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

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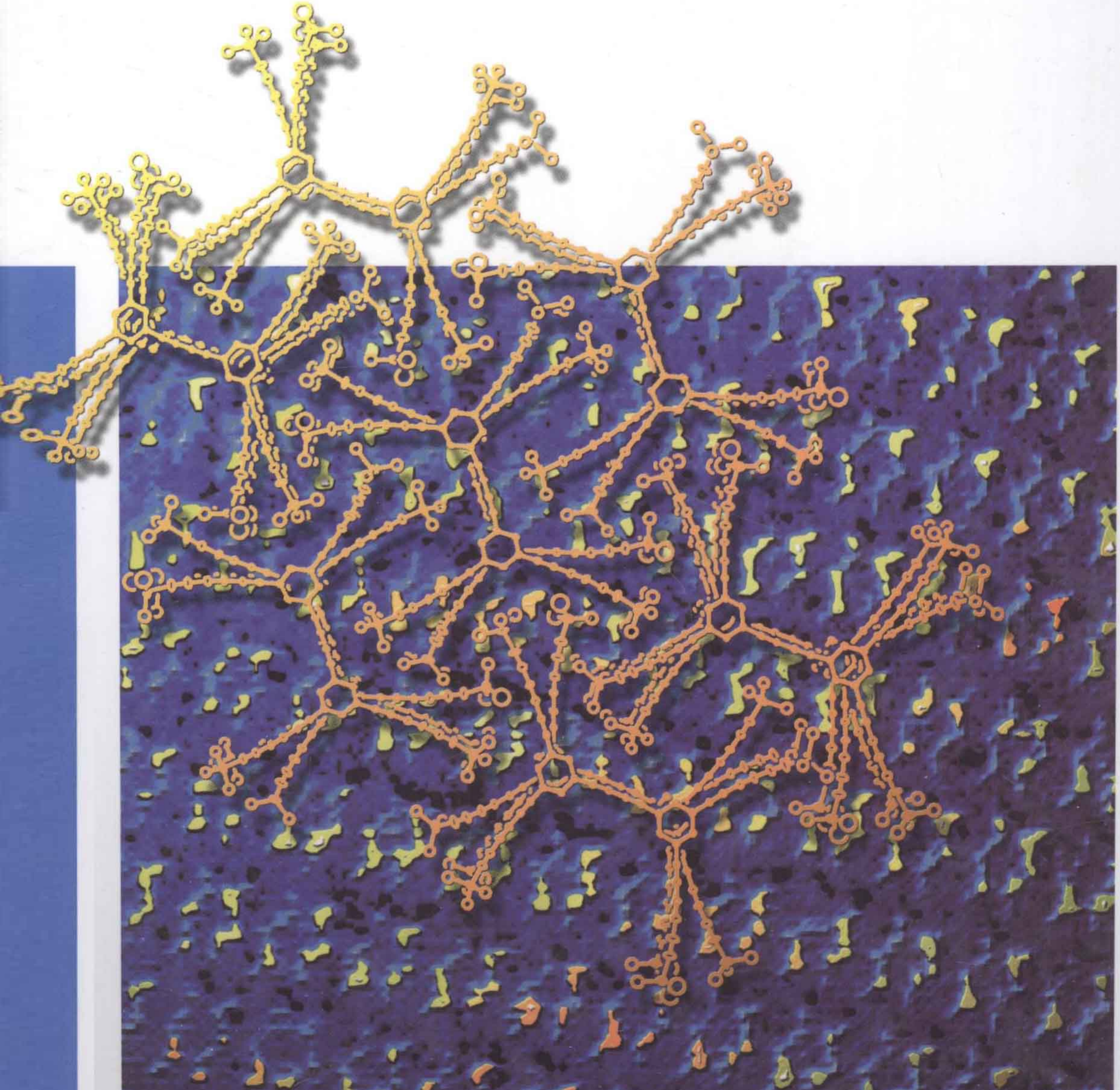
Acetylene Chemistry

Chemistry, Biology, and Material Science



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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.

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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.

November, 2004 F. Diederich, P. J. Stang, R. R. Tykwinski

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
BTEACl	benzyltriethylammonium chloride
$BTEAICl_2$	benzyltriethylammonium dichloroiodate
$BTEAICl_3$	benzyltrimethylammonium tribromide
BTMSA	bis(trimethylsilyl)acetylene
$BTMABr_3$	benzyltrimethylammonium tribromide
Bu	butyl
BuLi	butyllithium
Bz	benzoyl

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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 configuration 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	decyl
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	$SiMe_2CMe_2CH_2CH_2OSi(CHMe_2)_3$
DP	degree of polymerization
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
DSC	differential scanning calorimetry

EA	electron affinity
ebthi	ethylene-bis-tetrahydroindenyl
ED	electron diffraction
EDX	energy dispersed X-ray emission
ee	enantiomeric excess
EELS	electron energy loss spectroscopy
EEM	electronegativity equalization method
ELF	electron localization function
E_{max}	energy of maximum absorption
EP	ethynylphenylene
EPR	electron paramagnetic resonance
equiv	equivalents
esu	electrostatic unit
Et	ethyl
FBW	Fritsch-Buttenberg-Wiechell
FC	flash chromatography
fs	femtosecond
fur	furyl
FVP	flash vacuum pyrolysis
FWHM	full width at half maximum
γ	molecular second hyperpolarizability
Gal	galactose
GGA	gradient generalized affroximation
Glc	glucose
GPC	gel permeation chromatography
$h\nu$	light
Hep	heptyl
Hex	hexyl
HF	Hartree-Fock
HMPA	hexamethylphosphoramide
HOMO	highest occupied molecular orbital
HOPG	highly oriented pyrolytic graphite
ICR	ion cyclotron resonance
INDO	intermediate neglect differential orbital
IP	ionization potential
K_{assoc}	association constant
l	contour length
λ_{max}	wavelength of maximum absorption
LB	Langmuir–Blodgett

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
T	thymine
TBAF	tetrabutylammonium fluoride
TBDMS	*tert*-butyldimethylsilyl
TBS	*tert*-butyldimethylsilyl
TCNQ	7,7,8,8-tetracyanoquinodimethane
TD	Time dependent
TDDFT	time-dependent DFT

TEBAC	triethylbenzylammonium 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
Tol	4-tolyl (4-methylphenyl)
Ts	*p*-toluenesulfonyl
Tr	trityl (triphenylmethyl)
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

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