structure, conformation and thermodynamic properties</i>	17

1.3.2.1	<i>General</i>	17
	(a) <i>Conformational analysis by molecular orbital methods</i>	17
	(b) <i>Valence force-field calculations</i>	17
	(c) <i>Strain calculations</i>	18
1.3.2.2	<i>Three-membered rings</i>	19
1.3.2.3	<i>Four-membered rings</i>	19
1.3.2.4	<i>Five- and six-membered rings</i>	20
1.3.2.5	<i>Eight-, nine- and ten-membered rings</i>	20
1.3.2.6	<i>Bicyclic and other systems</i>	20
1.4	<b>GENERAL SPECTROSCOPIC AND OTHER METHODS</b>	21
1.4.1	<i>Ultraviolet spectroscopy, circular dichroism and optical rotatory dispersion</i>	21
1.4.1.1	<i>General</i>	21
1.4.1.2	<i>Three-membered rings</i>	21
1.4.1.3	<i>Five- and six-membered rings</i>	22
1.4.1.4	<i>Eight- and nine-membered rings</i>	22
1.4.1.5	<i>Bicyclic and other systems</i>	23
1.4.2	<i>Infrared spectroscopy</i>	23
1.4.2.1	<i>Three- and four-membered rings</i>	23
1.4.2.2	<i>Five- and six-membered rings</i>	24
1.4.2.3	<i>Seven-membered and larger ring systems</i>	26
1.4.2.4	<i>Bicyclic and other systems</i>	27
1.4.3	<i>Mass spectroscopy</i>	27
1.4.3.1	<i>Three- and four-membered rings</i>	27
1.4.3.2	<i>Five- and six-membered and larger rings</i>	28
1.4.3.3	<i>Bicyclic ring systems</i>	29
1.4.3.4	<i>Polycyclic ring systems</i>	29
1.4.4	<i>Resonance spectrometry</i>	30
1.4.4.1	<i>Electron spin resonance studies</i>	30
1.4.4.2	<i>Nuclear quadrupole and nuclear magnetic resonance studies</i>	31
1.4.5	<i>Miscellaneous methods</i>	35

## 1.1 INTRODUCTION

In this review attention is directed towards the geometric and electronic structures of alicyclic compounds. The literature, from late 1969 to the end of 1971, has been surveyed and priority given to the more direct and unambiguous methods of structure elucidation, i.e. x-ray, neutron and electron diffraction, microwave spectroscopy and the pertinent aspects of infrared and ultraviolet spectroscopies. More indirect methods, such as electron spin resonance, nuclear magnetic and quadrupole resonance, circular dichroism and optical rotatory dispersion, mass spectrometry and other techniques which often rely on empirical relationships, are included when the information obtained has precise structural significance or is of well-defined diagnostic value.

Theoretical treatments of conformation, electronic energy, supporting thermodynamic and photo-electron studies are also included. General aspects of dynamic conformational equilibria are covered in Chapter 2.

The heading alicyclic compounds has been defined rigorously and material associated with annulenes, terpenoid and steroidal systems is not included even though much relevant data lies in these areas. SI units are used except for ionisation potentials, given in electron volts (eV) and molar decadic extinction coefficients, given as  $M^{-1} \text{ cm}^{-1}$ . Where abbreviations have been used they are defined on first mention.

### 1.1.1 General reviews

The determination of relative and absolute configuration has been reviewed<sup>1,2</sup> and a reference list<sup>3</sup> of structures, including alicyclics, whose absolute configurations were determined by x-ray diffraction is now complete to early 1970. Structure determination by gas-phase electron diffraction<sup>4</sup> and the application of microwave spectroscopy<sup>5</sup> in the study of conformation and internal molecular motion have been surveyed. An exhaustive general review<sup>6</sup> of optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) has been made. A less recent but significant appraisal of the strained double bond in cyclic systems is available<sup>7</sup>.

Theoretical calculations of structural, spectral and thermodynamic properties of organic molecules have been reviewed and include the use of molecular orbital (MO) methods<sup>8</sup>, all-valence electron self-consistent field (SCF) calculations of large molecules<sup>9</sup>, and semi-empirical molecular orbital calculations for saturated organic compounds<sup>10</sup>. A short introductory summary of the principles of conformational analysis has appeared<sup>11</sup>.

The implications and use of the intramolecular nuclear Overhauser effect (NOE) in structural organic chemistry has appeared<sup>12</sup> as has a critique<sup>13</sup> of the use of nuclear magnetic resonance (n.m.r.) for establishing conformational preferences. An extensive compilation<sup>14</sup> has been published of n.m.r. long-range proton spin-spin coupling constants which contains a large amount of pertinent alicyclic data. The conformational preferences of six-membered alicyclics have been reviewed<sup>15</sup> and the requisite methods used evaluated. An assessment of infrared (i.r.) and Raman spectroscopic studies of conformational isomerism in three- to ten-membered cycloalkyl monohalides has been made<sup>16</sup>. Conformational mobility in seven-membered rings<sup>17</sup> and the results of x-ray studies and strain minimisation calculations on medium rings<sup>18</sup> have also been reviewed. The physical, structural and chemical properties of bicyclo[*n.m.0*]alkanes<sup>19</sup>, bicyclo[3.3.1]nonanes<sup>20</sup>, and adamantanes<sup>21</sup> have been summarised.

The proceedings of a recent Symposium include the structures<sup>22</sup> of small alicyclic compounds (microwave structures of methylcyclopropyl ketone, 4-chloronortricyclene, benzocyclopentene, benzocyclobutene and 6-hydroxy-2-formyl fulvene), detailed i.r. studies of cyclobutane and cyclohexane and an assessment<sup>23</sup> of the scope and limitations of conformational analysis. In the latter instance many important topics such as the geometry of five-membered rings, n.m.r. studies of conformation, conformational analysis

by *ab initio* SCF-LCAO-MO methods and general quantitative conformational analysis are included.

## 1.2 DIRECT DETERMINATION OF MOLECULAR STRUCTURE

### 1.2.1 Microwave spectroscopy

#### 1.2.1.1 Three-membered rings

The molecular structures and dipole moments of a number of monosubstituted cyclopropanes have been determined by microwave spectroscopy. In cyclopropylamine<sup>24</sup> (dipole moment,  $\mu = 1.19$  D\*) the C—N bond length, 0.1428(1) nm, is shortened somewhat for a single bond, possibly because of an appreciable conjugative interaction of the nitrogen lone-pair electrons with the three-membered ring. Similarly, the C—P bond, 0.1834(1) nm, in cyclopropylphosphine<sup>25</sup> ( $\mu = 1.16$  D) is less than that in other organophosphines. In the case of cyclopropylcarbinol<sup>26</sup> and its O—D analogue ( $\mu = 1.87$  and 1.84 D, respectively) only one of the possible rotamers was identified and it was suggested that internal rotation of the substituent is hindered by hydrogen bonding between the hydroxyl group and the cyclopropyl ring. Further evidence of such hindered rotation is found in the observation of both ground state and torsional excited states in the microwave spectra of cyclopropane carboxaldehyde<sup>27</sup> and cyclopropane carbonyl fluoride<sup>28</sup>. As expected, the *cis*- conformers (i.e. those with the oxygen atom *cis* with respect to the ring plane) have dipole moments ( $\mu = 2.74$  and 3.28 D, respectively) lower than those in the *trans* species ( $\mu = 3.26$  and 3.46 D). The rotational barriers present were also investigated.

The spectrum of 1-methylcyclopropene ( $\mu = 0.84$  D) also showed the presence of torsionally excited molecules and has yielded<sup>29</sup> a value of 5.82 kJ mol<sup>-1</sup> for the barrier to rotation of the methyl group in addition to the structure of the molecule. It was found that the double bond, 0.1300(1) nm, is shortened and that the methyl group-to-ring C—C bond distance, 0.1476(1) nm, is closer to that in methylacetylene than to that in propylene, implying the bond has more s character than in a pure sp<sup>2</sup> situation. In the case of methylene cyclopropene<sup>30</sup> ( $\mu = 0.402$  D) the double bond 0.13317(14) nm and the other C—C bonds 0.14570(14) nm for C-2—C-3 and 0.15415(3) nm for C-3—C-3 have lengths consistent with the formal hybridisation of the atoms involved.

#### 1.2.1.2 Four- and five-membered rings

A detailed microwave study<sup>31</sup> of 1-methylcyclobutene ( $\mu = 0.357$  D) has shown the molecule to be planar and that the barrier to methyl group rotation is 6.96 kJ mol<sup>-1</sup>. The observed rotational constants and dipole moment components of cyclopentene oxide<sup>32</sup> ( $\mu = 2.00$  D) can only be

\*1 D = 1 Debye =  $3.335640 \times 10^{-30}$  C m

explained if the boat conformer of the molecule is most stable. A preliminary note<sup>33</sup> on the microwave structure of cyclopent-3-en-1-one has stated that the molecule is planar in the vibrational ground state but in several successive excited states an out-of-plane vibration is present. From a study<sup>34</sup> of the microwave spectrum and other structural properties of bicyclo[2.1.0]pent-2-ene ( $\mu = 0.398$  D) it has been deduced that the molecule has a dihedral angle between the ring planes of 114 degrees and a charge distribution similar to that in cyclobutene itself. The degree of electron delocalisation present is held to be significantly less than that in cyclopentadiene.

### 1.2.1.3 Six-membered rings

Observed<sup>35</sup> dipole moment components and moments of inertia in cyclohex-2-en-1-one imply that the oxygen atom and all the carbon atoms except C-5 are co-planar unlike cyclopent-2-en-1-one which is planar.

### 1.2.1.4 Bicyclic systems

The structure of bicyclo[2.1.1]hexan-2-one has been reported<sup>36</sup> ( $\mu = 3.35$  D) and the potential-energy function for the lowest energy vibrational mode (perpendicular to the plane of symmetry) is close to harmonic with no barrier at the symmetry position. A large amplitude internal motion has been detected<sup>37</sup> in the symmetric rotor 1-fluorobicyclo[2.2.2]octane and the spectrum of the 1-chloro-compound has been re-investigated. A shortening of the C-1—C-2 bond and a narrowing of the halogen- $\hat{C}$ -1—C-2 were noted. The double-minimum potential required to match the observed behaviour of the molecule has a barrier of  $800 \pm 220$  J mol<sup>-1</sup> and  $560 \pm 280$  J mol<sup>-1</sup> in the fluoro- and chloro-derivatives respectively. The corresponding equilibrium angle is about 16 degrees in both compounds. Microwave data for five isotopic forms of 1-chlorobicyclo[1.1.1]pentane have been analysed<sup>38</sup> and the bond lengths, for C—C1, C-1—C-2 and C-2—C-3, of 0.1761, 0.1536 and 0.1556 nm respectively, obtained. The C-1— $\hat{C}$ -2—C-3 is 73.5 degrees.

## 1.2.2 Gas-phase electron diffraction

### 1.2.2.1 Three-membered rings

It has been shown<sup>39</sup> that the C—F bonds in perfluorocyclopropane are normal, 0.1314(1) nm, and that the C—C distance, 0.1505(3) nm, is close to that in cyclopropane. It was noted that F— $\hat{C}$ —F of 112.2(1.0) degrees is less than in the hydrocarbon and that this has been ascribed to a rehybridisation (produced by the *gem*-difluoro groups) of the bent-bond model sp<sup>2</sup>-carbon atomic orbitals to a more nearly normal sp<sup>3</sup> condition in the perfluorocyclopropane system. At least in part, this interpretation is borne out by the larger strain energy observed<sup>40</sup> for the fluorocarbon (288 kJ mol<sup>-1</sup>) cf. cyclopropane (115 kJ mol<sup>-1</sup>). The bond lengths and angles in



cyclopropene have also been determined<sup>41</sup> by electron diffraction in the gas phase. Structures, derived from the molecular-intensity curve, with an assumed  $C_{2v}$  symmetry, have been published<sup>42</sup> for perchlorocyclopropene. The double bond, 0.1320(6) nm, is somewhat longer than in cyclopropene while the C—C bonds are shortened, 0.1479(1) nm. The olefinic C—Cl bonds are also short, 0.1684(2) nm, suggesting that the carbon atom involved has more s character than if  $sp^2$ -hybridised.

#### 1.2.2.2 Four- and five-membered rings

Octafluorocyclobutane has been shown<sup>43</sup> to be non-planar with  $D_{2d}$  symmetry and hexafluorocyclobutene to be planar. In the former the C—C distance, 0.1566(2) nm, is only slightly longer than in the cyclobutane, however, the dihedral angle at 17.4 degrees is considerably less than the value of 27 degrees in the parent compound, and the tilt angle of the  $CF_2$  groups is increased by 1.4 degrees to  $-5.4$  degrees. In hexafluorocyclobutene the C-3—C-4 distance appears to be abnormally long (0.1595 nm); the double bond distance, 0.1342(6) nm; C-2—C-3, 0.1508(3) nm, and the internal angles, C-1—C-2—C-3, C-2—C-3—C-4, at 94.8 and 85.2 degrees respectively, have cast doubt on the data available for cyclobutene itself. Adams and Bartell<sup>44</sup> have found that cyclobutane carbonyl chloride exists almost entirely as the *gauche* conformer in the gas phase, unlike the corresponding cyclopropyl compound. The bond lengths and angles are as expected and there is some evidence to suggest that ring puckering and torsional displacements are coupled.

Gas-phase electron diffraction can provide an alternative and sensitive way of investigating pseudo-rotation via the pseudo-rotational puckering coordinate  $q$ , however, no direct information about the corresponding phase angle,  $\phi$ , has been obtained so far. In the case of cyclopentane<sup>45</sup>  $q_e = 0.0438$  nm, a value lower than effective puckering displacements based on thermodynamic or spectroscopic measurements. The observed C—C distance, 0.15460(12) nm, is longer (by 0.0013 nm) than in n-alkanes. Normal bond distances and angles have been found<sup>46</sup> in cyclopentene with a ring puckering angle of 29.0(2.5) degrees. Whereas in perfluorocyclopentene this is reduced<sup>47</sup> to 21.9(5) degrees, with C-4 out of the plane of the other carbon atoms. Perchlorocyclopentadiene is planar and shows<sup>47</sup> no structural abnormalities. The structure of cyclopentanone has also been determined<sup>48</sup> by gas-phase electron diffraction and a pseudo-rotational puckering potential ( $q_e = 0.038$  nm,  $\phi = 37.2$  degrees determined, which is lower than in cyclopentane. It is held that the lower torsional barrier and increased endocyclic valence angle in the C-5—C=O—C-2 moiety flattens the ring compared to that in the hydrocarbon. This is, of course substantiated by x-ray studies on the behaviour of ring D in steroids.

#### 1.2.2.3 Six- and eight-membered rings

Buys and Geise<sup>49</sup> have re-determined the molecular structure of cyclohexane and methylcyclohexane by gas-phase electron diffraction and found a higher ring puckering angle than previously reported. The new value, 55.9(4)

degrees, corresponds more closely to values obtained by x-ray diffraction (53.2–57.6 degrees), n.m.r. (58 degrees) and force-field calculations (55.2–56.1 degrees). Cyclohexene has been shown<sup>50</sup> to have a half-chair conformation with the expected bond lengths and angles, a comparison of the experimental endocyclic torsional angles with those derived from theoretical models is also given in this paper.

Cyclo-octa-1,3-diene adopts<sup>51</sup>  $C_i$  symmetry in the gas phase with an angle of 37.8 degrees between the planar ethylene groups, the double bonds are 0.1347 nm and that between them, C-2—C-3, is 0.1475 nm.

#### 1.2.2.4 Bicyclic and other systems

Two independent gas-phase electron diffraction studies<sup>52, 53</sup> of bicyclo[1.1.1]pentane have produced structures which do not agree. The Swedish group has discussed<sup>53</sup> the discrepancies in detail and it is suggested that a scaling error in one of the investigations may be the cause. Both  $D_{3h}$  and  $D_3$  symmetries have been used for refinement. For the latter, the C—C distance 0.1557(2) nm, is slightly longer than normal, and the non-bonded C-1...C-3 and C-2...C-4 distances are 0.1874 and 0.2151 nm respectively. The internal angle at the methylene carbon is 74.2(2) degrees, close to that in the 1-chlorobicyclo[1.1.1]pentane (see above). The structure<sup>54</sup> of bicyclo[2.1.0]pentane is notable for the short C-1—C-4 distance, 0.1439(15) nm, i.e. the zero-membered bridge, and long C-2—C-3 bond, 0.1622(16) nm. The cyclobutane ring is planar and a dihedral angle of 109.4(4) degrees is observed between the two ring planes present. Hexamethylbicyclo[2.2.2]hexa-2,5-diene (a Dewar benzene) has also been examined<sup>55</sup> and here the angle between the two cyclobutene rings is 124(1.5) degrees and the terminal methyl groups extend some 16 degrees out of the cyclobutene ring planes away from the bridge. At 0.163(1) nm the zero-membered bridge is the longest C—C single bond recorded, but the other C—C distances are close to the expected values. The molecule appears to be undergoing a large amplitude twisting motion about a minimum energy structure with  $C_{2v}$  symmetry, thus matching quite well the possible symmetry-correlation diagrams for the reversion path to benzene.

A comparison of the electron diffraction structures of bicyclo[2.2.1]heptane (norbornane) and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) shows<sup>56</sup> that the dihedral angles between the C-1—C-2—C-3—C-4 and C-4—C-5—C-6—C-1 planes are 113.1(1.8) and 115.6 (2.2) degrees respectively and all the carbon valence angles are less than tetrahedral and the C-1—C-7 bridge bonds are longer than C—C single bonds, the more so in the diene. The structure of bicyclo[2.2.2]octane has been determined<sup>57</sup>, and calculations on the potential function for twisting round the  $D_{3h}$  symmetry axis show a broad minimum with a barrier approximately 420 J mol<sup>-1</sup> in height at the  $D_{3h}$  conformation, i.e. the molecule has a quasi- $D_{3h}$  structure. A root-mean-square value of 12.0(1.5) degrees has been given for the dihedral angle of torsion round the C-2—C-3 axis along with a classical turning value of 21.5(5) degrees. The structures of bicyclo[2.2.2]octene and bicyclo[2.2.2]octadiene are essentially as expected<sup>58</sup>.