Acetylene Chemistry

Chemistry, Biology and Material Science

Edited by F. Diederich, P.J. Stang, R. R. Tykwinski



WILEY-VCH Verlag GmbH & Co. KGaA

Acetylene Chemistry

Edited by

F. Diederich, P. J. Stang,

R. R. Tykwinski

Further Reading from Wiley-VCH

A. de Meijere, F. Diederich (Eds.)

Metal-Catalyzed Cross-Coupling Reactions, 2nd Ed., 2 Vols.

2004, ISBN 3-527-30518-1

R. Mahrwald (Ed.)

Modern Aldol Reactions, 2 Vols.

2004, ISBN 3-527-30714-1

N. Krause, A.S.K. Hashmi (Eds.)

Modern Allene Chemistry, 2 Vols.

2004. ISBN 3-527-30671-4

R. Gleiter, H. Hopf (Eds.)

Modern Cyclophane Chemistry

2004, ISBN 3-527-30713-3

Acetylene Chemistry

Chemistry, Biology and Material Science

Edited by F. Diederich, P.J. Stang, R. R. Tykwinski



WILEY-VCH Verlag GmbH & Co. KGaA

Editors:

Prof. Dr. François Diederich Laboratorium für Organische Chemie ETH Hönggerberg, HCI CH-8093 Zürich Switzerland

Prof. Dr. Peter J. Stang
Department of Chemistry
University of Utah
315S 1400E, Rm. 2020
84112 Salt Lake City
USA

Prof. Dr. Rik R. Tykwinski Department of Chemistry University of Alberta T6G 2G2 Edmonton Canada All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, 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.

Library of Congress Card No.: applied for British Library Cataloguing-in-Publication Data:

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

Bibliographic information published by Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at http://dnb.ddb.de>.

© WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005

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.

Printed in the Federal Republic of Germany. Printed on acid-free paper.

Typesetting hagedorn kommunikation, Viernheim Printing betz-druck gmbh, Darmstadt Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN 3-527-30781-8

Preface

The carbon-carbon triple bond is a common structural motif in organic chemistry. Only during the past two decades, however, has it become a mainstay in the toolbox of synthetic organic chemists, biochemists, and materials scientists. Both as a building block and as a versatile synthon, the fascinating and sometimes unpredictable chemistry associated with the alkyne moiety has fueled many of the most recent advances. A decade ago, the monograph *Modern Acetylene Chemistry* documented an emerging renaissance in the chemistry of the carbon-carbon triple bond. Over the past ten years, this renaissance has evolved at an astounding rate and acetylenes now constitute a principal class of compounds in nearly all areas of chemistry and materials science.

The explosive growth of acetylene chemistry has particularly benefited from the development of new synthetic methodology based on transition metal catalysts and metal acetylides. An acetylene unit can now be introduced into nearly any desired molecule, large or small, often with surprising ease. Metal acetylides are key components for generating new nucleophilic reagents suitable for asymmetric addition reactions into electrophilic multiple bonds. The chemistry of early transition metal acetylides is especially rich, providing a fascinating class of compounds with remarkable synthetic potential. Acetylene chemistry has also driven the development of new methodology such as electrophilic addition reactions that allow the derivatization of this high-energy functional group into hetero- and carbocycles of significant interest to both synthetic and medicinal chemists. Alkynes are also versatile synthetic building blocks for the formation of natural product analogues and hybrid structures. For example, combining the hydrophobic, rigid, and linear attributes of acetylenes with the hydrophilic and chiral framework of carbohydrates affords derivatives with interesting structural properties and biological activity.

The advent of fullerene and nanotube chemistry in the 1990s inspired the search for other molecular carbon allotropes, and the hunt for both linear and cyclic allotropes consisting of sp-hybridized carbon continues in earnest. The study of carbon clusters, both linear and cyclic, spans from astrophysics to fullerene formation and advances in synthetic methodology are propelling efforts on all fronts. Acetylenic carbon rings can now be generated in the gas phase by a number of routes, while acyclic polyynes with lengths of several nanometers can be produced in unprecedented quantities with a range of terminal appendages. Cleverly designed acetylenic scaffolds can also serve as precursors to carbon-rich structures such as fullerenes and bucky onions. These recent discoveries provide for the tantalizing possibility of designer fullerenes with engineered shape and size.

Structural rigidity and electronic communication which is essentially unperturbed by conformational effects are the hallmarks of the acetylene moiety. These attributes make it a highly versatile component for conjugated scaffolds, especially when coupled with the extraordinary advances that have been achieved in metal catalyzed cross-coupling reactions. Nowhere is this more evident than in the spectacular array of molecules that have been assembled based on an arylene ethynylene framework. The synthesis of macrocycles based on arylacetylenes has now evolved to the point where constitution, physical properties, and chemical reactivity can be controlled in exquisite detail. Many of these molecules have been structurally tailored to exhibit specific properties of use in semiconductors, nonlinear optical media, liquid crystals, and sensors. Shape persistent acetylenic macrocycles can provide ordered systems based both on super- and supramolecular chemistry, resulting in tubular superstructures, two-dimensional networks, hosts for molecular recognition, and even adaptable systems that conform to external stimuli. Oligomeric, dendrimeric, and polymeric systems based on arylene ethynylene subunits are now widely viewed as some of the most important semiconducting organic materials. Vital to the successful application of these materials is the development of a much more thorough understanding of the key aspects of their synthesis, electronic structure, and organization into well-ordered films. The fruits of these efforts include synthetic polymers with programmed solid-state organization and ultra-sensitive molecular sensors for TNT. Arylene ethynylene structures incorporating chiral 1,1'-binaphthyl subunits provide yet another appealing dimension to these materials, and optically active acetylenic scaffolds suitable for asymmetric catalysis, nonlinear optics, and polarized emission have all been realized.

Complementing the efforts of synthetic and experimental chemists are the substantial achievements of theoretical chemists in their ability to both model and predict the properties of acetylene-rich molecules. The ever-increasing power of computational hardware, coupled with the development of new and improved numerical methods, have made theoretical modeling a vital tool in the evolution of modern acetylene chemistry. These efforts have shed light on topics ranging from the fundamentals of homoconjugation to the prospect of utilizing acetylene-based molecular wires as components in molecular electronics.

The eleven expert authors that have contributed to this monograph collectively offer a rich overview of the modern face of acetylene chemistry, as well as a detailed analysis of more subtle aspects that can dictate the success or failure of a particular experiment. Considerable emphasis has been placed on outlining the most recent advances in key areas of this discipline. We hope that this monograph offers to the novice a taste of the fundamental issues that motivate this exciting field of science, and to the expert the specific details on synthesis and applications necessary to stimulate the future of acetylene chemistry.

The editors wish to thank Dr. Elke Maase at Wiley-VCH for an enjoyable collaboration in the preparation of this book and Ms. Annie Tykwinski for designing the cover art.

Contents

1	Theoretical Studies on Acetylenic Scaffolds 1
1.1	Introduction 1
1.2	Linear Acetylenic Scaffolds 2
1.2.1	The Dicarbon Molecule and Acetylene 2
1.2.2	Uncapped Pure sp Carbon Chains 3
1.2.3	Capped All-sp Oligoacetylenic Chains 5
1.2.4	Hybrid sp-sp ² Oligoacetylenic Molecules 9
1.2.5	Hybrid sp-sp ³ Oligoacetylenic Molecules 14
1.3	Cyclic Acetylenic Scaffolds 15
1.3.1	Hybrid sp-sp ³ Rings 15
1.3.2	Hybrid sp-sp ² Rings (Dehydroannulenes) 20
1.3.3	carbo-Heteroannulenes 32
1.4	Star-Shaped Acetylenic Scaffolds 34
1.4.1	Atomic Cores 34
1.4.2	Rod Cores 34
1.4.3	Cyclic Cores 37
1.5	Cage Acetylenic Scaffolds 40
1.6	Conclusion 41
	Acknowledgements 42
2	Synthesis of Heterocycles and Carbocycles by
	Electrophilic Cyclization of Alkynes 51
2.1	Introduction 51
2.2	Cyclization of Oxygen Compounds 51
2.2.1	Cyclization of Acetylenic Alcohols 51
2.2.2	Cyclization of Acetylenic Phenols 55
2.2.3	Cyclization of Acetylenic Ethers 57
2.2.4	Cyclization of Acetylenic Acids and Derivatives 59
2.2.5	Cyclization of Acetylenic Aldehydes and Ketones 63
2.3	Cyclization of Sulfur and Selenium Compounds 66
2.4	Cyclization of Nitrogen Compounds 67
2.4.1	Cyclization of Acetylenic Amines 67
2.4.2	Cyclization of Acetylenic Amides 70

Ca		+ ~		+-
L۷	rı	w	rı	us

2.4.3		
2.7.3	Cyclization of Acetylenic Carbamates 73	
2.4.4	Cyclization of Acetylenic Sulfonamides 75	
2.4.5	Cyclization of Acetylenic Enamines and Imines 77	
2.4.6	Cyclization of Other Acetylenic Nitrogen Functional Groups 79	
2.5	Cyclization of Carbon onto Acetylenes 81	
2.5.1	Cyclization of Acetylenic Carbonyl Compounds and Derivatives 81	
2.5.2	Cyclization of Diacetylenes 83	
2.5.3	Cyclization of Aryl Acetylenes 84	
2.5.4	Cyclization of Acetylenic Organometallics 89	
2.6	Conclusions 90	
2.7	Representative Experimental Procedures 90	
2.7.1	Synthesis of α -Methylene- γ -butyrolactones by Carbonylation of	
	1-Alkyn-4-ols 90	
2.7.2	Synthesis of 1-Alkoxyisochromenes by Cyclization of	
0.7.0	2-(1-Alkynyl)benzaldehydes 90	
2.7.3	Synthesis of 3-Aryl(vinylic)indoles by Palladium-catalyzed	
	Cross-coupling of Aryl Halides or Vinylic Triflates and	
27.4	2-(1-Alkynyl)trifluoroacetanilides 90	
2.7.4	Synthesis of Pyridines by the Gold-catalyzed Cross-coupling of	
275	Ketones and Propargyl Amine 91	
2.7.5	Synthesis of 4-Iodoisoquinolines by the Cyclization of Iminoalkynes 91	
2.7.6	Synthesis of Cyclic Amines by Acetylene-Iminium Ion Cyclizations 91	
	A also assol a discourants — 0.2	
	Acknowledgements 92	
3	Acknowledgements 92 Addition of Terminal Acetylides to CO and CN Electrophiles 101	
	Ç	
3	Addition of Terminal Acetylides to CO and CN Electrophiles 101	
3 3.1	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101	
3 3.1 3.2	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103	
3 3.1 3.2 3.3	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106	
3.1 3.2 3.3 3.4	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114	
3 3.1 3.2 3.3 3.4 3.5	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125	
3 3.1 3.2 3.3 3.4 3.5 3.6	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1 3.7.2	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132 General Procedure for the Zn(OTf) ₂ -Catalyzed Diastereoselective	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1 3.7.2 3.7.3	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132 General Procedure for the Zn(OTf) ₂ -Catalyzed Diastereoselective Alkynylation of N-Glycosyl Nitrones 133	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1 3.7.2	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132 General Procedure for the Zn(OTf) ₂ -Catalyzed Diastereoselective Alkynylation of N-Glycosyl Nitrones 133 General Procedure for the Et ₂ Zn-Catalyzed Diastereoselective	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1 3.7.2 3.7.3	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132 General Procedure for the Zn(OTf) ₂ -Catalyzed Diastereoselective Alkynylation of N-Glycosyl Nitrones 133 General Procedure for the Et ₂ Zn-Catalyzed Diastereoselective Alkynylation of Chiral Nitrones 133	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1 3.7.2 3.7.3	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132 General Procedure for the Zn(OTf) ₂ -Catalyzed Diastereoselective Alkynylation of N-Glycosyl Nitrones 133 General Procedure for the Et ₂ Zn-Catalyzed Diastereoselective Alkynylation of Chiral Nitrones 133 General Procedure for the CuBr-Catalyzed Enantioselective Preparation	
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.7.1 3.7.2 3.7.3	Addition of Terminal Acetylides to CO and CN Electrophiles 101 Introduction 101 Background 103 Additions with Stoichiometric Amounts of Metal Acetylides 106 Nucleophilic CO Additions involving the Use of Zn(II) Salts 114 Acetylene Additions to CN Electrophiles 125 Conclusion 131 Experimental Procedures 131 General Procedure for the Enantioselective Alkynylation of Aldehydes by the Use of Stoichiometric Amounts of Zn(OTf) ₂ 131 General Procedure for the Zn(OTf) ₂ -Catalyzed Enantioselective Alkynylation of Aldehydes 132 General Procedure for the Enantioselective Alkynylation of Ketones Catalyzed by Zn(salen) Complexes 132 General Procedure for the Zn(OTf) ₂ -Catalyzed Diastereoselective Alkynylation of N-Glycosyl Nitrones 133 General Procedure for the Et ₂ Zn-Catalyzed Diastereoselective Alkynylation of Chiral Nitrones 133 General Procedure for the CuBr-Catalyzed Enantioselective Preparation of Propargylamines 133	134

4	Transition Metal Acetylides 139
4.1	Introduction 139
4.2	General Comments 140
4.2.1	Structure and Bonding 140
4.2.2	Syntheses 141
4.2.3	Reactions 144
4.3	Titanocene- and Zirconocene-Acetylides 146
4.3.1	MCCR 146
4.3.2	M(CCR) ₂ 148
4.3.3	M(CCR) ₃ 148
4.3.4	Products of $[Cp_2M(\eta^2-RC_2R)]$ and $[Cp_2^*M(\eta^2-RC_2R)]$ with Acetylenes 149
4.3.5	Reactions 151
4.4	Complexation of MCCM 160
4.4.1	Examples 160
4.4.2	Molecular Dynamics of Acetylides 161
4.4.3	Acetylides in the Topomerization of Alkynes 163
4.5	Summary and Outlook 165
4.6	Typical Experimental Procedures 166
4.6.1	Synthesis of a Monomeric Ti(111) Monoacetylide [Cp*2TiCC'Bu] 166
4.6.2	Synthesis of a Ti(111) Bisacetylide Tweezer [Cp ₂ Ti(CC ^t Bu) ₂][Li(THF)] 160
4.6.3	Synthesis of a Dinuclear Ti(111) Monoacetylide [Cp ₂ TiC ₂ SiMe ₃)] ₂
	by CC Cleavage of a 1,3-Butadiyne 167
4.6.4	Synthesis of a Zr(IV) Bisacetylide [Cp*2Zr(CCSiMe3)2] 167
4.6.5	Synthesis of a Zirconacyclocumulene
	$[Cp*_{2}Zr(\eta^{4}-1,2,3,4-Me_{3}SiC_{4}SiMe_{3})]$ 167
	Acknowledgments 168
5	Acetylenosaccharides 173
5.1	Introduction 173
5.2	Isolation of Acetylenosaccharides from Natural Sources 174
5.3	Preparation of Monoalkynylated Acetylenosaccharides 177
5.3.1	Preparation of Linear Acetylenosaccharides 177
5.3.2	Preparation of Branched-Chain Acetylenosaccharides 188
5.4	Preparation of Dialkynylated Acetylenosaccharides 193
5.4.1	Linear Dialkynylated Acetylenosaccharides 193
5.4.2	Branched Dialkynylated Acetylenosaccharides 194
5.4.2.1	4-O-Alkynyl-β-D-glucopyranosylacetylenes 195
5.5	Transformations of Acetylenosaccharides 203
5.5.1	Ring-Forming Reactions 204
5.5.2	Coupling Reactions 212
5.5.2.1	Homocoupling of Acetylenosaccharides 213
5.6	Biological and Medicinal Uses of Acetylenosaccharides 215
5.7	Experimental Protocols 215
	Acknowledgements 219

	_
(Content
١.	Conveni.

6	Semiconducting Poly(arylene ethylene)s 233
6.1	Introduction 233
6.2	Synthesis 234
6.3	Conducting Properties of PArEs 236
6.4	Photophysical Properties and Interpolymer Electronic Interactions
6.5	Sensor Applications 247
6.6	Superstructures 249
6.7	Summary 255
6.8	General Procedures for Synthesis of PPEs 255
	Acknowledgements 256
7	Polyynes via Alkylidene Carbenes and Carbenoids 259
7.1	Introduction 259
7.2	Alkylidene Carbene and Carbenoid Species 260
7.3	Alkyne Formation from Carbenes and Carbenoids 261
7.3.1	Synthesis of Acetylenes: the Fritsch–Buttenberg–Wiechell
7.00	Rearrangement 261
7.3.2	Synthesis of 1,3–Butadiynes 265
7.3.3	Synthesis of 1,3,5–Hexatriynes 268
7.3.4	Tri- and Pentaynes from Free Alkylidene Carbenes 273
7.4 7.4.1	Toward applications 274
7.4.1 7.4.2	Natural Products Synthesis 274 Extended Arylenethynylene Derivatives 276
7.4.2	Cyclo[n]carbons 283
7. 1 .5	Linear Conjugated Polyynes 284
7.5.1	Synthesis of Triisopropylsilyl End-Capped Polyynes 285
7.5.2	Solid-State Characterization 289
7.5.3	Linear Optical Properties 291
7.5.4	Third-Order Nonlinear Optical Properties 294
7.6	Conclusions 296
7.7	Experimental Procedures 297
7.7.1	General Procedure for Friedel–Crafts Acylation 297
7.7.2	General Procedure for Dibromoolefination 297
7.7.3	General FBW Rearrangement Procedure 297
7.7.4	General Oxidative Coupling Procedure 298
	Acknowledgements 298
8	Macrocycles Based on Phenylacetylene Scaffolding 303
8.1	Introduction 303
8.2	Synthetic Strategies 304
8.2.1	Intermolecular Approach 304
8.2.2	Intramolecular Approach 307
8.2.3	Comparison of the Two Pathways 311
8.3	Phenylacetylene Macrocycles 312
8.3.1	Ortho PAMs 312

8.3.2	
	Meta-PAMs 323
8.3.3	Para-PAMs 334
8.3.4	Mixed PAMs 335
8.4	Phenyldiacetylene Macrocycles 338
8.4.1	Ortho-PDMs 339
8.4.2	Meta-PDMs 356
8.4.3	Para-PDMs 361
8.4.4	Mixed PDMs 362
8.5	Phenyltriacetylene Macrocycles 373
8.6	Phenyltetraacetylene Macrocycles 374
8.7	Phenyloligoacetylene Macrocycles 377
8.8	Conclusions 378
8.9	Experimental 378
8.9.1	Preparation of 8 from [(t-BuO) ₃ WCt-Bu)] Catalysis of 13 378
8.9.2	Synthesis of 8 and 10 from Copper (2-Iodophenyl)acetylide 379
8.9.3	Preparation of 31 by Pd-Catalyzed Cyclization of 29 379
8.9.4	Preparation of 122 by Pd-Mediated Cyclization of 136 379
8.9.5	Synthesis of 148 from 149 and Mo(CO) ₆ 380
8.9.6	Preparation of 189 and 190 from 1,2-Diiodotetrafluorobenzene
	under Hay Conditions 380
8.9.7	Preparation of 1 by Deprotection and Cyclization of 223 380
8.9.8	Synthesis of 304 by Photolysis of Dewar Benzene 305 381
8.9.9	Preparation of 332 and 333 by Deprotection/Cyclization of 335 in situ 381
	Acknowledgments 381
_	
9	Carbon-Rich Compounds: Acetylene-Based Carbon Allotropes 387
9.1	Introduction 387
9.1 9.2	Introduction 387 Linear Carbon Clusters 388
9.1 9.2 9.3	Introduction 387 Linear Carbon Clusters 388 Carbyne 394
9.1 9.2 9.3 9.4	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397
9.1 9.2 9.3 9.4 9.5	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410
9.1 9.2 9.3 9.4 9.5 9.6	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415
9.1 9.2 9.3 9.4 9.5	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420
9.1 9.2 9.3 9.4 9.5 9.6	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415
9.1 9.2 9.3 9.4 9.5 9.6	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420
9.1 9.2 9.3 9.4 9.5 9.6 9.7	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420
9.1 9.2 9.3 9.4 9.5 9.6 9.7	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427
9.1 9.2 9.3 9.4 9.5 9.6 9.7	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427
9.1 9.2 9.3 9.4 9.5 9.6 9.7	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427 Ordered Systems 429 Host-Guest Complexes 429
9.1 9.2 9.3 9.4 9.5 9.6 9.7 10 10.1 10.2 10.2.1 10.2.2	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427 Ordered Systems 429 Host-Guest Complexes 429 Tubular Superstructures in Solution 433
9.1 9.2 9.3 9.4 9.5 9.6 9.7 10 10.1 10.2 10.2.1 10.2.2 10.2.3	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427 Ordered Systems 429 Host-Guest Complexes 429 Tubular Superstructures in Solution 433 Thermotropic Liquid Crystals 438
9.1 9.2 9.3 9.4 9.5 9.6 9.7 10 10.1 10.2 10.2.1 10.2.2	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427 Ordered Systems 429 Host-Guest Complexes 429 Tubular Superstructures in Solution 433 Thermotropic Liquid Crystals 438
9.1 9.2 9.3 9.4 9.5 9.6 9.7 10 10.1 10.2 10.2.1 10.2.2 10.2.3 10.2.4	Introduction 387 Linear Carbon Clusters 388 Carbyne 394 Linear Polyynes 397 Monocyclic Carbon Clusters: Cyclo[n]carbons 410 Three-Dimensional Multicyclic Polyynes 415 Conclusion 420 Acknowledgements 420 Shape-Persistent Acetylenic Macrocycles for Ordered Systems 427 Introduction 427 Ordered Systems 429 Host-Guest Complexes 429 Tubular Superstructures in Solution 433 Thermotropic Liquid Crystals 438 Two-Dimensional Organization 442

10.4.2	Template-Based Oxidative Cyclodimerization of a Rigid Bisacetylene	447
10.4.3	Deprotection of a Macrocyclic THP-Protected Tetraphenol 448	
10.4.4	Alkylation of a Macrocyclic Tetraphenol 448	
10.4.5	Hydrolysis of a Macrocycle with Two Intraannular Ester Groups 44	18

10.4.6 Formation of a Macrocycle with Two Intraannular Thioether Groups 449 Acknowledgements 449

11	Chiral	Acetylenic	Macromolecules	453

- 11.1 Introduction 453
- 11.2 Chiral Acetylenic Dendrimers 454
- 11.3 Chiral Acetylenic Polymers 460
- 11.3.1 Chiral Polymers Containing Main-Chain para-Phenyleneethynylenes
- 11.3.2 Chiral Polymers Containing Main-Chain *ortho*-Phenyleneethynylenes 468
- 11.3.3 Chiral Polymers Containing Main-Chain *meta*-Phenyleneethynylenes
- 11.3.4 Chiral Polymers Containing Main-Chain Thienylene-Ethynylenes 483
- 11.3.5 Chiral Polymers Containing Side-Chain Phenyleneethynylenes 485
- 11.4 Summary 490 Acknowledgements 491
- 11.5 Experimental Procedures 491
- 11.5.1 Preparation of the Chiral Dendrimers A Typical Procedure 491
- 11.5.2 Preparation of the Chiral Polymer (R)-18e 491
- 11.5.3 Preparation of the Chiral Polymer (R)-45 492
- 11.5.4 Preparation of the Helical Polymer (R)-85 492

Index 495

Symbols and Abbreviations

A adenine

ABLA absolute bond length alternation parameter

Ac acetyl

ADF Amsterdam density functional
AFM atomic force microscopy
AIBN azobis(isobutyronitrile)
AIM atoms in molecules

All allyl

AM1 Austin model 1

APCI atmospheric pressure chemical ionization

ARCS aromatic ring current shielding ASE aromatic stabilization energy

ATRP atom transfer radical polymerization

B3LYP hybrid funtional by Becke and Lee-Yang-Parr B3PW91 hybrid functional by Becke and Perdew-Wang

BHT 3,5-di-*tert*-butyl-4-hydroxytoluene
BINOL 1,1'-binaphthalene-2,2'-diol
BLYP Bekce/Lee-Yang-Parr functional
bmim 1-butyl-3-methylimidazolium

Bn benzyl

Boc tert-butoxycarbonyl
BPO benzoyl peroxide
bpy 2,2'-bipyridyl

BRE Breslow resonance energy

 $\begin{array}{ll} \text{BTEACl} & \text{benzyltriethylammonium chloride} \\ \text{BTEAICl}_2 & \text{benzyltriethylammonium dichloroiodate} \\ \text{BTEAICl}_3 & \text{benzyltrimethylammonium tribromide} \end{array}$

BTMSA bis(trimethylsilyl)acetylene

BTMABr₃ benzyltrimethylammonium tribromide

Bu butyl

BuLi butyllithium Bz benzoyl CAN ceric ammonium nitrate

CASSCF complete active-space self consistent field

CC coupled cluster

CCSDT/ CCSD(T) coupled cluster singles doubles triples

CD circular dichroism

CNDO/S-CI complete neglect differential orbital/singles configura-

tion interaction

COD 1,5-cyclooctadiene Cp cyclopentadienyl

Cp' differently substituted cyclopentadienyl

Cp* pentamethylcyclopentadienyl
CPDMS 3-cyanopropyldimethylsilyl
CRD cavity ring-down (spectroscopy)

CSA camphorsulfonic acid

<d> average diameter

DABCO 1,4-diazabicyclo[2.2.2]octane dba dibenzylideneacetone

DBU 1,8-diazabicyclo[5.4.0]undec-7-ene

DCC dicyclohexylcarbodiimide
DCE 1,2-dichloroethane
DE dissociation energy
DEAD diethyl azodicarboxylate

Dec decvl

DET diethyl tartrate

DFT density functional theory

"D+G" band "disorder-induced" + "graphite" band

DIB diffuse interstellar band
DIBAH diisobutylaluminium hydride
DIC N,N'-diisopropylcarbodiimide

DL diode laser

DLS dynamic light scattering
DMAP 4-dimethylaminopyridine
DME 1,2-dimethoxyethane
DMF N,N-dimethylformamide
DMI 1,3-dimethyl-2-imidazolidinone

DMSO dimethylsulfoxide

Dod dodecyl

DOKE differential optical Kerr effect DOPS-TIPS SiMe₂CMe₂CH₂CH₂OSi(CHMe₂)₃

DP degree of polymerization

dppe1,2-bis(diphenylphosphino)ethanedppp1,3-bis(diphenylphosphino)propaneDSCdifferential scanning calorimetry

EΑ electron affinity

ebthi ethylene-bis-tetrahydroindenyl

ED electron diffraction

EDX energy dispersed X-ray emission

enantiomeric excess ee

FFLS electron energy loss spectroscopy electronegativity equalization method EEM

ELF electron localization function energy of maximum absorption Emax

ΕP ethynylphenylene

EPR electron paramagnetic resonance

equivalents equiv electrostatic unit esu

ethvl Et

FBW Fritsch-Buttenberg-Wiechell flash chromatography FC

fs femtosecond

fur furvl

FVP flash vacuum pyrolysis full width at half maximum **FWHM**

molecular second hyperpolarizability

Gal

GGA gradient generalized affroximation

Glcglucose

GPC gel permeation chromatography

hν light Hep heptyl hexyl Hex

ΗF Hartree-Fock

HMPA hexamethylphosphoramide

highest occupied molecular orbital HOMO HOPG highly oriented pyrolytic graphite

ion cyclotron resonance ICR

INDO intermediate neglect differential orbital

ΙP ionization potential

association constant $K_{\rm assoc}$

1 contour length

wavelength of maximum absorption λ_{max}

Langmuir-Blodgett I.B

LC liquid crystal

LDA lithium diisopropylamide LD-TOF laser desorption time of flight

LE locally excited
LLS laser light scattering

LiHMDS lithium hexamethyldisilazide

LUMO lowest unoccupied molecular orbital

MALDI-TOF matrix-assisted laser desorption/ionization time-of-flight

Me methyl

MINDO modified intermediate neglect differntial orbital

min minutes

MMC molecular mechanics for clusters

MM3 molecular mechanics 3

 M_n number average molecular weight

MNDO/3 modified neglect differential orbital number 3

MOM methoxymethyl

MP2, MP4 Moller Plesset 2, Moller Plesset 4

MRD-CI multi-reference single and doubly excitation configuration

MRTD molecular resonant tunneling diode

Ms mesyl

M_w weight average molecular weight

NBO natural bond order
NBS N-bromosuccinimide
NCS N-chlorosuccinimide

NDR negative differential resistance NICS nucleus independant chemical shift

NIS N-iodosuccinimide
NLO nonlinear optics
NLP nonlinearity parameter
NME N-methylephedrine

NMO N-methylmorpholine N-oxide NMP N-methyl-2-pyrrolidone

ns nanosecond

Oct octyl

ODCB ortho-dichlorobenzene
ODf difluoromethanesulfonate
OEP oligoethynylphenylene

OITB orbital interaction through bonds
OITS orbital interaction through space
ORTEP Oak Ridge thermal ellipsoid plot

OTf trifluoromethanesulfonate

PArE poly(arylene ethynylene)
PAM phenylacetylene macrocycle
PCC pyridinium chlorochromate
PDI polydispersity index

PDM phenyldiacetylene macrocycle PM3 parametric method number 3

PDA poly(diacetylene)

Ph phenyl
PhLi phenyllithium
PHT phenylheptatriyne

Pic picrate

Piv pivaloyl (*tert*-butylcarbonyl)
PmB para-methoxybenzyl

PPE poly(phenylene ethynylene) PPV poly(phenylene vinylene)

Pr propyl
PS polystyrene
PTA poly(triacetylene)
PTFE polytetrafluoroethylene

PTeM phenyltetraacetylene macrocycle PTrM phenyltriacetylene macrocycle

py pyridine

QUINAP 1-(2-diphenylphosphanyl-naphthalen-1-yl)-isoquinoline

R2CPD resonance two-color photodetachment

REMPED resonance-enhanced multi-photon detachment

RHF restricted Hartree-Fock rt room temperature

SAM self-assembled monolayer SCF self consistent field

SERS surface plasmon polariton-enhanced Raman spectra

SHG second harmonic generation

SSH Su-Schrieffer-Heeger

STM scanning tunneling microscopy

STO-3G minimal Pole basis set

Γ thymine

TBAF tetrabutylammonium fluoride

TBDMS tert-butyldimethylsilyl
TBS tert-butyldimethylsilyl

TCNQ 7,7,8,8-tetracyanoquinodimethane

TD Time dependent TDDFT time-dependent DFT

VIII Symbols and Abbreviations

TEBAC	riethylbenzylamn	nonium	chloride
-------	------------------	--------	----------

TEE tetraethynyl-ethylene

TEM transmission electron microscopy

Tf trifluoromethanesulfonyl
TFA 2,2,2-trifluoroacetic acid
TGA thermal gravimetric analysis
Th Thexyl, 1,1,2-trimethylpropyl

THF tetrahydrofuran
THP tetrahydropyranyl
TIPS triisopropylsilyl

TIPSA triisopropylsilylacetylene
TLC thin layer chromatography

TMEDA N, N, N', N'-tetramethylethylenediamine

TMS trimethylsilyl

TMSA trimethylsilylacetylene
TMU tetramethylurea
TNT trinitrotoluene

TOF-MS time-of-flight mass spectrometry

U uracil

UPS ultraviolet photoelectron spectroscopy

VEH/SOS valence effective Hamiltonien/sum over states

VSEPR valence shell electron pair repulsion

VPO vapor pressure osmometry

VUV vacuum UV

ZINDO Zerner intermediate neglect differential overlap

List of Contributors

Patrick Aschwanden

Laboratorium für Organische Chemie ETH Zürich 8093 Zürich Switzerland

Bruno Bernet

Laboratorium für Organische Chemie ETH Zürich 8093 Zürich Switzerland

Erick M. Carreira

Laboratory of Organic Chemistry ETH Hoenggerberg, HCI 8093 Zürich Switzerland

Rémi Chauvin

CNRS

Laboraoire de Chimie de Coordination 205 Route Narbonne 31077 Toulouse, Cedex 4 France

Sara Eisler

Department of Chemistry University of Alberta Edmonton, Alberta T6G 2G2 Canada

Michael M. Haley

Department of Chemistry 1253 University of Oregon Eugene, Oregon 97403-1253 USA

Carissa S. Jones

Department of Chemistry and the Materials Science Institute 1253 University of Oregon Eugene, Oregon 97403-1253 USA

Sigurd Höger

Polymer Institut Universität Karlsruhe Hertzstraße 16 76187 Karlsruhe Germany

Richard C. Larock

Department of Chemistry 1605 Gilman Hall Iowa State University Ames, IA 50011-3111 USA

Christine Lepetit

CNRS

Laboraoire de Chimie de Coordination 205 Route Narbonne 31077 Toulouse, Cedex 4 France

Matthew J. O'Connor

Department of Chemistry and the Materials Science Institut 1253 University of Oregon Eugene, Oregon 97403-1253 USA

Lin Pu

Department of Chemistry Universtiy of Virginia PO Box 400319 Charlottesville, VA 22904-4319 **USA**

Uwe Rosenthal

Institut für Organische Katalyseforschung Universität Rostock e.V. Buchbinderstraße 5-6 18055 Rostock Germany

Timothy M. Swager

Department of Chemistry Massachusetts Institute of Technolgov 77 Massachusetts Ave. Cambridge, MA 02139 USA

Yoshito Tobe

Department of Chemistry Faculty of Engineering Science Osaka University Toyonaka, Osaka 560-8531 **Japan**

Rik R. Tykwinski

Department of Chemistry University of Alberta Edmonton, Alberta T6G 2G2 Canada

Andrea Vasella

Laboratory of Organic Chemistry ETH Hoenggerberg, HCI 8093 Zürich Switzerland

Tomonari Wakabayashi

Department of Chemistry, School of Science and Engineering Kinki University Higashi-Osaka 557-8502 Japan

Theoretical Studies on Acetylenic Scaffolds

Remi Chauvin and Christine Lepetit

1.1 Introduction

Ten years ago, Houk demonstrated that along with experimental analysis, theoretical analysis could not be ignored for advanced understanding of the specific properties of acetylenic compounds [1]. In recent years, the growing power of computational facilities, the optimized implementation of performant methods in various software packages, and the development of new theoretical tools (faster and extended coupled cluster (CC) methods, new density functional theory (DFT) functionals, time-dependent DFT (TDDFT), advanced topological treatments of the information contained in the electron density through the atoms in molecules (AIM) [2], and electron localization function (ELF) [3] methods,...) prompted more and more chemists to consider theoretical modeling as a key tool. This tool is used at either of two levels: (i) a posteriori, for analysis of the properties of known compounds, or (ii) a priori, for selection of synthetic targets with specific properties among potential molecular structures suggested by empirical laws governing the chemist's intuition. This intuition is formally sustained by more systematic suggestion tools, such as the "analogy principle" (variation of some structural unit through structural units with the same valence, such as a terminal atom through all the halogens), the "vinylogy", "cumulogy", or "ethynylogy" principles (insertion of CH=CH, C=C, or C≡C units between a few pairs of conjugated atoms), or the "carbo-mer principle" (insertion of C_{sp}-C_{sp} units into at least all symmetry-related bonds of a Lewis structure (Scheme 1.1)) [4]. The last of these principles allows for fine-tuning of the notion of carbon-rich molecules [5] to a notion of carbon-

Scheme 1.1 Acetylenic expansions, becoming *carbo*-meric expansions if applied to complete sets of symmetry-related bonds of a parent molecule [4].

enriched molecules: indeed, *carbo*-merization does not corrupt the personality of a parent molecule "too much", as it preserves many of its basic features (connectivity, symmetry, shape, π-electron resonance, CIP configuration of asymmetric centers, …), while just expanding its size through its acetylenic content.

A natural question concerns the variation of pre-existing or emerging properties as a function of the acetylenic content. Theoretical modeling allows for systematic screening and targeting prior to the undertaking of possibly tedious experimental syntheses. It should be emphasized, however, that many constructed expanded acetylenic scaffolds intentionally contain butadiynyl units (C_4) and are quite symmetrical. This holds to the efficiency and variety of oxidative C_{sp} - C_{sp} coupling procedures from terminal alkynes, which also motivated theoretical investigations of their mechanism [6].

This chapter presents selected advances (with special emphasis on results published since 1995) in the theoretical analysis or prediction of the properties of acetylenic scaffolds in a sequence based on dimensionality [7]:

- 1.2 Linear acetylenic scaffolds
- 1.3 Cyclic acetylenic scaffolds
- 1.4 Star-shaped acetylenic scaffolds
- 1.5 Cage acetylenic scaffolds

1.2 Linear Acetylenic Scaffolds

1.2.1

The Dicarbon Molecule and Acetylene

The empirically observed statistical even/odd carbon atom disparity in organic molecules [8] can be arithmetically interpreted by saying that the latter are made of "carbon pairs" rather than of carbon atoms. The bonded carbon pair, C_2 , is the unitary "brick" of acetylenic scaffolds. This molecule can be observed in the form of the blue light of hot hydrocarbon flames [9] (e.g., during the pyrolysis of acetylene itself [10]), but also occurs under various conditions (diamond vapor deposition, laser ablation of graphite, in carbon-rich stars and comets...), and it was quickly proposed that it might assemble into the C₆₀ fullerene [11]. The MO diagram of the $^1\Sigma_g^{\ +}$ ground state corresponds to the $(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$ configuration, and is nearly degenerate with the first triplet state $({}^{3}\Pi_{\rm u})$. For the ${}^{1}\Sigma_{\rm g}^{+}$ state, the simplest orbital criterion (six bonding and two anti-bonding electrons) corresponds to the :C=C: description. Higher bond orders (approximately 3.7) were, however, assigned by Wiberg or natural population analysis (NPA) [12], in accordance with the experimentally determined bond length (1.242 Å) and harmonic frequency (1855.0 cm⁻¹) [13], which are well reproduced by CCSDT methods and non-iterative approximation thereof [14]. The bond is indeed shorter than more stable $C_{sp} = C_{sp}$ double bonds (e.g., approximately 1.280 Å for butatriene at various experimental and theoretical levels [15]). The ${}^{1}\Sigma_{g}^{+}$ state was thus depicted as a resonance hybrid

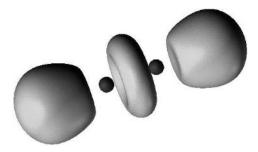


Figure 1.1 Localization domains of the acetylene molecule (ELF = 0.8) [3a]. The two red basins represent the carbon inner shells; the two blue ones the C-H bonds, and the green torus the $C \equiv C$ bond.

 $:C=C:\leftrightarrow:C \odot C \leftrightarrow C \odot C:$, as derived from Feynman's diagrams [16]. If the formal C≣C octet form is excluded [12], the classical Lewis resonance accounting both for the spin state and for the bond length of the ${}^{1}\Sigma_{g}^{+}$ state would be: $:C=C:\leftrightarrow^+C\equiv C:^-\leftrightarrow^-:C\equiv C^+$. Similarly, a consistent picture for the ${}^3\Pi_u$ state would be $:C-C:\leftrightarrow C\equiv C$. These pictures suggest that the C_2 units might efficiently transmit π electron delocalization (vide infra).

In unstrained bonding situations, the biscarbenic character of the C₂ unit disappears. In acetylene, for example, the chemical shape of the three-bond rod can be visualized through the ELF localization domains (Figure 1.1) [3a]. According to the axial symmetry of the molecule, the three bond domains expected for the triple C-C bond are degenerate and merged into a torus: there is no σ/π separation, in variance with the classical view of organic chemists.

1.2.2 Uncapped pure sp Carbon Chains [1]

Many theoretical studies of all-sp carbon clusters C_n show that the open linear form is preferred over the cyclic form for n < 10, though cyclic forms of short *n*-even chains (C_4, C_6, C_8) do compete [17]. The converse holds for $n \ge 10$ (see Section 1.3.2.4), but open chains are known for odd n = 3-29 [18].

Optimized geometries at various level of theory indicate that the octet deficiency of carbon chains is partly made up by a strong cumulenic character both for C_{2m+1} chains (${}^{1}\Sigma_{g}^{+}$ ground state with equal bond lengths of approximately 1.30 Å) and for C_{2m} chains (${}^{3}\Sigma_{g}^{-}$ ground state with less than 2% bond length alternation). Although DFT calculations did not accurately reproduce experimentally determined or CCSD(T) singlet-triplet separation, both the local density approximation (LDA) [19] and the use of gradient-corrected (BLYP) [20] or hybrid (B3LYP) functionals gave relevant results in terms of geometries and harmonic frequencies [21]. Hund rule-reliable Lewis representations of small carbon chains are given in Scheme 1.2. With regard to the contribution of zwitterionic forms, it should be mentioned that a TD-LDA treatment showed that the longitudinal polarizability increases from approximately 7 Å³ (n = 3) to approximately 490 Å³ (n = 21), namely more rapidly than n, and more rapidly than the polarizability of the corresponding polyenes with the same number of valence electrons [18].

1 Theoretical Studies on Acetylenic Scaffolds

Scheme 1.2 Main Lewis forms for ground state C_{2m+1} and C_{2m} (m=1-8) accounting for both the bond orders and the spin state.

Calculations of various excited or charged (C_n^-, C_n^+) states of linear carbon chains have been carried out at high levels of theory, especially by coupled cluster methods, which proved to be useful for reproduction or prediction of experimentally measured electronic spectra [22], electron affinities (EAs), ionization potentials (IPs), or dissociation energies (DEs) [17].

Efforts devoted to theoretical studies of linear carbon chains are motivated by their uniques properties, such as their role in fullerene growth or, more recently, in the field emission of electrons from carbon nanotubes or in the origin of the diffuse interstellar bands (DIBs) [18].

- C_n chains of nanometer sizes (n = 10-100) can be generated by electric field-induced unraveling of the inner graphene wall layers of carbon nanotubes, and are then responsible for emission currents of 0.1–1 μ A under bias voltages of less than 80 V [23]. Indeed, linear C_n chains (n = 3-11) were calculated to pass relevant tests to qualify as metallic atomic wires with ease, but open-shell n-even chains give currents 100 times as intense as their closed-shell n-odd neighbors [19].
- A challenging goal in radio-astronomy is understanding of the origin of the DIBs, silent bands of frequency in the visible-IR spectra of interstellar clouds [22]. DIBs were previously proposed to be caused by linear carbon chains [24], and some of them could recently be identified with optical gas-phase electronic transitions of anionic representatives [25]. An alternative to the difficult experimental determination of the characteristics of such transitions is their calculation. A partial attempt using experimental energies and theoretical (TD-LDA) oscillator strengths of C_5 – C_{21} carbon chains provided a few qualitative coincidences with observed DIBs [18].

The octet deficiency of carbon chains can be completed by closure to $\operatorname{cyclo}[n]\operatorname{carbons}$ (see Section 1.3.2.4), by simple doping, by end-capping, or by passing from the molecular status to a material status through infinite expansion [26]. Whereas end-capping is the topic of the next section, doping can be exemplified by neutral and charged carbon clusters $[C_{2n}X]^q$, which have been studied at the DFT level when X is a main group metal atom [27]: the cyclic ω -diacetylide-type structures C = C - X - C = C are favored over the open-chain isomers for q = 0 and X divalent (e. g., X = Mg) [28], or for q = -1 and X monovalent (e. g., X = Na) [27]. Similar studies have been conducted with transition metal atoms, including with X = Pt at the B3LYP level [29].

Finally, infinite expansion affords carbyne (1D sp carbon allotrope), the missing link between atomic carbon and graphite (2D sp² carbon allotrope), which may be hybridized with the latter to design graphyne and related allotropic structures [30]. Although the carbon allotropes are beyond the scope of this chapter [31], it should be mentioned that several theoretical studies have focused on the possible structures and promising properties of these challenging materials [32].

1.2.3

Capped all-sp Oligoacetylenic Chains

1.2.3.1 all-sp Oligoacetylenic Chains between Redox-Silent Organic Groups

The recently surveyed state of the art of the characterization of doubly capped acetylenic chains XC_{2n}Y prompted a comprehensive study of lower representatives (Scheme 1.3, $n \le 6$) at various level of theory (HF, MP2, MP4, CCSD(T), B3P86, B3LYP, with various basis sets) [33a].

$$X \leftarrow C = C \rightarrow Y$$
 $X, Y = H, CH_3, Ph, Na, F, I, CN, O, S, Se,...$

Scheme 1.3 Capped polyacetylenics.

For X = Y = H, let us first remind ourselves that the possible structures of small C_mH_2 molecules (m = 3, 5, 6, 7) have been investigated by various ab initio calculations (see, for example, refs. [33b-f]). For larger polyacetylenic representatives (m = $2n, n \leq 6$), geometrical, vibrational, and energetic (heats of formation, ionization potentials, electronic affinities (EAs)) properties display regular variations with respect to n [33a]. At the HF level, the C=C and C-C bond lengths were found to converge to different values (1.190 Å and 1.366 Å, respectively), while the EAs decrease from 4.15 eV for n = 1 to 1.19 eV for n = 5. These results were extended by DFT studies of higher representatives (n = 6-12) [33]. The B3LYP level was argued to be relevant not only for the ${}^{1}\Sigma_{g}^{+}$ ground states of the neutral species, but also for the ${}^2\Pi_{11}$ or ${}^2\Pi_{12}$ ground states of the radical anions [HC_{2n}H]. In the latter, the bond length equalization increases with increasing n, while the adiabatic EAs of the neutral species increase continuously from 1.78 eV (n = 6) to 2.95 eV (n = 6) 12). The number of calculated stretches in the 1900–2200 cm⁻¹ region support the hypothesis that long $[HC_{2n}H]^q$ species $(q = 0, -1, n \ge 6)$ could contribute to the DIBs [34]. It may be commented that the results from references [33a] and [34], though referring to different methods, could suggest that the EA is at its minimum around $n \approx 5$.

Chaquin et al. recently reported a comprehensive structural and vibrational study of the $HC_{2n}H$ molecules up to n=20 at the B3LYP level [35]. The results confirm the persistency of bond length alternation with increasing n, and a systematic correlation scheme afforded asymptotic values of 1.229 Å and 1.329 Å for triple and single bonds, respectively. As would be expected, the asymptotic bond length alternation (0.10 Å) is smaller than that obtained at the HF level (0.17 Å) [33a], but the DFT estimate is supported by excellent fits with experimentally obtained data. The alternation was also visualized through the ELF localization domains in $C_{30}H_{7}$ [35].

Polyynes have also received much attention, as they are predicted to exhibit large second hyperpolarizabilities [36]. Beyond ab initio calculations on simple diacety-lene derivatives [36d–e], high level ab initio studies (SCF, MP, CCSD(T)) with large basis sets show that the static hyperpolarizability increases with increasing C=C bond lengths [37]. The bond length alternation (BLA) parameter, which is a determining factor of nonlinear optical properties, was compared for polyyne chains at various calculation levels (PM3, ab initio, DFT) [38, 39]. The static second hyperpolarizabilities (γ of linear polyynes up to C₁₆₀H₂) was calculated [36b, 39] and, as in the case of polyenes, γ/n_C versus the number of carbon atoms n_C saturates beyond $n_C \approx 50$. Similarly, deprotonation and double deprotonation energies of polyynes containing up to 40 carbon atoms were shown to decrease towards an asymptotic limit of 370 kcal mol⁻¹ [38b].

For X = Y = Ph (Scheme 1.3, $n \le 6$), DFT studies of α,ω -diphenyl polyynes of D_{2h} symmetry accounted for the effects both of the chain length and of the phenyl endcaps on the fluorescence properties [40]. The fluorescent excited state switches from $1^1B_{2u}(\pi_x\pi_x^*)$ for $n \le 2$ to 1^1A_u ($\pi_x\pi_v^*$ or $\pi_v\pi_x^*$) for $n \ge 3$.

For X = Y = O, S, Se, the acetylenic character is expected a priori for the triplet states (Scheme 1.3). The $OC_{2n}O$ molecules are much less stable than the cumulenic "odd" carbon suboxides $OC_{2n+1}O$. The first member of this series is ethylenedione C_2O_2 (i. e., the dimer of CO or the *carbo*-mer of CO), which has hitherto evaded unambiguous experimental observation. On the basis of CCSD(T) calculations, it was recently suggested to be an intrinsically short-lived molecule [41]. The monosulfur analogue C_2OS [42] and the higher cumulogue C_4O_2 could, however, be identified by comparison between calculated and experimentally measured IR or COSD(T) spectra [43]. Recent calculations at the COSD(T) representable support the view that all triplet structures COSD(T) (COSD(T)) possess a COSD(T) representable structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures COSD(T) representable support the view that all triplet structures are considered to the view that all triplet structures are considered to the view that all triplet structures are considered to the view that all triplet structures are considered to the view that all triplet structure

For X, Y = H, CN (Scheme 1.3, $n \le 9$), the corresponding cyanopolyynes H-(C₂)_n-CN and dicyanopolyynes NC-(C₂)_n-CN are regarded as isolable model substances of the carbyne allotrope [45]. The variation of the HOMO-LUMO gap (AM1, HF or MP2) and of the ZINDO-calculated UV spectra accounts for the experimentally observed Lewis–Calvin bathochromic shift with increasing n ($\lambda^2 = kn$). The observed regioselectivity of dienophile cycloadditions at the $C_{\beta} = C_{\gamma}$ bonds is consistent with the highest positive Mulliken charges at the C_{β} and C_{γ} atoms (Scheme 1.4). Since the positive charge is greater at C_{β} than at C_{γ} , the weight of the long-range charge separation (y) is greater than that of the shorter-range one (x) (Scheme 1.4). The increase in cumulenic character with increasing n, also systematically evidenced at the B3LYP level [35], would thus be consistent with a parallel increase in the y/x ratio. The occurrence of the zwitterionic resonance forms would also account for the σ-coordination ability of the nitrogen atoms toward main group metals as evidenced by DFT calculations [46]. From a more applied

Scheme 1.4 Schematic charge separations in dicyanopolyynes.

standpoint, DFT-calculated low vibration frequencies of cyanopolyynes have also been claimed to be relevant for possible assignments of spectroscopic absorptions in interstellar media [35].

For X, Y = H, F, or Na (Scheme 1.3, $n \le 5$), the electron distribution in the corresponding polyynes has been studied at the MP2/6-31G** level within the formalism of the electronegativity equalization method (EEM) [47]. In contrast to the atomic charges, the charges of the X-C≡C- and -C≡C-Y termini and those of the (n-2) intermediate -C \equiv C- units were found to be additive. For example, given n = 5 and X, Y = Na, F, the charges of the i^{th} unit in the heteronuclear and homonuclear molecules are bound through: $[Q_i(FC_{10}F) + Q_i(NaC_{10}Na)] \approx [Q_i(NaC_{10}F)$ + Q_i(FC₁₀Na)]. This gives support to the view of the C₂ units as "compact" building blocks (see Section 1.2.1).

Much weaker than conventional hydrogen bonds, intermolecular $\pi...\pi$ or $C-H...\pi$ interactions have been attracting increasing attention [48]. In particular, several ab initio and DFT studies have focused on the hydrogen bond-accepting ability of triple bonds [49]. The ab initio intermolecular potential for acetylene sliding perpendicularly along a polyyne (Figure 1.2) was calculated at the MP2 level and was used to refine an MMC (molecular mechanics for clusters) model potential for polyynes [50]. The T-shaped interaction energy of acetylene with the triple bond at the end of the chain reaches an asymptote of -372 cm⁻¹. As the acetylene molecule slides along the chain, the intermolecular potential is essentially flat with only small bumps (Figure 1.2) (acetylene interacts slightly more with the triple C≡C bonds than with the single C-C bonds). This extended smooth intermolecular potential zone produces weak bonding slipperiness of acetylene along the polyyne chain.

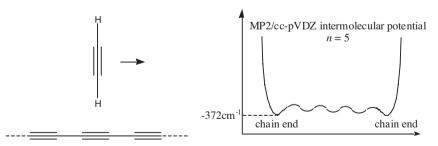


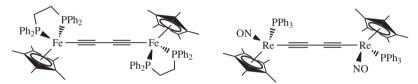
Figure 1.2 Perpendicular sliding of acetylene along a polyyne $H(C \equiv C)_n H$ (n = 2-5) at fixed distance between the center of mass of acetylene and the polyyne molecular axis (4.5 Å) [50].

1.2.3.2 All-sp Oligoacetylenic Chains between Organometallic Termini

Besides their potential applications in homogeneous and heterogeneous catalysis, alkynylmetal complexes are thermally robust, available in high yield, and attractive for their conducting and nonlinear optical properties. Among a very large number of theoretical studies on such complexes, a few recent results are highlighted below.

In monometallic complexes, theoretical studies have aimed at better understanding of metal-alkynyl bonding [51]. Through the use of the ADF program and the bond energy decomposition scheme designed by Ziegler and Rauk [52], metal-to-ligand backbonding energies were calculated for a set of σ -acetylide complexes of electron-rich metal centers such as $M(X)(PH_3)_n$, with M=Fe, Ru, Os (X=Cl and n=4, or $X=C_5H_5$ and n=2) [53, 54]. As expected, the π backbonding increases with the electron-withdrawing ability of the η^1 -acetylide substituent and increases from Fe to Os. However, π bonding effects are relatively small in relation to the dominant metal-alkyne σ bonding. The backbonding energy is accurately correlated with the experimentally determined or calculated quadratic hyperpolarizability [55], but not with the $\nu(MC=C)$ IR stretching frequency, which is indeed lowered by coupling with the stretching of the adjacent bonds. A similar DFT study of the influence of terminal substituents on the π backbonding in metallacumulene complexes has also been reported [56].

Studies of the homo- and heterobimetallic complexes have focused on the electronic communication between the metal centers through the polyyne bridge (Scheme 1.5) [57, 58, 59].



Scheme 1.5 Examples of homobimetallic complexes where electronic communication is assumed by polyyne bridges [64b].

In L_mM —C—C— ML_m complexes, the C_2 molecule (Section 1.2.1) is stabilized as a μ -diacetylide ligand [31, 60]. DFT calculations allow two classes of dicarbido complexes to be identified, the metals lying in pseudotetrahedral coordination spheres [61]. For early metals of the Ti, V, and Cr triads in high oxidation states with π -donor ligands, the coordination mode (M–C=C–M, M=C–C=M) depends on the d^n configuration. In contrast, for metals of the late triads (from Mn onwards) in low oxidation states with π -acceptor ligands, only the M–C=C-M coordination mode is observed whatever the metal d^n configuration.

The generalized valence flexibility (M–C \Longrightarrow \leftrightarrow M=C \Longrightarrow \leftrightarrow M \equiv C \rightarrow) has been elegantly studied by natural bond order (NBO) and AIM analyses for even- [62] or odd-numbered [63] carbon chains, depending on the metallic end-caps. In the case of C₄ chains bonded to electron-rich metal fragments (M = Fe, Re, Ru,