

Contents

Foreword V

Preface VII

List of Contributors XVII

- 1 Introduction 1**
- 1.1 Initial Remarks 1
Helena Dodziuk
- 1.2 Hydrocarbons with Unusual Spatial Structure: the Need to Finance Basic Research 5
Helena Dodziuk
- 1.3 Computations on Strained Hydrocarbons 12
Andrey A. Fokin and Peter R. Schreiner
- 1.4 Gallery of Molecules That Could Have Been Included in This Book 18
Helena Dodziuk
- 1.4.1 Introductory Remarks 18
- 1.4.2 Saturated Hydrocarbons 18
- 1.4.3 Distorted Double Bonds 21
- 1.4.4 Benzene Rings with Nontypical Spatial Structures 22
- 1.4.5 Cumulenes 25
- 1.4.6 Acetylenes 26
- References 27
- 2 Distorted Saturated Hydrocarbons 33**
- 2.1 Molecules with Inverted Carbon Atoms 33
Kata Mlinarić-Majerski
- 2.1.1 Introduction 33
- 2.1.2 Small-ring Propellanes: Computational and Physicochemical Studies 35
- 2.1.3 Small-ring Propellanes: Experimental Results 38
- 2.1.3.1 Preparation and Reactivity of [1.1.1]Propellane 38

Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis. Edited by Helena Dodziuk
Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-31767-7

- 2.1.3.2 Preparation and Reactivity of [2.1.1]Propellane and [2.2.1]Propellane 41
- 2.1.3.3 [1.1.1]Propellane as the Precursor for the Synthesis of Other Unusual Molecules 42
- 2.1.4 New Hypothetical Molecules with Inverted Carbon Atoms 43
- 2.2 Molecules with Planar and Pyramidal Carbon Atoms 44
Helena Dodziuk
- 2.3 A Theoretical Approach to the Study and Design of Prismane Systems 49
Tatyana N. Gribanova, Vladimir I. Minkin and Ruslan M. Minyaev
- 2.3.1 Introduction 49
- 2.3.2 Prismanes 49
- 2.3.3 Expanded Prismanes 52
- 2.3.3.1 Asteranes 52
- 2.3.3.2 Ethynyl-expanded Prismanes 54
- 2.3.4 Dehydroprismanes 55
- 2.3.5 Polyprismanes 56
- 2.3.5.1 Cubane Oligomers 56
- 2.3.5.2 Fused Prismanes 57
- 2.3.6 Conclusions 58
- 2.4 $(\text{CH})_{2n}$ Cage Structures, 'in'-'out' Isomerism in Perhydrogenated Fullerenes and Planar Cyclohexane Rings 59
Helena Dodziuk
- 2.4.1 $(\text{CH})_{2n}$ Cage Structures 59
- 2.4.1.1 Tetrahedrane 61
- 2.4.1.2 Triprismane 62
- 2.4.1.3 Cubane 61, Cuneane 100 and Octabisvalene 101 C_8H_8 62
- 2.4.1.4 $\text{C}_{10}\text{H}_{10}$ Saturated Cages 63
- 2.4.1.5 $\text{C}_{12}\text{H}_{12}$ Saturated Cages 63
- 2.4.1.6 Higher $[n]$ Prismanes, Dodecahedrane 64
- 2.4.1.7 'In'-'out' Isomerism in Perhydrogenated Fullerenes $\text{C}_{60}\text{H}_{60}$ 64
- 2.4.1.8 Summary 67
- 2.4.2 Planar Cyclohexane Rings 67
- 2.5 Ultralong C–C Bonds 70
Takanori Suzuki, Takashi Takeda, Hidetoshi Kawai and Kenshu Fujiwara
- 2.5.1 Introduction 70
- 2.5.2 Ultralong C–C Bonds Confined in a Stiff Molecular Frame 72
- 2.5.3 Tetraphenylnaphthocyclobutene as a Scaffold to Produce Ultralong C–C Bonds 73
- 2.5.4 'Clumped' Hexaphenylethane Derivatives with Elongated and Ultralong C–C Bonds 74
- 2.5.5 HPE Derivatives with a Super-ultralong C–C Bond 78
- 2.5.6 'Expandability' of the Ultralong C–C Bond: Conformational Isomorphs with Different Bond Lengths 79
- 2.5.7 Future Outlook 82

2.6	Ultrashort C–C Bonds	82
	<i>Vladimir Y. Lee and Akira Sekiguchi</i>	
2.6.1	Introduction	82
2.6.2	Tricyclo[2.1.0.0 ^{2,5}]pentanes: Ultrashort Endocyclic Bridging C–C Bonds	83
2.6.3	Coupled Cage Compounds: Ultrashort Exocyclic Intercage C–C Bonds	86
2.6.4	Sterically Congested <i>in</i> -Methylcyclophanes: Ultrashort C–C(Me) Bonds	91
2.6.5	Conclusions	91
	References	92
3	Distorted Alkenes	103
3.1	Nonplanar Alkenes	103
	<i>Dieter Lenoir, Paul J. Smith and Joel F. Liebman</i>	
3.1.1	Introduction and Context	103
3.1.2	Bridgehead Alkenes	103
3.1.2.1	<i>t</i> -Butyl-substituted Ethylenes	104
3.1.2.2	Investigations of <i>t</i> -Butylated Ethylenes and Other Acyclic Alkenes	106
3.1.2.3	Cyclo and Bicycloalkenes ... and on to Polycyclic Analogs	107
3.1.2.4	Adamantylideneadamantane and its Derivatives	108
3.1.2.5	<i>t</i> -Butyl-substituted and Cyclic Stilbenes	108
3.1.3	Multiply Unsaturated Bicycloalkenes, Homoaromaticity and Cyclophanes	109
3.1.3.1	The Most Distorted Ethylenes and Seemingly Simple Analogs	111
3.2	Small Ring and Cage Structures Involving Nonplanar C=C Bonds	112
	<i>Athanassios Nicolaidis</i>	
3.2.1	Pyramidalized Alkenes	112
3.2.1.1	Tricyclo[3.3.11.0 ^{3,7}]undec-3(7)-ene 38	115
3.2.1.2	Tricyclo[3.3.10.0 ^{3,7}]dec-3(7)-ene 39 and tricyclo[3.3.9.0 ^{3,7}]non-3(7)-ene 40	117
3.2.1.3	Tricyclo[3.3.0.0 ^{3,7}]oct-1(5)-ene 41	119
3.2.1.4	(Ph ₃ P) ₂ Pt Complexes	119
3.2.2	Conclusions	121
3.3	Strained Cyclic Allenes and Cumulenes	122
	<i>Richard P. Johnson and Kaleen M. Konrad</i>	
3.3.1	Introduction	122
3.3.2	Allene π Bond Deformations and Strain Estimates	123
3.3.3	Four- and Five-membered Ring Allenes	124
3.3.4	1,2-Cyclohexadienes	125
3.3.5	1,2,4-Cyclohexatrienes	127
3.3.5.1	6-Methylene-1,2,4-Cyclohexatrienes and Related Structures	131
3.3.6	Seven-membered Ring Allenes	131

- 3.3.6.1 Cycloheptatetraenes 132
- 3.3.7 Eight-membered Ring Allenes 134
- 3.3.8 Polycyclic Allenes 135
- 3.3.9 Cyclic Bisallenenes 136
- 3.3.10 Cyclic Butatrienes 136
- 3.3.10.1 Butatriene π Bond Deformations and Strain Estimates 137
- 3.3.10.2 Five- to Nine-membered Ring Cyclic Butatrienes 137
- 3.3.11 Conclusions 139
- References 140

- 4 Strained Aromatic Molecules 147**
- 4.1 Nonstandard Benzenes 147
Paul J. Smith and Joel F. Liebman
- 4.1.1 Introduction and Context 147
- 4.1.2 Alkylated Aromatics 148
- 4.1.3 Helicenes 148
- 4.1.4 [n]Circulenes 149
- 4.1.5 Cyclophanes 150
- 4.2 Distorted Cyclophanes 153
Henning Hopf
- 4.2.1 Introduction 153
- 4.2.2 The [n]Cyclophanes 154
- 4.2.2.1 [n]Paracyclophanes 154
- 4.2.2.2 [n]Metacyclophanes 160
- 4.2.3 The [m.n]Paracyclophanes 161
- 4.2.4 Distorted Aromatic Rings and 'Aromatic Character' 164
- 4.2.5 NMR Characteristics of Cyclophanes 165
- 4.3 Helicenes 166
Ivo Starý and Irena G. Stará
- 4.3.1 Introduction 166
- 4.3.2 Synthesis of Helicenes 166
- 4.3.3 Nonracemic Helicenes 171
- 4.3.4 Intriguing Helicene Structures 172
- 4.3.5 Physicochemical Properties and Applications 173
- 4.3.6 Theoretical Studies 175
- 4.3.7 Outlook 176
- 4.4 Cycloproparenes 176
Brian Halton
- 4.4.1 Introduction 176
- 4.4.2 Synthetic Considerations 177
- 4.4.3 Chemical Considerations 183
- 4.4.4 Heteroatom Derivatives 187
- 4.4.5 Physicochemical and Theoretical Considerations 188
- References 193

5	Fullerenes	205
5.1	Introduction	205
	<i>Helena Dodziuk</i>	
5.2	Chemistry Influenced by the Nontypical Structure: Modification of [60]Fullerene	208
	<i>Takuma Hara, Takashi Konno, Yosuke Nakamura and Jun Nishimura</i>	
5.2.1	Introduction	208
5.2.2	General Overview	209
5.2.3	Modification Reactions	215
5.2.3.1	Reduction and Oxidation	215
5.2.3.2	Alkylation	217
5.2.3.3	Cycloadditions	218
5.2.4	Conclusions	224
5.3	Physicochemical Properties and the Unusual Structure of Fullerenes	225
5.3.1	Single-crystal X-ray Structures of Fullerenes and Their Derivatives	225
	<i>Olga V. Boltalina, Alexey A. Popov and Steven H. Strauss</i>	
5.3.1.1	Introduction	225
5.3.1.2	Disorder	226
5.3.1.3	Nonplanar Steric Strain	226
5.3.1.4	Nonplanar Steric Strain Parameters	229
5.3.1.5	Are Non-IPR Fullerenes Sterically Unstable?	232
5.3.1.6	Long and Short C(sp ²)-C(sp ²) Bonds in Fullerene Cages	232
5.3.1.7	Steric Strain in C ₆₀ (X) _n Isomers	236
5.3.2	Vibrational and Electronic Spectra	238
	<i>Alexey A. Popov</i>	
5.3.2.1	Introduction	238
5.3.2.2	Vibrational Spectra of Fullerenes	239
5.3.2.3	The Orbital Picture of Fullerenes: High-energy Electronic Spectra	243
5.3.2.4	Electronic Excitations. UPS, UV/Vis/NIR Absorption and Fluorescence Spectroscopy	246
5.3.3	Nuclear Magnetic Resonance	250
	<i>Toni Shiroka</i>	
5.3.3.1	Introduction	250
5.3.3.2	NMR of Fullerenes	251
5.3.3.3	Concluding Remarks	259
5.3.4	Electrochemistry	259
	<i>Renata Bilewicz and Kazimierz Chmurski</i>	
5.3.4.1	Electronic Properties of Fullerenes	259
5.3.4.2	Electrochemical Properties of Soluble Fullerene Derivatives	263
5.3.4.3	Electrocatalytic Activity of Fullerenes	270
5.3.4.4	Conclusions and Outlook	272
5.4	Fullerene Aggregates	273

	<i>Tommi Vuorinen</i>	
5.4.1	Film Preparation Methods	274
5.4.2	Fullerene Film Properties	277
5.4.3	Conclusions	282
5.5	Endohedral Fullerenes with Neutral Atoms and Molecules	282
	<i>Sho-ichi Iwamatsu</i>	
5.5.1	Introduction	282
5.5.2	Preparation	282
5.5.2.1	Direct Approach Using an Existing Fullerene	282
5.5.2.2	Molecular Surgery Approach via an Open-cage Fullerene	284
5.5.2.3	Open-cage Fullerenes, Reversible Molecular Incorporations and Ejections	285
5.5.3	Properties	287
5.5.3.1	Host Fullerenes	287
5.5.3.2	Guest Substrates	288
5.5.4	Binding Energies, Theoretical Investigations	290
5.5.5	Summary	291
5.6	Hydrogenated Fullerenes	291
	<i>Mark S. Meier</i>	
5.6.1	Synthesis and Structure	291
5.6.2	C ₇₀ Chemistry	295
5.6.3	Higher Fullerenes	297
5.6.4	Reactivity of Hydrogenated Fullerenes	297
5.7	Applications of Fullerenes	299
	<i>Rosimiriã Pereira de Freitas and Jean-François Nierengarten</i>	
5.7.1	Introduction	299
5.7.2	Applications in Materials Science	299
5.7.2.1	C ₆₀ Derivatives for Optical Limiting Applications	299
5.7.2.2	C ₆₀ Derivatives for Photovoltaic Applications	304
5.7.3	Biological Applications	310
5.7.4	Conclusions	314
	References	315
6	Carbon Nanotubes	335
6.1	The Structure and Properties of Carbon Nanotubes	335
	<i>Anke Krueger</i>	
6.1.1	Introduction	335
6.1.2	The Structure of Single-walled Carbon Nanotubes	335
6.1.3	The Structure of Multi-walled Carbon Nanotubes	342
6.1.4	The Aromaticity of Carbon Nanotubes	345
6.1.5	Conclusions	347
6.2	The Functionalization of Carbon Nanotubes	347
	<i>Anke Krueger</i>	
6.2.1	Introduction	347
6.2.2	Functionalization of the Nanotube Tips	348

6.2.3	Non-covalent Functionalization of Carbon Nanotubes	349
6.2.4	Covalent Side-wall Functionalization of Carbon Nanotubes	352
6.2.5	Endohedral Functionalization of Carbon Nanotubes	355
6.2.6	Conclusions	356
6.3	Applications of Carbon Nanotubes	356
	<i>Marc Monthieux</i>	
6.3.1	Introduction	356
6.3.2	Properties of CNTs	357
6.3.2.1	Which CNT for Which Application?	357
6.3.2.2	Why is 'Nano' Beautiful?	358
6.3.2.3	Potential Problems Related to the Use of CNTs	360
6.3.3	Applications of CNTs	362
6.3.3.1	Prospective Applications	362
6.3.3.2	Applications Under Development	364
6.3.3.3	Applications on the Market	366
6.3.4	Conclusions	367
	References	368
7	Angle-strained Cycloalkynes	375
	<i>Henning Hopf and Jörg Grunenberg</i>	
7.1	Introduction	375
7.2	Cyclopropyne and Cyclobutyne: Speculations and Calculations on Non-isolable Cycloalkynes	376
7.2.1	Cyclopropyne and Related Systems	376
7.2.2	Cyclobutyne	378
7.3	Cyclopentyne, Cyclohexyne, Cycloheptyne: from Reactive Intermediates to Isolable Compounds	379
7.3.1	Cyclopentyne and its Derivatives	379
7.3.2	Cyclohexyne and its Derivatives	382
7.3.3	Cycloheptyne and its Derivatives	384
7.4	The Isolable Angle-strained Cycloalkynes: Cyclooctyne, Cyclononyne, and Beyond	385
7.4.1	Cyclooctyne and its Derivatives	385
7.4.2	Cyclononyne and Cyclodecyne	386
7.5	Cyclic Polyacetylenes	387
7.6	Spectroscopic Properties of Angle-strained Cycloalkynes	392
	References	393
8	Molecules with Labile Bonds: Selected Annulenes and Bridged Homotropilidenes	399
	<i>Richard V. Williams</i>	
8.1	Introduction	399
8.2	Annulenes	399
8.2.1	Cyclobutadiene	399
8.3	Cyclooctatetraene	403

8.4	Bond Shifting, Ring Inversion and Antiaromaticity	405
8.5	Valence Isomerization	409
8.6	Ions Derived from COT	410
8.7	The Higher Annulenes	411
8.8	Bridged Homotropilidenes	413
8.9	Recent Developments	415
8.9	Conclusions	419
	References	420
9	Molecules with Nonstandard Topological Properties: Centrohexaindane, Kuratowski's Cyclophane and Other Graph-theoretically Nonplanar Molecules	425
	<i>Dietmar Kuck</i>	
9.1	Introduction	425
9.1.1	Is All This Trivial?	425
9.2	Topologically Nonplanar Graphs and Molecular Motifs	427
9.2.1	The Centrohexasquinacene Core	427
9.2.2	The Nonplanar Graphs K_5 and $K_{3,3}$ and Some Molecular Representatives	428
9.3	Centrohexaindane	430
9.3.1	Centrohexaindane and Structural Regularities of the Centropolyindane Family	431
9.3.2	Syntheses of Centrohexaindane	433
9.3.3	Multiply-functionalized Centrohexaindanes	436
9.4	K_5 versus $K_{3,3}$ Molecules	438
9.4.1	Topologically Nonplanar Polyethers and Other $K_{3,3}$ Compounds	438
9.5	Kuratowski's Cyclophane	441
9.5.1	Synthesis of Kuratowski's Cyclophane	441
9.5.2	The Structure of Kuratowski's Cyclophane	443
9.6	Conclusions	444
	References	445
10	Short-lived Species Stabilized in 'Molecular' or 'Supramolecular Flasks'	449
	<i>Helena Dodziuk</i>	
	References	456
11	Concluding Remarks	459
	<i>Helena Dodziuk</i>	
	References	461
	Index	463