

Contents

Foreword 5

Introduction 9

Part One. Methods of Studying the Geometrical Structure of Free Molecules 11

Chapter I. Gas Phase Electron Diffraction Method 11

- I.1. General 11
- I.2. Atomic Scattering of Electrons 12
 - I.2.1. Elastic Scattering 13
 - I.2.2. Inelastic Scattering 16
 - I.2.3. Total Atomic Scattering Intensity 17
- I.3. Molecular Electron Scattering 17
 - I.3.1. Molecular Contribution to Scattering Intensity 17
 - I.3.2. The Application of the Fourier Transform to the Electron Diffraction Problem 20
 - I.3.3. Diatomic Molecules 21
 - I.3.4. Radial Distribution Curve for a Diatomic 24
 - I.3.5. Polyatomic Molecules 24
- I.4. Gas Phase Electron Diffraction Experiment 29
 - I.4.1. Basic Scheme of Electron Diffraction Unit 30
 - I.4.2. Microphotometer Measurements 33
 - I.4.3. Determination of Molecular Contribution to Scattering Intensity 33
- I.5. Interpretation of Electron Diffraction Patterns 35
 - I.5.1. Estimation of Uncertainties in Parameter Values 37
- I.6. Vibrational Effects in Molecular Structures Determined by Gas Phase Electron Diffraction 39
- I.7. Scope of Gas Phase Electron Diffraction Method 43

Chapter II. Spectroscopic Methods 46

- II.1. The Method of Microwave Spectroscopy 46
 - II.1.1. Rotational Spectra of Molecules 47
 - II.1.2. Scheme of the Microwave Experiment 52
 - II.1.3. Methods of Calculating Geometrical Parameters of Molecules 54
 - II.1.4. Structural Potential of the Microwave Method 60
- II.2. Other Spectral Methods 62
 - II.2.1. Pure Rotational Raman Spectra 63
 - II.2.2. High Resolution Infrared Spectra 63

Chapter III. Comparison of Electron Diffraction and Microwave Molecular Parameters 65

- III.1. Physical Meaning of Electron Diffraction and Spectroscopic Parameters 65
- III.2. Determination of the Geometry of Molecules by Combined Analysis of Electron Diffraction and Spectroscopic Experiments 69

Part Two. The Principal Stereochemical Results of the Study of Free Molecules of Organic and Organoelement Compounds 73

- Chapter IV. Acyclic Hydrocarbons 74**
- IV.1. Normal Saturated Hydrocarbons 74
 - IV.1.1. Bond Lengths 75
 - IV.1.2. Valence Angles 76
 - IV.1.3. Dihedral Angles or Conformations 77
 - IV.2. Branched Saturated Hydrocarbons 80
 - IV.3. Molecular Mechanics Calculations 82
 - IV.4. Alkenes and Cumulenes 83
 - IV.4.1. Bond Lengths 83
 - IV.4.2. Valence Angles 85
 - IV.4.3. Conformations 86
 - IV.5. Alkynes 87
 - IV.6. Environmental Effects on C—C Distances 88
- Chapter V. Compounds with Conjugated Bonds and Aromatic Hydrocarbons 90**
- V.1. Compounds with Conjugated Multiple Bonds 90
 - V.1.1. Hydrocarbons with Conjugated Double Bonds 90
 - V.1.2. Compounds with Conjugated C=C—C=O and O=C—C=O Bond Systems 91
 - V.1.3. Conformations of Molecules with Conjugated Double Bonds 98
 - V.1.4. Enynes and Polyynes. The Dependence of the Central Bond Length on the Type of Conjugated Multiple Bonds 101
 - V.2. Aromatic Hydrocarbons 103
 - V.2.1. Benzene and Its Homologues 103
 - V.2.2. Diphenyl and Its Derivatives 107
 - V.2.3. Condensed Aromatic Hydrocarbons 110
- Chapter VI. Alicyclic Hydrocarbons 113**
- VI.1. Saturated Monocyclic Hydrocarbons 113
 - VI.1.1. Bond Lengths 113
 - VI.1.2. Valence Angles 114
 - VI.1.3. Conformations 117
 - VI.2. Unsaturated Monocyclic Hydrocarbons 122
 - VI.2.1. Multiple Bonds in Cycles 122
 - VI.2.2. Multiple Bonds in Side Chains 124
 - VI.3. Spiranes 128
 - VI.4. Bicyclic Hydrocarbons 128
 - VI.4.1. Bicyclo[*m.n.0*]alkanes (alkenes) 128
 - VI.4.2. Bicyclo[*m.n.1*]alkanes (alkenes) 130
 - VI.4.3. Bicyclo[*m.n.2*]alkanes (alkenes) 133
 - VI.5. Polycyclic Hydrocarbons 134
- Chapter VII. Halogenated Hydrocarbons 135**
- VII.1. Bond Length and Bond Angle Variations 143
 - VII.2. Some Problems of Conformational Behaviour of Halogenated Hydrocarbons 146
- Chapter VIII. Compounds Containing Oxygen 148**
- VIII.1. Alcohols and Ethers 148
 - VIII.2. Aldehydes and Ketones 154
 - VIII.2.1. Formaldehyde, Acetaldehyde, Acetone and Their Homologues 154

Contents

VIII.2.2. Halogenated Derivatives of Acetone and Acetylacetone	157
VIII.2.3. Acetyl Halides	159
VIII.2.4. Ketenes	161
VIII.3. Carboxylic Acids, Their Dimers and Anhydrides	161
VIII.3.1. Carboxylic Acids and Their Dimers	161
VIII.3.2. Substituted Carboxylic Acids	163
VIII.3.3. Esters and Anhydrides of Carboxylic Acids	164
VIII.4. Derivatives of Hydrogen Peroxide	167
<i>Chapter IX. Compounds Containing Nitrogen</i>	169
IX.1. Simpler Aliphatic and Aromatic Amines	169
IX.1.1. Ammonia and Methylamines	169
IX.1.2. Halogenoamines	172
IX.1.3. Hydroxylamine Derivatives	173
IX.1.4. Organoelement Amine Compounds	174
IX.1.5. Derivatives of Hydrazine and Hydrazones	176
IX.1.6. Aromatic Amines	177
IX.2. Amides of Organic Acids	180
IX.3. Compounds Containing Two-Coordinate Nitrogen	183
IX.4. Nitriles and Cyanamide Derivatives	185
IX.5. Nitrocompounds	188
IX.6. Nitrosocompounds	197
<i>Chapter X. Organoelement Compounds</i>	198
X.1. Compounds Containing Group II Elements	198
X.2. Compounds Containing Group III Elements	200
X.2.1. Simple AX ₃ Compounds and Their Dimers	200
X.2.2. Carboranes	202
X.2.3. Donor-Acceptor Complexes	204
X.3. Compounds Containing Group IV Elements	206
X.4. Compounds Containing Group V Elements	210
X.5. Compounds Containing Group VI Elements	217
X.6. Compounds Containing Element-Halogen Bonds	224
X.7. Metal π -Complexes	226
X.8. Metal Acetylacetonates	230
<i>Chapter XI. Heterocyclic Compounds</i>	231
XI.1. Heterocyclic Compounds with Three- to Six-Membered Rings	231
XI.2. Discussion of Structural Data	238
XI.2.1. Saturated Heterocyclic Compounds	238
XI.2.2. Aromatic Heterocyclic Compounds	243
<i>Chapter XII. Free Radicals</i>	245
XII.1. General	245
XII.2. Experimental Data on Unstable and Stable Free Radicals	245
Conclusion	249
References	257
Index of Chemical Compounds	271