

# Molecular Catenanes, Rotaxanes and Knots

A Journey  
Through the World  
of Molecular Topology

Edited by  
J.-P. Sauvage and  
C. Dietrich-Buchecker



Weinheim · New York · Chichester  
Brisbane · Singapore · Toronto

This Page Intentionally Left Blank

Molecular Catenanes,  
Rotaxanes and Knots

Edited by  
J.-P. Sauvage and  
C. Dietrich-Buchecker

 **WILEY-VCH**

## Further Titles of Interest

N. V. Gerbeleu, V. B. Arion, J. Burgess

**Template Synthesis of Macrocyclic Compounds**

1999, ISBN 3-527-29559-3

K. Rück-Braun, H. Kunz

**Chiral Auxiliaries in Cycloadditions**

1999, ISBN 3-527-29386-8

F. T. Edelman, I. Haiduc

**Supramolecular Organometallic Chemistry**

1999, ISBN 3-527-29533-X

O. I. Kolodiaznyi

**Phosphorus Ylides**

Chemistry and Application in Organic Synthesis

1999, ISBN 3-527-29531-3

# Molecular Catenanes, Rotaxanes and Knots

A Journey  
Through the World  
of Molecular Topology

Edited by  
J.-P. Sauvage and  
C. Dietrich-Buchecker



Weinheim · New York · Chichester  
Brisbane · Singapore · Toronto

Prof. Dr. Jean-Pierre Sauvage  
Prof. Dr. Christiane Dietrich-Buchecker  
Faculté de Chimie  
Université Louis Pasteur  
4, rue Blaise Pascal  
F-67070 Strasbourg Cédex  
France

This book was carefully produced. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Cover Illustration: Prof. Dr. J.S. Siegel, La Jolla, USA / Dr. K. Baldrige, San Diego, USA

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloging-in-Publication Data:

**Molecular catanes, rotaxanes and knots** : a journey through the world of molecular topology / E. Wassermann ... Ed. by J.-P. Sauvage and C. Dietrich-Buchecker. – Weinheim ; New York ; Chichester ; Brisbane ; Singapore ; Toronto : Wiley-VCH, 1999  
ISBN 3-527-29572-0

© WILEY-VCH Verlag GmbH, D-69469 Weinheim (Federal Republic of Germany), 1999

Printed on acid-free and chlorine-free paper.

All rights reserved (including those of translation in other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition: K+V Fotosatz GmbH, D-64743 Beerfelden. Printing: betz-druck GmbH, D-64291 Darmstadt. Bookbinding: J. Schäffer GmbH & Co. KG., D-67269 Grünstadt.

Printed in the Federal Republic of Germany.

# Foreword

Almost a century has elapsed between Willstätters 'visionary' speculation about a molecule made of two interlocked rings – a catenane – and the today's outspreading molecular chemistry concerned with topology.

After the very early achievements due to the real pioneers of chemical topology who forty years ago first succeeded to that intriguing molecule that is a catenane (by statistical threading approach: Wasserman, 1960 or by a directed approach: Lüttringhaus and Schill, 1964), this peculiar field of research concerned with molecules whose prime feature rests without doubt on beauty and non trivial spacial arrangement, has in the beginning of the 80's literally exploded with the apparition of various templated approaches.

Creative imagination led chemists to use as templates either transition metals,  $\pi$  donor-acceptor effects or hydrogen bondings in order to build up around a central core or by multi-fragment interactions, more and more complex molecules, from the plain [2]-catenanes to higher entwined and complex molecular edifices like knots, doubly interlocked or poly-catenanes. Step by step, with an ever increasing rate and more and more sophisticated targets, the actual achievements realized by molecular chemists today go far beyond Willstätters original early dream.

But if in the beginning such molecules were mainly perceived as synthetic challenges, they were soon connected to nature and reality with the discovery in the early 60's of catenated or knotted DNA.

Unexpectedly, this field of research, actively supported by rigorous mathematical theories, glided furtively from pure curiosity towards much more concrete and tangible domains.

After numerous answers were brought to the synthetic challenge itself, there arose ever more insistently the quest for functions and properties of such special compounds. Already, even if still far from real applications, one can imagine, based on interlocked, threaded or knotted multi-component molecules, new organic materials, specific polymers, molecular devices or machines able to process and transfer energy, electrons or information.

We hope that the present book which gathers articles from very different scientific horizons will allow the reader to gain an overview on a fascinating broad area of science and to appreciate the long way covered in only a few decades.

## VI      *Foreword*

We would particularly like to thank each of the authors for making time in their busy schedules to contribute a chapter to this book.

*Jean-Pierre Sauvage, Christiane Dietrich-Buchecker*  
Strasbourg, September 1998



# Contents

<b>1</b>	<b>Chemical Topology – Statistical Musings</b>	<b>1</b>
1.1	Catenanes	1
1.2	Olefin Metathesis	3
1.3	Knots	4
	References	6
<b>2</b>	<b>A Knot Theoretic Approach to Molecular Chirality</b>	<b>7</b>
2.1	Topological Chirality of Knots and Links	7
2.2	Topological Chirality of Embedded Graphs	14
2.3	Topological Chirality of Molecular Knots and Links	16
2.4	Topological Chirality of Molecular Cell Complexes	18
2.5	Molecular Möbius Ladders and Related Molecules	21
2.6	Using Automorphisms to Prove Intrinsic Chirality	31
	References	34
<b>3</b>	<b>Soft and Hard Molecule-Based Magnets with a Fully Interlocked Three-Dimensional Structure</b>	<b>37</b>
3.1	Introduction	37
3.2	Molecular Magnetism	37
3.3	Magnetic Bricks	39
3.4	A Game of Bricks and Pieces of Mortar	40
3.5	Structure of Molecule-Based Magnets Containing Three Spin Carriers, with a Fully Interlocked Structure	44
3.6	Magnetic Properties	48
3.6.1	The Temperature Dependence of Magnetic Susceptibility	48
3.6.2	Field Dependencies of the Magnetization	51
3.7	Some Further Considerations	53
3.8	A Few Words to Conclude	54
	References	55

<b>4</b>	<b>Transition Metal-Incorporating Catenanes</b>	<b>57</b>
4.1	Introduction	57
4.2	Interlocked Compounds Containing Metals	58
4.2.1	Metal-Containing Rotaxanes	59
4.2.2	Metal-Templated Synthesis of Catenanes	59
4.2.3	Organometallic Catenanes and Rotaxanes	60
4.2.4	Self-Assembly of a [2]Catenane Incorporating (en)Pd(II) Units	62
4.2.4.1	Quantitative Self-Assembly of a Coordination Catenane	62
4.2.4.2	Mechanism of the Rapid Interconversion: Möbius Strip Mechanism	64
4.2.4.3	Irreversible Interlock of Molecular Rings	64
4.2.4.4	Electronic Effects in the Self-Assembly of Pd(II)-Linked Catenanes	66
4.2.5	Made-to-Order Assembling of Pd(II)-Linked Catenanes	68
4.2.5.1	Quantitative Formation of Catenanes from Rectangular Molecular Boxes	68
4.2.5.2	Selective Formation of Catenanes from Three Species-Eight Components	69
4.2.5.3	Scope and Limitations	71
4.3	Conclusion	74
	References	75
<b>5</b>	<b>Catenane and Rotaxane Motifs in Interpenetrating and Self-Penetrating Coordination Polymers</b>	<b>77</b>
5.1	Introduction	77
5.1.1	Nets	77
5.1.2	Interpenetration of Nets	79
5.2	Interpenetrating 1D Polymers	80
5.3	Interpenetrating 2D Networks	83
5.3.1	Parallel Interpenetration of 2D Frameworks	83
5.3.1.1	Interpenetrating Pairs of Sheets	83
5.3.1.2	Parallel Interpenetration of more than Two Sheets	87
5.3.1.3	Parallel Interpenetration of Sheets Other than (6,3) and (4,4)	87
5.3.1.4	Parallel Interpenetration of 2D Nets to Give a 3D Interlocked Composite	87
5.3.2	Inclined Interpenetration of 2D Frameworks	88
5.3.2.1	More Than One Sheet Passing Through Any Ring	89
5.4	Interpenetrating 3D Networks	91
5.4.1	Interpenetrating 3-Connected 3D Nets	91
5.4.1.1	Interpenetrating (10,3)-a Nets	92
5.4.1.2	Interpenetrating (10,3)-b Nets	93
5.4.1.3	Interpenetrating (8,3)-c Nets	94
5.4.2	Interpenetrating 4-Connected 3D Nets	94
5.4.2.1	Interpenetrating Diamond-Like Nets	94
5.4.2.2	Interpenetrating Quartz-Like Nets	95
5.4.2.3	Interpenetrating PtS-Like Nets	95

5.4.3	Interpenetrating 6-Connected 3D Nets . . . . .	95
5.4.3.1	Interpenetrating <i>a</i> -Po-Like Nets . . . . .	95
5.4.3.2	Interpenetrating 6-Connected Nets Unrelated to <i>a</i> -Po . . . . .	98
5.4.4	Interpenetrating 3D Nets Each Containing Two Types of Nodes with Different Connectivities . . . . .	99
5.4.5	Interpenetrating 3D Nets with Different Chemical Compositions . . .	101
5.4.5.1	Interpenetrating Nets of the Same Topology but Different Chemical Composition . . . . .	101
5.4.5.2	Interpenetrating 3D Nets of Different Topology . . . . .	102
5.5	Self-Penetrating and Self-Catenating Networks . . . . .	103
5.6	Closing Comments – Properties and Applications . . . . .	104
	References . . . . .	105
<b>6</b>	<b>Molecular Knots – From Early Attempts to High-Yield Template Syntheses . . . . .</b>	<b>107</b>
6.1	Introduction . . . . .	107
6.1.1	Topology – From Arts to Mathematics . . . . .	107
6.1.2	Biological Topology – DNA and Proteins . . . . .	109
6.1.3	Historical Perspectives – Catenanes and Chemical Knots . . . . .	111
6.1.4	The Various Routes Towards a Molecular Knot – Early Attempts . . . . .	112
6.1.4.1	Approaches Involving Randomness . . . . .	112
6.1.4.2	Attempts using Directed Syntheses . . . . .	114
6.1.4.3	Attempts Based on Templated Synthesis . . . . .	115
6.2	First Synthesis . . . . .	116
6.2.1	Strategy . . . . .	116
6.2.2	A Synthetic Molecular Trefoil Knot – First Results . . . . .	119
6.3	Generalization and Improvements . . . . .	123
6.3.1	Formation of Double-Stranded Helical Precursors with Polymethylene Linkers . . . . .	123
6.3.2	A Dramatic Improvement – Use of 1,3-Phenylene Spacer Between the Coordinating Units . . . . .	125
6.3.3	High-Yield Synthesis of a Dicopper(I) Trefoil Knot using Ring-Closing Metathesis Methodology . . . . .	126
6.4	Trefoil Knots as Transition Metal Ligands – Specific Kinetic, Electrochemical, and Photochemical Properties . . . . .	129
6.4.1	Topological Effect – The Polymethylene Bridged Complexes . . . . .	129
6.4.2	Structural Effect – The Phenylene Bridged Trefoil Knot Cu <sub>2</sub> (K-84) <sub>p</sub> <sup>2+</sup> . . . . .	132
6.5	Resolution of a Molecular Knot into its Enantiomers . . . . .	135
6.5.1	Strategy and Achievements . . . . .	135
6.5.2	Optical Properties and Perspectives . . . . .	137
6.6	Conclusion . . . . .	138
	References . . . . .	139

<b>7</b>	<b>Organic Template-Directed Syntheses of Catenanes, Rotaxanes, and Knots</b> .....	143
7.1	Brief History and Background .....	143
7.2	Pseudorotaxanes and Rotaxanes Incorporating Macrocyclic Polyethers and Secondary Dialkylammonium Salts as their Components .....	146
7.3	Pseudorotaxanes, Catenanes, Rotaxanes, and Knots Incorporating $\pi$ -Electron-rich and Deficient Components .....	153
7.4	Catenanes and Rotaxanes Incorporating Amide Recognition Sites in Their Components .....	163
7.5	Catenanes and Rotaxanes Incorporating Cyclodextrins as their Macrocyclic Components .....	166
7.6	Reflections and Opportunities .....	169
	References .....	170
<b>8</b>	<b>Amide-Based Catenanes, Rotaxanes and Pretzelanes</b> .....	177
8.1	Introduction .....	177
8.2	Amide-Based Catenanes .....	178
8.3	Amide-Based Rotaxanes .....	189
8.3.1	Clipping .....	190
8.3.2	Threading .....	191
8.3.3	Slipping .....	203
8.4	Chemistry with Amide-Based Catenanes and Rotaxanes .....	205
8.5	Stereochemistry of Amide-Based Catenanes and Rotaxanes .....	211
8.6	Conclusion and Outlook .....	216
8.7	Addendum .....	217
	References .....	219
<b>9</b>	<b>Polymer Chains in Constraining Environments</b> .....	223
	Synopsis .....	223
9.1	Introduction .....	224
9.2	Chains Constrained in Homogeneous (One-Phase) Systems .....	225
9.2.1	Inter-Chain Entanglements .....	225
9.2.2	Chain-Junction Entanglements and 'Constrained-Junction' Theory .....	225
9.2.3	'Constrained-Chain' Theory .....	227
9.2.4	'Diffused Constraints' Theory .....	227
9.2.5	'Slip-Link' Theory .....	228
9.2.6	Some Relevant Experiments .....	228
9.3	Sorption and Extraction .....	229
9.3.1	General Approach .....	229
9.3.2	Linear Diluents .....	230
9.3.3	Cyclic Diluents .....	231
9.4	Trapping of Cyclics .....	231

9.4.1	Experimental Results	231
9.4.2	Theoretical Interpretations	232
9.4.3	'Olympic' Networks	233
9.5	Chains Constrained within Second Phases or at Interfaces	233
9.5.1	Essentially One-Dimensional Systems	233
9.5.1.1	Zeolites as Illustrative Systems	233
9.5.1.2	Simple Mixing of a Polymer and a Zeolite	234
9.5.1.3	Polymerizing Monomer within Zeolite Cavities	234
9.5.2	Essentially Two-Dimensional Systems	236
9.5.2.1	Some Important Examples	236
9.5.2.2	Polymers Between Two Surfaces	236
9.5.2.3	Polymeric Coatings	237
9.5.2.4	Elastomers Bound to Reinforcing Filler Particles	238
9.5.3	Essentially Three-Dimensional Systems	238
9.5.3.1	General Features	238
9.5.3.2	Tubules	238
9.5.3.3	Mesoporous Silica	238
9.5.3.4	Vycor Glass	239
9.5.3.5	Thermoporimetry	239
	References	240
<b>10</b>	<b>Polycatenanes, Poly[2]catenanes, and Polymeric Catenanes</b>	<b>247</b>
10.1	Introduction	247
10.2	Polycatenanes Linked by Topological Bonds	250
10.3	Poly[2]catenanes Linked by Alternating Topological and Covalent Bonds	256
10.4	Catenated Cyclic Polymers	268
10.5	Conclusions and Perspective	272
	References	274
<b>11</b>	<b>Polyrotaxanes – Syntheses and Properties</b>	<b>277</b>
11.1	Introduction	277
11.2	General Principles of Polyrotaxane Syntheses	278
11.2.1	Nomenclature	278
11.2.2	Structural Requirements – Size of the Cyclic Species and Blocking Groups	280
11.2.3	Driving Forces for Threading	280
11.2.3.1	Statistical Threading and Chemical Conversion	281
11.2.3.2	Threading Driven by Enthalpy	281
11.3	Syntheses of Polyrotaxanes	285
11.3.1	Statistical Approaches	285
11.3.2	Hydrophilic-Hydrophobic Interactions	288
11.3.3	Hydrogen Bonding	294
11.3.4	Metal Templates	303

11.3.5	Self-Assembly – $\pi$ - $\pi$ Stacking and Charge Transfer	304
11.3.6	Other Complexes	307
11.4	Characterization	309
11.5	Properties and Potential Applications	311
11.5.1	Phase Behavior – Glass Transitions and Melting Temperatures	312
11.5.2	Electronic Properties	313
11.5.3	Solubility	313
11.5.4	Solution Viscosity and Melt Viscosity	315
11.5.5	Mechanical Properties	315
11.6	Conclusions and Some Perspectives	316
	References	318
<b>12</b>	<b>Synthetic DNA Topology</b>	<b>323</b>
12.1	Introduction	323
12.1.1	DNA Helicity Leads to Linked Topological Species	323
12.1.2	DNA Branching Topology	325
12.1.3	DNA as a Synthetic Material	326
12.2	Polyhedral Catenanes	328
12.2.1	A DNA Cube	328
12.2.2	A Solid-Support Methodology	329
12.2.3	A Truncated Octahedron	331
12.3	Knots	331
12.3.1	Knots, Catenanes and Nodes	331
12.3.2	DNA Knots	334
12.3.3	Topoisomerization of DNA Knots	335
12.3.4	An RNA Topoisomerase	335
12.4	Junctions, Antijunctions, and Mesojunctions	337
12.5	Borromean Rings	339
12.6	Topological Protection	341
12.7	DNA Double-Crossover Molecules	341
12.7.1	Motifs and Properties	341
12.7.2	Crossover Topology	344
12.7.3	Ligation of Double Crossover Molecules	344
12.7.4	Double-Crossover Molecules as a Route to Linear Catenanes and Rotaxanes	348
12.7.5	Two-Dimensional Arrays of Double-Crossover Molecules	349
12.8	Concluding Comments	351
12.8.1	Applications of Synthetic DNA Topology	351
12.8.2	Synthetic DNA Topology Leads to DNA Nanotechnology	353
	References	354
<b>Index</b>		<b>357</b>

# List of Authors

Stuart R. Batten  
Department of Chemistry  
Monash University  
Clayton Vic. 3168  
Australia

Christiane Dietrich-Buchecker  
Laboratoire de Chimie  
Organo-Minérale  
CNRS UMR 7513  
Faculté de Chimie  
Université Louis Pasteur  
67070 Strasbourg  
France

Erica Flapan  
Pomona College  
Department of Mathematics  
Claremont  
CA 91711  
USA

Makoto Fujita  
Institute for Molecular Science  
Laboratory of Coordination Chemistry  
Myodaiji, Okazaki 444-8585  
Japan

Yves Geerts  
Chercheur Qualifié au FNRS  
Université Libre de Bruxelles  
Chimie Macromoléculaire CP 206/1  
Boulevard du Triomphe  
1050 Bruxelles  
Belgique

Harry W. Gibson  
Department of Chemistry  
Virginia Polytechnic Institute  
and State University  
Blacksburg  
VA 24061  
USA

Caiguo Gong  
Department of Chemistry  
University of California  
Berkeley  
CA 94720  
USA

Christiane Heim  
Kekulé-Institut für Organische Chemie  
und Biochemie  
Universität Bonn  
Gerhard-Domagk-Str. 1  
53121 Bonn  
Germany

Olivier Kahn  
Laboratoire des Sciences Moléculaires  
Institut de Chimie de la Matière  
Condensée de Bordeaux  
UPR CNRS No 9048  
33608 Pessac  
France

J.E. Mark  
Department of Chemistry  
University of Cincinnati

XIV *List of Authors*

Cincinnati  
OH 45221-0172  
USA

Corine Mathonière  
Laboratoire des Sciences Moléculaires  
Institut de Chimie de la Matière  
Condensée de Bordeaux  
UPR CNRS No 9048  
33608 Pessac  
France

Lahcène Ouahab  
Laboratoire de Chimie du Solide  
et Inorganique Moléculaire  
UMR CNRS No 6511  
Université de Rennes I  
35042 Rennes  
France

Gwénaél Rapenne  
Laboratoire de Chimie  
Organo-Minérale  
CNRS UMR 7513  
Faculté de Chimie  
Université Louis Pasteur  
67070 Strasbourg  
France

Françisco M. Raymo  
Department of Chemistry  
and Biochemistry  
University of California Los Angeles  
405 Hilgard Avenue  
Los Angeles  
CA 90095-1569  
USA

Richard Robson  
School of Chemistry  
University of Melbourne  
Parkville 3052  
Victoria  
Australia

Jean-Pierre Sauvage  
Laboratoire de Chimie  
Organo-Minérale  
CNRS UMR 7513

Faculté de Chimie  
Université Louis Pasteur  
67070 Strasbourg  
France

Nadrian C. Seeman  
Department of Chemistry  
New York University  
New York  
NY 10003  
USA

J. Fraser Stoddart  
Department of Chemistry  
and Biochemistry  
University of California, Los Angeles  
405 Hilgard Avenue  
Los Angeles  
CA 90095-1569  
USA

Humberto O. Stumpf  
Departamento de Quimica ICEx  
Universidade Federal de Minas Gerais  
Belo Horizonte  
MG 31.270-901  
Brazil

Dirk Udelhofen  
Kekulé-Institut für Organische Chemie  
und Biochemie  
Universität Bonn  
Gerhard-Domagk-Str. 1  
53121 Bonn  
Germany

Fritz Vögtle  
Kekulé-Institut für Organische Chemie  
und Biochemie  
Universität Bonn  
Gerhard-Domagk-Str. 1  
53121 Bonn  
Germany

E. Wasserman  
E.I. DuPont de Nemours & Co.  
Wilmington  
DE 19880-0328  
USA



# 1 Chemical Topology – Statistical Musings

E. Wasserman

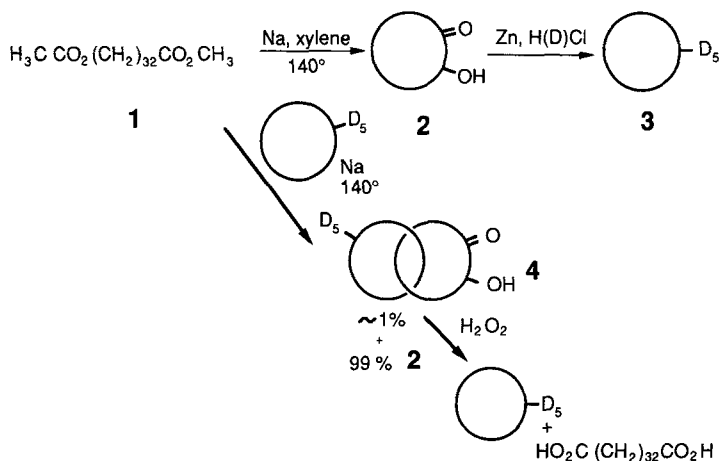
Chemical topology was undoubtedly discussed for decades before serious laboratory efforts began. When cyclic compounds were known, the imagination could play with conjectures about catenanes and knotted rings. In 1961, on a visit to V. Prelog at the ETH, he told me about a conversation with L. Ruzicka many years earlier. Ruzicka mentioned that R.M. Willstätter had discussed the possibility of interlocked rings in a talk in Zurich before 1912 [1]. The awareness of these three chemists, major contributors to our knowledge of small- and medium-sized rings ( $\lesssim 30$  carbon atoms), suggests that the concept of catenated cycles had been in the air for many years.

The broad landscape of chemical topology and topoisomerism has been summarized in comprehensive reviews [2–5]. The accomplishments of Schill, Walba, Sauvage, Stoddart, and others are landmarks in organic synthesis. This chapter describes a personal odyssey in which the focus is on statistical approaches – tinged by polymer science in their continual reference to the flexibility of chains. Some early laboratory efforts, and the technical considerations which led to them, are discussed, as is more recent activity.

## 1.1 Catenanes

I was introduced to interlocked rings in 1956 by M.S. Newman, a seminar speaker at Harvard. In informal discussion after the talk he described the proposal of a graduate student at Ohio State, L. Friedman, for a many-step synthesis of a catenane. The final reaction was cleavage of the two bonds connecting the linked and chemically bound rings.

I was intrigued. Mulling over the problem later that evening, and considering the need both to form and to detect catenanes, a statistical approach seemed attractive. Synthesis of a  $C_{30}$  ring from a linear precursor in the presence of an inert  $C_{20}$  cyclic compound should enable threading of some of the smaller rings before cyclization. A  $C_{50}$  product would indicate the presence of an interlocked system.



**Figure 1.** Experimental route to a 34,34-catenane.

At Bell Laboratories the following year, I manipulated space-filling models and found that a ring  $\gtrsim \text{C}_{24}$  was required for a polymethylene chain to pass through. Larger rings were preferred as they should be more likely to have sufficiently open conformations. The acyloin condensation of an  $\alpha, \omega$  diester offered a particularly efficient route to carbocycles. With the largest reported diacid containing 34 carbon atoms, these considerations pointed to a 34,34-catenane as the goal. The experimental route is given in Figure 1 [6].

After chromatographic removal of **3**, the cleavage of the catenane, **4**, to **3** and **1** was critical evidence of the structure. Numerous blank experiments excluded other possibilities. Figure 1 essentially describes a double-labeling experiment; deuterium for one ring and the acyloin function for the other, the labels detected by their infrared absorption [6]. The few milligrams of purified **3** could not be crystallized. The name ‘catenane’ was based on the Latin ‘catena’ for ‘chain’.

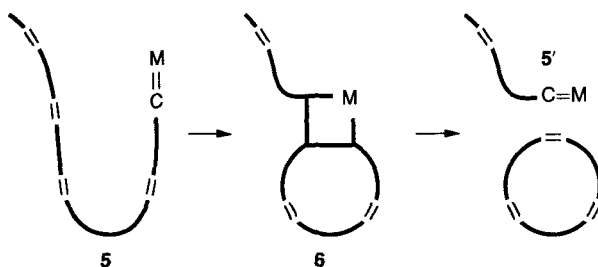
The stability of the catenated link under laboratory conditions, e.g. chromatography, is essentially demonstrated in Figure 1. Simple calculations of the probability of tunneling of one C-C bond through another gave unobservably small values. Although expected, the evidence for the robust structure was reassuring.

More information on threading was reported by Harrison and Harrison in some elegant studies. They demonstrated that a polymethylene could thread a  $\text{C}_{30}$  ring bound to a Merrifield resin to form a hooplane or rotaxane when the ends were capped [7]. Using a mixture of rings alkane chains were found to thread  $\text{C}_{24}$  and larger cycles with a probability which increased with ring size. Values of  $\sim 1\%$  were found near  $\text{C}_{30}$  [8]. The low probability of threading [6, 7] made the formation of multiply-threaded polymeric systems unlikely [9–11]. Attempts at synthesis were made by Lüttringhaus et al. [12] and by Lemal [13]. They constructed systems in which the closure of a second ring would have led to catenanes in high yield.

## 1.2 Olefin Metathesis

Another route to catenated structures became possible via the olefin metathesis reaction of Calderon et al. [14, 15]. With cyclododecene, oligomers up to  $C_{192}$  could be identified by mass spectrometry [16]. The original suggested mechanism involved a transient metal-complexed cyclobutane [14, 15]. With oligomers arising from repeated metathesis, twisting of the intermediate rings and another metathesis defines a Möbius-strip approach to catenated and knotted rings [17]. The mass spectral evidence [17] was consistent with catenanes.

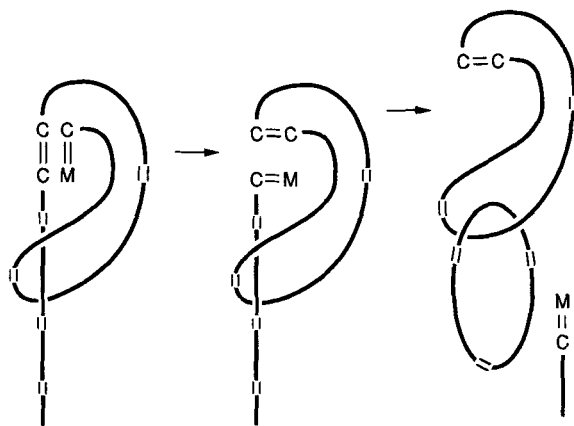
Shortly after these reports, mechanistic studies by Grubbs [18] established that metal-carbenes **5** and metalocyclobutane **6** are the critical intermediates, as shown in Scheme 1.



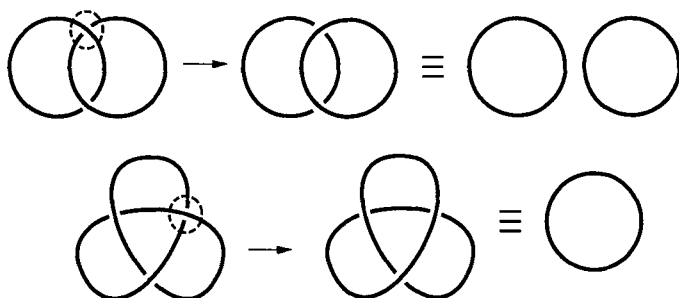
Scheme 1

This route provides access to catenanes (and knotted rings) without having to thread closed cycles, sharing an important feature of the Möbius path. The more complex ring structures arise from the tangling motions of the pendant chain before formation of the four-membered ring **6** (Scheme 2).

More generally, the metathesis reaction provides a laboratory analog of an important theorem in topology. Any linked or knotted structure can be converted to simple cycles (unknots) by selective interconversion of overcrossings and under-



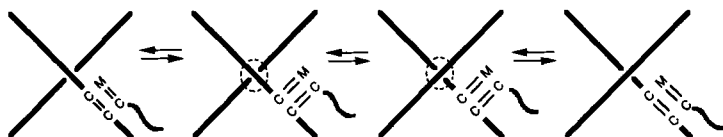
Scheme 2



Scheme 3

crossings – Scheme 3 [18]. Conversely, unknots of adequate size can be converted into any other linked or knotted species.

The metalocarbene, containing one carbon of a potential double bond, is a catalyst for the reversible breaking of an olefinic bond. Once broken the conversion of an overcrossing to an undercrossing is a change of conformation. Reforming the bond can freeze this new arrangement – Scheme 4.



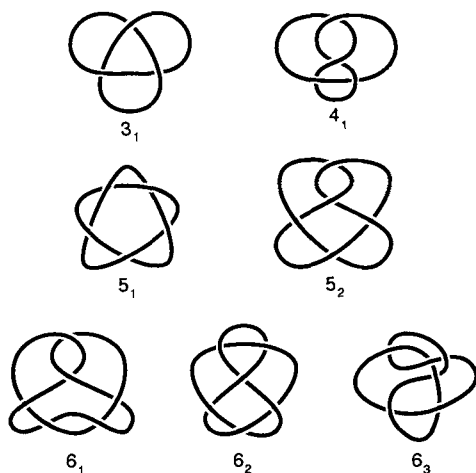
Scheme 4

The mass spectra [17] give a grossly simplified picture of the complex mixture which can result from a ring-opening polymerization. Knotted isomers can have almost identical mass spectra, dominated by the parent ion. With the reversibility of metathesis, the polyolefin mixture near equilibrium is expected to contain a large variety of knotted and linked species.

A molecular biology analog of Scheme 4 is the ability of topoisomerases to interchange different knots in DNA [19].

### 1.3 Knots

In reference 1 we noted that a cycloalkane with >50 carbon atoms could exist as a (chiral) trefoil, and one with >72 carbon atoms as a figure-of-eight. The minimum values are for a ‘tight’ knot, one with little flexibility. These numbers were obtained from models and the examination was not extended to larger molecules. In the intervening years the ability to synthesize more complex systems has greatly improved. A dramatic demonstration of this progress was the directed synthesis of a trefoil by C. Dietrich-Buchecker and J.-P. Sauvage in 1989 [20].



**Figure 2.** Threefold, fourfold, fivefold, and sixfold knots.

To examine the possibilities for knotted isomers in larger rings we note that two 5-fold knots (Figure 2) require  $\sim 83$  and  $\sim 92$  methylenes; the three 6-fold  $\sim 100$ ,  $\sim 102$ , and  $\sim 105$ . Thus a  $C_{100}$  cycloalkane might exist as one of  $\sim 5$  isomeric knots.

This sparse set of choices becomes richer with larger rings. With more crossings,  $n$ , the number of possible knots increases exponentially [21]. There are 21 for  $n=8$ , 165 for  $n=10$ , and 2176 for  $n=12$  [22]. Models indicate that many 12-fold knots should be stable in a cycloalkane of  $\sim C_{200}$ . The rapid increase in the number of possible knots between  $C_{100}$  ( $\sim 5$ ) and  $C_{200}$  ( $\sim 3000$ ) results from the dependence of allowed values of  $n$  on ring size.

One can excise  $\sim 4$  carbon atoms, and the loop in the shape of a lock-washer which pivots around them, to convert an  $n$ -crossing knot into an  $n-2$  knot. Some 30 carbon atoms are removed in this transformation. Examples would be the conversion of the 6-fold knots (Figure 2) into the figure-of-eight, removing 28, 30, or 33 carbon atoms. In general we expect the allowed  $n$  for tight knots to increase approximately linearly with the size of the ring.

There are  $>10^6$  knots for  $n=16$  [23] and by extrapolation there will be  $>10^7$  for  $n=18$ . Thus a ring of  $\sim 300$  carbon atoms has the potential for tens of millions of knotted isomers, most of which will be chiral. The laboratory tests of these conjectures are left as an exercise for the reader.

### Acknowledgments

Dr. L. Barash performed the Herculean labor of preparing the catenane, **3**. Drs A.M. Trozzolo and H.L. Frisch were always willing to engage in thought-provoking conversation. More recently, discussion with Professors D.W. Sumners, S.G. Whittington, and J. Simon familiarized me with recent mathematical advances relevant to chemical topology.

## References

- [1] (a) H.L. Frisch and E. Wasserman, *J. Am. Chem. Soc.* **83**, 3789 (1961); (b) Ruzicka, a student of Staudinger, moved with him to Zurich when the latter replaced Willstätter in 1912. (Y. Furukawa, *Inventing Polymer Science*, University of Pennsylvania Press, 1998, p. 54). Thus Ruzicka probably did not hear Willstätter's first discussion of the subject.
- [2] G. Schill, *Catenanes, Rotaxanes, and Knots*. Academic Press, 1971.
- [3] D.M. Walba, *Tetrahedron* **41**, 3161 (1985).
- [4] C.O. Dietrich-Buchecker and J.P. Sauvage, *Chem. Rev.* **87**, 795 (1987).
- [5] D.M. Amabilino and J.F. Stoddart, *Chem. Rev.* **95**, 2725 (1995).
- [6] E. Wasserman, *J. Am. Chem. Soc.* **82**, 4433 (1960).
- [7] I.T. Harrison and S. Harrison, *J. Am. Chem. Soc.* **89**, 5723 (1967).
- [8] I.T. Harrison, *J. Chem. Soc., Chem. Comm.*, 1972, 231; *J. Chem. Soc., Perkin Trans. I*, 1974, 301.
- [9] H. Frisch, I. Martin, and H. Mark, *Monatsh.* **84**, 250 (1953).
- [10] H. Frisch of references 9 and 1 was a colleague at Bell with a continuing interest in statistical and topological subjects.
- [11] P. Patat and P. Derst, *Angew. Chem.* **71**, 105 (1959).
- [12] A. Lüttringhaus, F. Cramer, H. Prinzbach, and F.M. Henglein, *Ann.*, **613**, 185 (1958).
- [13] D. Lemal, personal communication.
- [14] N. Calderon, H.Y. Chen, and K.W. Scott, *Tetrahedron Lett.* **34**, 3327 (1967).
- [15] N. Calderon, E.A. Ofstead, J.P. Ward, W.A. Judy, and K.W. Scott, *J. Am. Chem. Soc.* **90**, 4133 (1968).
- [16] E. Wasserman, D.A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.* **90**, 3286 (1968). Oligomers  $C_{132}$  to  $C_{192}$  were identified after this publication (with M.L. Kaplan).
- [17] (a) D.A. Ben-Efraim, C. Batich, and E. Wasserman, *J. Am. Chem. Soc.* **92**, 2133 (1970); (b) R. Wolovsky, *J. Am. Chem. Soc.* **92**, 2132 (1970).
- [18] C.C. Adams, *The Knot Book*. W.H. Freeman and Co., New York, 1994, Chapter 3.
- [19] (a) C.C. Adams, *The Knot Book*, W.H. Freeman and Co., New York, 1994, Chapter 7; (b) S.A. Wasserman and N. Cozzarelli, *Science* **232**, 951 (1986).
- [20] C. Dietrich-Buchecker and J.P. Sauvage, *Angew. Chem.* **28**, 189 (1989).
- [21] C. Ernst and D.W. Sumners, *Proc. Cambridge Phil. Soc.* **102**, 303–315, (1987).
- [22] C.C. Adams, *The Knot Book*. W.H. Freeman and Co., New York, 1994, p. 33. In addition to the prime knots listed we expect several dozen composite knots for  $n=12$ .
- [23] M. Thistlethwaite, personal communication.

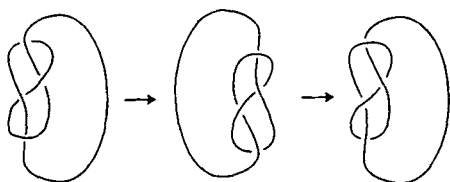
## 2 A Knot Theoretic Approach to Molecular Chirality

Erica Flapan

This chapter will begin by explaining some topological techniques to prove that a knot, link, or embedded graph cannot be deformed to its mirror image. We shall explain how to use these topological techniques to prove that the graphs of many of the recently synthesized chemical knots and links cannot be deformed to their mirror images. Then we present an alternative approach to analyzing whether a molecular structure can be deformed to its mirror image, by using a molecular cell complex rather than a molecular graph to represent a molecule. We will present examples of molecular cell complexes, and explain how to prove that an embedded cell complex cannot be deformed to its mirror image. Finally, we give examples of chiral molecules whose molecular cell complexes cannot be deformed to their mirror images yet whose molecular graphs can be deformed to their mirror images. Thus in these examples, the topology of the molecule is more accurately represented by a molecular cell complex than by a molecular graph.

### 2.1 Topological Chirality of Knots and Links

Topologists became interested in chirality with the development of knot theory, which itself grew out of chemistry. In the late nineteenth century, Lord Kelvin developed the theory that atoms were vortex rings which were knotted or linked in different ways according to what element they were [1]. Motivated by this theory, Peter Guthrie Tait created tables of different knots and links with the hope of building a periodic table [2]. Tait defined a *knot* to be a simple closed curve in 3-space, and a *link* to be one or more disjoint simple closed curves in 3-space. He defined two knots or links to be topologically equivalent if one can be deformed to the other, where a deformation of a knot or link does not permit the knot or link to pass through itself. In order to provide a list of topologically distinct knots and links, Tait tried to determine whether or not each knot and link could be deformed to its mirror image.



**Figure 1.** A deformation of a figure eight knot to its mirror image.

Ever since Tait's seminal papers on knot theory [2], topologists have been interested in which knots and links are topologically distinct from their mirror image. Nonetheless, the word 'chirality' was not used to describe knots and links until the 1980s. Prior to that time, topologists utilized Tait's terminology which defined a knot or link to be *amphichiral* if it could be deformed to its mirror image. There was no specific word to refer to a knot or a link which was not amphicheiral. As a result of the increase in communication between topologists and chemists since the early 1980s, the term *topologically achiral* is now commonly used as a synonym for amphicheiral, and knots or links which are not amphicheiral are said to be *topologically chiral*. Note that for molecular graphs the word 'achiral' can have different meanings depending on how flexible the graph is. In order to make it clear that the knots and links we are considering are completely flexible, we always speak of topological achirality rather than simply achirality.

For a knot or link which has few crossings, it may not be too difficult to see how to deform it to its mirror image. For example, Figure 1 illustrates how the figure eight knot can be deformed to its mirror image. To get from the first picture in Figure 1 to the second picture, you rotate the knot by  $180^\circ$  about a vertical axis. Then to get to the third picture, you flip the long string over the knotted arc without moving the knotted arc. This final picture is the mirror image of the first picture, where the mirror is in the plane of the paper. This means that the mirror has the effect of interchanging all of the overcrossings and undercrossings.

In most cases, simply examining a knot or link is not sufficient to determine whether or not it is topologically chiral. If we cannot find a deformation of it to its mirror image this does not necessarily mean that such a deformation does not exist. Perhaps if we just kept trying we would eventually find the deformation, or perhaps the knot or link is actually topologically chiral. In order to avoid this uncertainty, topologists have developed techniques to recognize when knots and links are topologically chiral. One important technique is to make use of one of the collection of link polynomials which have recently been created. We project our knot or link onto a plane in such a way that at most two points of the knot or link are projected down to the same point. Then we indicate each undercrossing by drawing a gap where one strand is meant to go under another strand. For example, Figure 1 illustrates several projections of the figure eight knot. We orient a knot by drawing an arrow to indicate in which direction we shall traverse the knot. A link is oriented by putting an arrow on every component of the link.

There are several link polynomials which are convenient to use, notably the Jones polynomial [3], the Kauffman polynomial [4], and the 2-variable HOMFLY polynomial [5]. These polynomials are all easy to explain and somewhat similar



in flavor, so we present only one, the HOMFLY polynomial named after five of the authors who discovered it, Hoste, Ocneanu, Millett, Freyd, Lickorish, and Yetter. It was also independently discovered by Przytycki and Traczyk [6]. This polynomial is sometimes simply called the P-polynomial. All the link polynomials are actually Laurent polynomials, which means that the variables in the polynomials can be raised to negative as well as positive powers.

Before we define the P-polynomial we need to clarify our terminology. Recall that the word ‘link’ refers to one or more simple closed curves, so when it is convenient, we shall use the word ‘link’ to mean a knot or link. The *unknot* is defined as any simple closed curve which can be deformed into a plane, and the *unlink* is defined as any collection of one or more simple closed curves which can be deformed into the plane. We begin by fixing a particular projection of an oriented link  $L$ . The P-polynomial of  $L$  will be defined in terms of the crossings of this oriented projection. We want to distinguish two different types of oriented crossings which we will call positive crossings and negative crossings. These two types of crossings are illustrated in Figure 2. Every crossing can be rotated to look like one of the two crossings in Figure 2. Furthermore, no matter how a positive crossing is rotated, it will never become a negative crossing, and no matter how a negative crossing is rotated, it will never become a positive crossing.



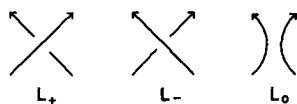
**Figure 2.** A positive crossing and a negative crossing.

The P-polynomial is defined recursively. This means that we compute the P-polynomial of an oriented link in terms of the polynomials of simpler oriented links, which in turn are computed in terms of the polynomials of oriented links which are simpler still, and so on until we get a collection of unknots each of whose polynomial is known to equal 1.

The P-polynomial  $P(L)$  has variables  $m$  and  $l$  and is formally defined from the oriented projection of  $L$  by using the following two axioms.

Axiom 1.  $P(\text{unknot}) = 1$ ,

Axiom 2. Suppose  $L_+$ ,  $L_-$ , and  $L_0$  are oriented link projections which are identical except near a single crossing where they differ by a positive, negative, or null crossing respectively (these three possibilities are illustrated in Figure 3). Then we have  $lP(L_+) + l^{-1}P(L_-) + mP(L_0) = 0$ .



**Figure 3.**  $L_+$ ,  $L_-$ , and  $L_0$  are identical except at this crossing.

From its definition, the P-polynomial appears to depend on the particular projection of the link which we are working with. However, when this polynomial was defined it was proven that given any oriented link, no matter how it is deformed or projected, the link will always have the same P-polynomial [5, 6]. This means that two oriented links which are topologically equivalent have the same P-polynomial. In particular, if an oriented link can be deformed to its mirror image then it and its mirror image will have the same P-polynomial.

We illustrate how to compute the P-polynomial by evaluating a couple of examples. First let  $L_0$  consist of the oriented unlink of two components which is illustrated in Figure 4. Then  $L_+$  and  $L_-$  are as shown in the figure. Now we use the second axiom of the definition of the P-polynomial, together with the observation that both  $L_+$  and  $L_-$  are topologically equivalent to the unknot, in order to obtain the equation  $l + l^{-1} + mP(L_0) = 0$ . Hence, we conclude that  $P(L_0) = -m^{-1}(l + l^{-1})$ .



Figure 4.  $L_+$ ,  $L_-$ , and  $L_0$ .

We shall use this result to enable us to compute the P-polynomial of the oriented link, illustrated as  $L_-$  in Figure 5. This link is known as the *Hopf link*. We choose the upper crossing to change so that we have  $L_+$  and  $L_0$  as indicated in the figure.

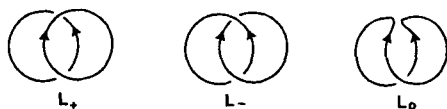


Figure 5. We compute the P-polynomial of the oriented Hopf link which is represented by  $L_-$ .

Now we see that  $L_0$  can be deformed to the unknot and  $L_+$  can be deformed to the link whose polynomial we computed previously. So we substitute these polynomials into the equation of Axiom 2, in order to get the equation  $l(-m^{-1}(l + l^{-1})) + l^{-1}P(L_-) + m = 0$ . Thus, after some simplification, we get  $P(L_-) = l^3m^{-1} + lm^{-1} - lm$ .

It can be seen from these simple examples that computing the P-polynomial of any complicated oriented link will be quite cumbersome. However, there are a number of excellent computer programs which will compute all of the link polynomials for any oriented link which can be drawn with up to about 50 crossings (for example, the program KNOTTHEORY by COMPUTER written by M. Ochiai, and available through anonymous ftp [7]).

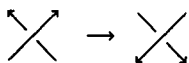
Notice that the orientation of a link may affect its polynomial. For example, the Hopf link in Figure 6 has one component which is oriented in a different di-



**Figure 6.** A Hopf link with a different orientation from that of  $L_-$  in Figure 5.

resection from the Hopf link which is illustrated as  $L_-$  in Figure 5. The P-polynomial of this new Hopf link turns out to equal  $l^{-3}m^{-1} + l^{-1}m^{-1} - l^{-1}m$ . The roles of  $l$  and  $l^{-1}$  in this polynomial have been reversed relative to the P-polynomial of the Hopf link illustrated as  $L_-$  in Figure 5.

In contrast with links, we can see as follows that the orientation of a knot has no effect on its polynomial. Suppose that  $L$  is a knot. Then reversing the orientation of  $L$  results in reversing all of the arrows in the diagram. In particular, it reverses the direction of both arrows occurring at any crossing. As can be seen from the positive crossing illustrated in Figure 7, a positive crossing remains positive after both arrows are reversed. Reversing the arrows simply has the effect of rotating the crossing by  $180^\circ$ . Similarly, negative crossings and null crossings remain unchanged by reversing all of the arrows of a diagram. Thus the P-polynomial of a knot  $L$  is independent of the orientation of the knot.



**Figure 7.** A positive crossing in a knot is independent of the orientation of the knot.

The link polynomials can be quite helpful if we wish to show that a specific oriented link is topologically chiral. So far we have only defined topological chirality for unoriented links. We now define an oriented link  $L$  to be *topologically achiral* if there is deformation taking the oriented link  $L$  to the mirror image of  $L$  with the corresponding orientation. An oriented link which is not topologically achiral is said to be *topologically chiral*. The theorem below, which follows from [5] and [6], tells us how to use the P-polynomial to prove that an oriented link is topologically chiral. For knots, we saw that the P-polynomial is independent of the choice of orientation. So we do not have to specify a knot's orientation in order to compute its polynomial. Thus the theorem tells us how to use the P-polynomial to prove that an unoriented knot is topologically chiral.

**Theorem.** Let  $L$  be an oriented link with P-polynomial  $P(L)$ . Let  $\bar{P}(L)$  denote the polynomial obtained from  $P(L)$  by interchanging  $l$  and  $l^{-1}$ . If  $P(L) \neq \bar{P}(L)$  then the oriented link  $L$  is topologically chiral. If  $K$  is a knot and  $P(K) \neq \bar{P}(K)$  then the unoriented knot  $K$  is topologically chiral [5, 6].

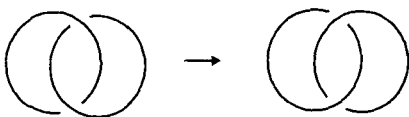
In order to see how to apply this theorem we can consider the oriented Hopf link which was illustrated in Figure 5. We determined above that the P-polynomial of this oriented Hopf link  $L$  is  $P(L) = l^3m^{-1} + lm^{-1} - lm$ . If we interchange  $l$  and  $l^{-1}$  we will obtain the polynomial  $\bar{P}(L) = l^{-3}m^{-1} + l^{-1}m^{-1} - l^{-1}m$ . Since  $P(L) \neq \bar{P}(L)$ , the theorem tells us that the oriented Hopf link is topologically chiral. This



**Figure 8.** An oriented Hopf link is topologically chiral.

means that there is no deformation which takes the Hopf link on the left side of Figure 8 to the Hopf link on the right side of Figure 8.

On the other hand, as an unoriented link the Hopf link is topologically achiral. This can be seen in Figure 9. In order to go from the first to the second picture we turn over the right hand component of the link. We can see that the second diagram is the mirror image of the first where the mirror is in the plane of the paper. However, for the oriented Hopf link of Figure 8, turning over one component would have the effect of reversing the orientation of the corresponding component of the mirror image.



**Figure 9.** By turning over one component we obtain the mirror image of the unoriented Hopf link.

For knots, we can apply the theorem without having to worry about the orientations. For example, the right handed trefoil knot, which is drawn in Figure 10, has P-polynomial  $P(L) = -l^{-4} + l^{-2}m^2 - 2l^{-2}$  regardless of how it is oriented. This polynomial is clearly not symmetric with respect to  $l$  and  $l^{-1}$ , so we can immediately conclude that the trefoil knot is topologically chiral. With the help of one of the computer programs to compute link polynomials, we can use the above theorem to recognize many topologically chiral knots and oriented links.



**Figure 10.** A trefoil knot is topologically chiral.

Note that the theorem does not detect all topologically chiral knots and oriented links, because there are topologically chiral knots and oriented links whose P-polynomials are nonetheless symmetric with respect to  $l$  and  $l^{-1}$ . For example, consider the knot which is illustrated in Figure 11. This knot is known by knot theorists as  $9_{42}$  because this is the forty second knot with 9 crossings listed in the standard knot tables (see the tables in Rolfsen's book [9]). Using a computer program we find that the P-polynomial of the knot  $9_{42}$  is  $P(9_{42}) = (-2l^{-2} - 3 - 2l^2) + m^2(l^{-2} + 4 + l^2) - m^4$ . Observe that this polynomial is symmetric with respect



**Figure 11.** The knot  $9_{42}$  is topologically chiral.

to  $l$  and  $l^{-1}$ . So we cannot apply the theorem. However, using more sophisticated techniques it is possible to show that this knot is topologically chiral.

We can also use link polynomials to prove that certain unoriented links are topologically chiral. For example, let  $L$  denote the  $(4,2)$ -torus link which is illustrated on the left in Figure 12. This is called a *torus link* because it can be embedded on a torus (i.e. the surface of a doughnut) without any self-intersections. It is a  $(4,2)$ -torus link, because, when it lies on the torus, it twists four times around the torus in one direction, while wrapping two times around the torus the other way. Let  $L'$  denote the oriented link that we get by putting an arbitrary orientation on each component of the  $(4,2)$ -torus link, for example, as we have done in Figure 12. Now the P-polynomial of  $L'$  is  $P(L') = -l^{-5}m^{-1} - l^{-3}m^{-1} + ml^{-5} - m^3l^{-3} + 3ml^{-3}$ .



**Figure 12.** The unoriented and oriented  $(4,2)$ -torus link.

We create the link  $L^*$ , the mirror image of the unoriented link  $L$ , by switching all of the crossings of  $L$ . Since  $L^*$  has two components, there are four ways to orient  $L^*$ . Two of these orientations for  $L^*$  are illustrated as  $L_1$  and  $L_2$  in Figure 13. There are two additional ways of orienting  $L^*$ , however, each one of these will reverse the direction of both arrows at each crossing relative to one of the oriented links in Figure 13 and so will have the same polynomial as  $L_1$  or  $L_2$ . We now compute the P-polynomial of each of the oriented links in Figure 13. These polynomials turn out to be  $P(L_1) = -l^5m^{-1} - l^3m^{-1} + ml^5 - m^3l^3 + 3ml^3$  and  $P(L_2) = -m^{-1}l^{-3} - m^{-1} - m^{-1}l^{-5} + ml^3$ . We prove that the unoriented  $(4,2)$ -torus



**Figure 13.** We orient the link  $L^*$  in two different ways to get  $L_1$  and  $L_2$ .

link is topologically chiral by contradiction. Suppose that the link  $L$  could be deformed to its mirror image. Hence the oriented (4,2)-torus link could be deformed to  $L^*$  with some orientation. The P-polynomial of the oriented (4,2)-torus link  $L'$  should therefore equal the P-polynomial of either  $L_1$  or  $L_2$ . As this is not the case, we can conclude that the unoriented (4,2)-torus link is topologically chiral.

## 2.2 Topological Chirality of Embedded Graphs

Stimulated by the development of the interdisciplinary field of topological chemistry, topologists have extended some of the techniques from knot theory to the theory of graphs in 3-space. Graph theorists typically study graphs as abstract objects made up of vertices and edges, while topologists study graphs which have a specified position in 3-space. Such a graph is viewed as a topological object in 3-space which can be deformed but cannot pass through itself. To make it clear that we are talking about graphs in 3-space rather than abstract graphs, we refer to such graphs as *spatial graphs* or *embedded graphs*. A molecular bond graph has a configuration in space and so is an example of an embedded graph. If we add a finite number of vertices to any knot or link, we have another example of an embedded graph. By analogy with knots and links, an embedded graph is said to be *topologically achiral* if it can be deformed to its mirror image, and otherwise it is said to be *topologically chiral*.

A graph is said to be *n-valent* if every vertex of the graph has  $n$  edges coming out of it. Various results in knot theory have been extended to 3-valent and 4-valent embedded graphs. In particular, Kauffman [9] has developed a polynomial for a specific type of 4-valent embedded graphs known as rigid vertex graphs, and Yamada [10] has developed a polynomial for 3-valent embedded graphs. These polynomials are related to link polynomials and can also be used to detect topological chirality for these specific types of embedded graphs. For arbitrary embedded graphs, Kauffman also has a method of associating a collection of knots and links to the embedded graph and using these knots and links to demonstrate the topological chirality of the embedded graph [9]. We shall explain Kauffman's method in detail below.

Let  $G$  be an embedded graph. Define  $T(G)$  to be the set of all knots and links which are contained in the embedded graph  $G$ . That is,  $T(G)$  contains every knot and link which can be obtained by joining two edges together at each vertex and disconnecting all other edges from that vertex. Performing this operation at all of the vertices may create a number of arcs which are not closed up, but  $T(G)$  does not include any of these arcs.

For example, consider the embedded graph  $G$  illustrated in Figure 14. The total collection of arcs and simple closed curves that we get by performing this operation at the vertices is illustrated in Figure 15, and the elements of the set  $T(G)$  are illustrated in Figure 16.