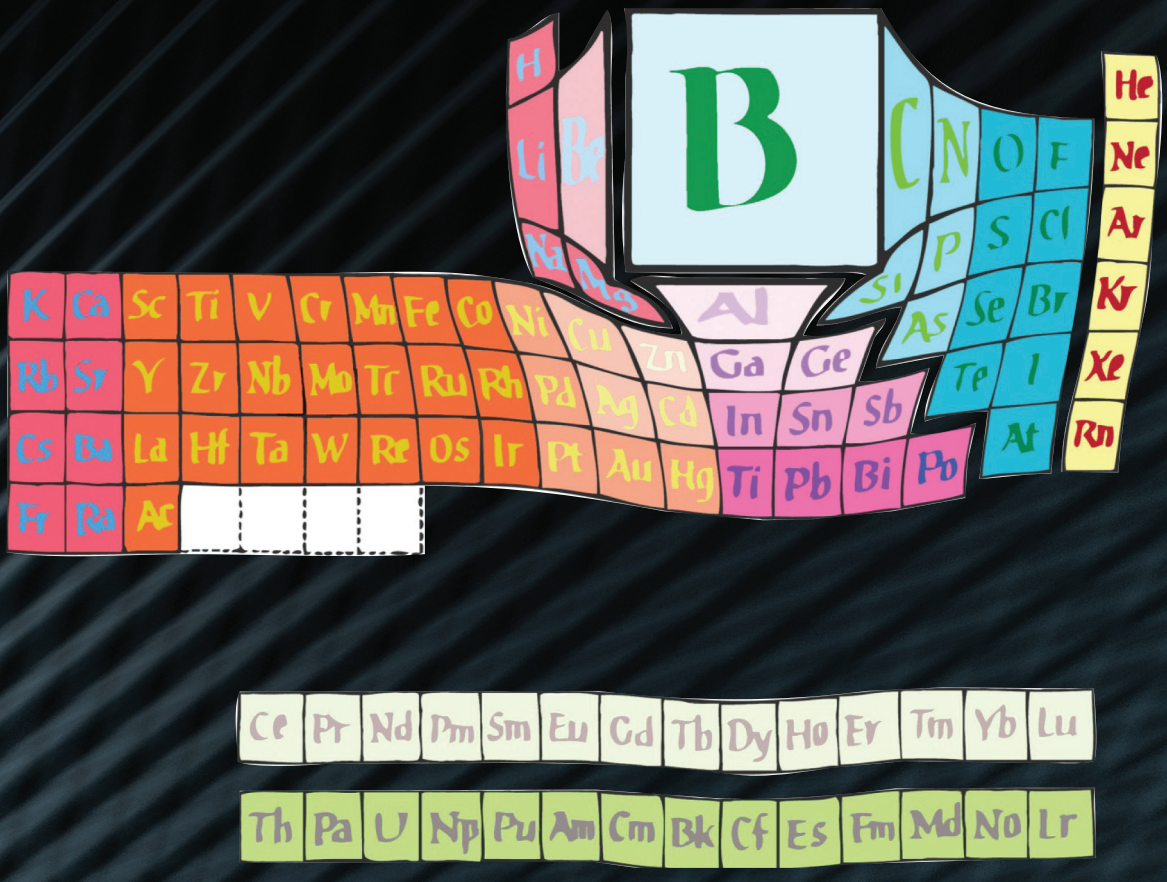
Boron Science

New Technologies and Applications



EDITED BY

NARAYAN S. HOSMANE

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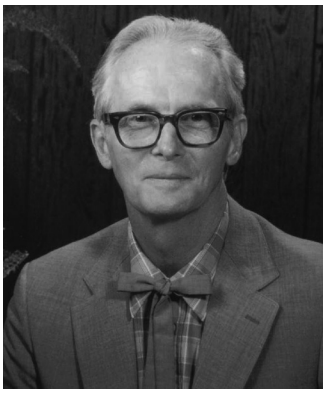
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This book is dedicated to William N. Lipscomb Jr. (December 9, 1919–April 14, 2011), Emeritus Professor at Harvard University and the winner of the 1976 Nobel Prize for Chemistry. Professor Lipscomb, one of the founders of theoretical and structural polyhedral boron chemistry, had dedicated much of his career to promoting boron science, which is the subject of this book. Much of the progress in these endeavors rests on Professor Lipscomb's original work on bonding in boranes. His dedication to our global society is hereby recognized and saluted. We miss him.

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Foreword

It has been observed many times but bears repeating: boron is a unique element. Of course, in a sense the same can be said of other elements, such as carbon and hydrogen, but the capacity of boron to confound established notions of structure and bonding—at times seeming to write its own rules—has fascinated and exasperated generations of workers. This seemingly innocuous element, tucked into the top of the periodic table between beryllium and carbon, appeared normal—even boring—for a century following its isolation in 1808 by Humphrey Davy and, independently, Gay-Lussac and Thenard. It behaved exactly as expected, forming trivalent compounds such as the boron trihalides, trialkylboranes, $B(OH)_3$, and borates, and everyone, including the eminent William Ramsey, a Nobel Laureate and discoverer of the noble gases, believed that its simplest hydride had to be BH_3 (what else could it be?). It took the great German chemist Alfred Stock to uncover the truth about the boron hydrides and, even he, working in the early twentieth century, had little notion of their incredible structures and assumed they must be similar to hydrocarbons despite their inconvenient shortage of electrons. Not until another half-century had passed did another towering scientist, William Nunn Lipscomb, finally crack the mystery of the three-center-bonded polyboranes, proving many of their structures with his ingenious apparatus that enabled the collection of x-ray diffraction data at ultracold temperatures and developing a theoretical foundation based on the concept of the three-center two-electron bond. For these achievements, Lipscomb was awarded the 1976 Nobel Prize in Chemistry.

It is highly appropriate that the editor of this volume highlighting recent advances in boron science across an amazingly broad spectrum of applications, with contributions by leading experts in their respective fields, has chosen to dedicate it to Lipscomb, a Kentuckian known as "the Colonel" to generations of his students, coworkers, and colleagues. I first met the Colonel in 1958 as a new graduate student in inorganic chemistry at the University of Minnesota, when it was suggested that I talk with him about joining his research group. I almost didn't go—after all, he was not a member of the inorganic faculty, in fact serving as physical chemistry division chair, and I had no interest in boranes (or so I thought). But I went anyway, and after an hour in his office I was hooked. The borane structures and bonding diagrams that filled several blackboards were exotic and strange to me, but there was something about this man and his mission that was irresistible, and I signed on. Only later did I discover that I was to be his first student who was neither a crystallographer nor a theoretician—it would be my job to learn how to build vacuum lines and manipulate such lovely materials as diborane and pentaborane. With the invaluable help of a summer in Riley Schaeffer's lab at Indiana University just prior to moving with the Colonel to Harvard in early 1960, I eventually managed to acquire these skills. But what struck me most forcefully about the Colonel, and still does, was his unconventional approach to research. In group discussions in which we were encouraged to think outside the box—the further outside, the better—I seldom, if ever, heard him dismiss an idea out of hand. Vacuum line explosions and other setbacks were shrugged off as the price of progress. (There were rare exceptions to his usual good humor, including an incident in which an expensive piece of x-ray diffraction equipment was dropped while being unloaded by crane from the second story of Gibbs Hall, gouging a large crater in the front lawn.)

Reflecting on the Lipscomb research philosophy after all these years, I think that a central attribute has been his uncommon willingness to risk error, as he acknowledged in an early classic paper on three-center bonding with Eberhardt and Crawford. This is not a universal attitude these days, as research funding agencies have little tolerance for false starts and dead ends, and pure exploratory synthesis is practically extinct. Moreover, it must be admitted that a free-wheeling approach is more likely to produce success when coupled with a consummate scientific imagination like the Colonel's.

To me, this book represents more than a fine up-to-date compilation of progress in the applied chemistry and physics of boron. It is, as well, a tribute to the groundbreaking studies of legions of workers over many years led by some truly inspired scientists including not only the late Lipscomb but Fred Hawthorne (who is still at it, full force, directing his new International Institute of Nano and Molecular Medicine at the University of Missouri), the late Herbert C. Brown, and their scientific protégés who together transformed boron science from a boring area to a compelling, exciting, vibrant, and growing one. One of the latter-day scientific descendants of these pioneers, Narayan Hosmane (a postdoc in my own laboratory over 30 years ago, and a major contributor in his own right) has performed a major service in bringing together this excellent fount of information in a rapidly moving field.

Russell N. Grimes
Charlottesville, Virginia

Preface

What is boron? The question itself may not seem very significant to many people. Their introduction to the word "boron" could come as the butt of a joke. Conan O'Brien made jokes about boron (http://www.wired.com/wiredscience/2009/02/conanchemistry/) by calling it either "Boring Boron" or "Boron Moron." Many people may connect boron to borax, which is one of its natural sources. Some of us with longer memories might recall a popular television show called *Death Valley Days*, aired in the 1950s, narrated by a young Ronald Reagan and sponsored by 20 Mule Team Borax. Although boron is one of the closest neighbors to carbon in the periodic table, it has neither gained the importance nor the popularity of carbon. But boron is not just about borax. How many of us know that a regular intake of boron can lessen the chance of prostate cancer? How many of us know that boron plays a direct and critical role in combating cancer through a treatment called boron neutron capture therapy (BNCT)?

If you were among those fortunate attendees of Professor M. Frederick Hawthorne's lecture at UCLA titled "From Mummies to Rockets and on to Cancer Therapy," you had the opportunity to explore the power of boron chemistry. Boron has made a significant impact in our lives through its use in fertilizers, fungicides, soaps, and detergents as well as many household glassware utensils; thus boron is silently present everywhere. Those involved in boron chemistry are beginning to realize that this silence needs to be broken. This book, titled *Boron Science: New Technologies and Applications*, attempts to do just that.

To illustrate the versatility of boron in all areas of applications, the 29 chapters of this book are divided into seven major sections, Boron for Living: Medicine (Part I); Boron for Living: Health and Nutrition (Part II); Boron for Living: Radioisotope (Part III); Boron for Living: Boron Neutron Capture Therapy (Part IV); Boron for Electronics: Optoelectronics (Part V); Boron for Energy: Energy Storage, Space, and Other Applications (Part VI); and Boron for Chemistry and Catalysis: Catalysis and Organic Transformations (Part VII). Each chapter has been rigorously reviewed by at least three reviewers. In order to maintain high quality, reviews were solicited not only from the expert authors of other chapters but also from renowned scientists who willingly shared their expertise and help in improving the quality of the chapters. The invaluable reviews from the following scientists are hereby gratefully acknowledged.

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While I would take this opportunity to thank all of the contributors for their timely submission and valuable input, the immense help from the senior project coordinator, Kari Budyk, and persuasive ability of Lance Wobus, the scientific editor of CRC Press, in making me edit this unique book will always be remembered, appreciated, and acknowledged.

Since the contributing authors are all renowned scientists in their respective disciplines, they truly deserve all of the credit for the success of this book. However, it would be a great mistake if I forgot to thank three most important individuals, Dr. Amartya Chakrabarti, his undergraduate research assistant Hiren Patel, and my wife, Sumathy Hosmane, for their immense support, patience, and help throughout the editing process, from drawing the figures to proofreading to contributing chapters.

We sincerely hope that the chapters in this book will make your reading more intriguing and fascinating than those derived from other elements, as they illuminate the multifaceted nature of the boron compounds beyond their normal place as chemical curiosities.

For the authors,
Narayan S. Hosmane

Editor



Narayan S. Hosmane was born in Gokarn near Goa, Karnatak state, Southern India, and is a BS and MS graduate of Karnatak University, India. He obtained a PhD degree in inorganic/organometallic chemistry in 1974 from the University of Edinburgh, Scotland, under the supervision of Professor Evelyn Ebsworth. After a brief postdoctoral research training in Professor Frank Glockling's laboratory at the Queen's University of Belfast, he joined the Lambeg Research Institute in Northern Ireland, and then moved to the United States to study carboranes and metallacarboranes. After postdoctoral work with Russell Grimes at the University of Virginia, in 1979 he joined the faculty at the Virginia Polytechnic Institute and State University. In 1982 he joined the faculty at the Southern Methodist University, where he became professor of chemistry in 1989. In 1998 he moved to Northern Illinois University and is currently a distinguished research professor and inaugural board of trustees professor. Dr. Hosmane is widely acknowledged to have an international reputation as "one of the world leaders in an interesting, important, and very active area of boron chemistry that is related to cancer research" and as "one of the most influential boron chemists practicing today." Hosmane has received numerous international awards that include but are not limited to the Alexander von Humboldt Foundation's Senior U.S. Scientist Award twice; the BUSA Award for Distinguished Achievements in Boron Science; the Pandit Jawaharlal Nehru Distinguished Chair of Chemistry at the University of Hyderabad, India; and the Gauss Professorship of the Göttingen Academy of Sciences in Germany. While his recent lecture at the Kishwaukee Community Hospital in DeKalb, Illinois, on "Boron and Gadolinium Neutron Capture Therapy: A New Perspective in Cancer Treatment" has resulted in the initiation of collaborative research efforts between NIU and the oncologists/surgeons at Kish Hospital, his featured lecture at the recent American Chemical Society's special symposium on nanomaterials, held in Philadelphia, brought special attention of Dr. Hosmane's work in utilizing magnetic nanomaterials for effective drug delivery in cancer research. He has published over 270 papers in leading scientific journals.

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Part I

Boron for Living: Medicine

INTRODUCTION

Boron lies next to carbon in the periodic table of elements. This causes compounds of boron to share some similarities with those of carbon but also preserves important differences. It is the combination of those similarities and differences that puts boron in a unique place for a variety of applications.

The physical and chemical properties of boron make it possible to the design boron-containing molecules with new biological characteristics and offer medicinal chemists a rare opportunity to explore and pioneer new areas of molecular design and medicinal applications. Emerging boron therapeutics show different modes of activity against a variety of biological targets. The utility of this class of compounds is likely to grow over the next decade, and boron could become widely accepted as a useful element in the development of future drugs.

The applications of boron in medicine are not limited to the development of new chemotherapeutics, but also include diagnostics and the modulation of many metabolic processes through dietary boron. The discovery of polyhedral boron compounds added new dimensions to the medicinal chemistry of boron, facilitating the quest for biologically active molecules containing boron clusters rather than only a single boron atom per molecule. Thus, boron is an essential element for life and living.

The first section consists of three chapters covering the medical uses of boron. Chapter 1 by Lesnikowski describes some of the properties of boron clusters that are important for medical applications and presents some examples of boron clusters in different types of medical applications. The following two chapters describe bioactivity of two specific types of boron compounds: carbaboranyl phosphonates (in Chapter 2 by Stadlbauer and Hey-Hawkins) and metal bis(dicarbollides) (Chapter 3 by Konvalinka et al). The former compounds are active as pesticides, bactericides and gameticides, while the later are useful as inhibitors of HIV protease. Both classes have been studied as boron delivery agents for boron neutron capture therapy in cancer treatment.

1 New Opportunities in Boron Chemistry for Medical Applications

Zbigniew J. Leśnikowski

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1.1 INTRODUCTION

The chemistry of boron has many facets. The pharmacological uses of boron compounds have been known for several decades. More recently it was found that some boron analogs of amino acids and their derivatives express hypolipidemic,[1] anti-inflammatory,[2] antineoplastic,[3] and antiostereoporotic[4] properties.

In animals and humans, at intracellular pH, nearly all natural boron exists as boric acid, which behaves as a Lewis acid, and forms molecular additive compounds with amino- and hydroxy acids, carbohydrates, nucleotides, and vitamins through electron donor–acceptor interactions. In most of the commercial dietary boron supplements now available, boron is chelated with amino acids or with hydroxy acids (i.e., glycine, aspartic acid, or citric acid) in combination with vitamins. However, little is known about the molecular structure of these boron chelates.[5,6]

The real stimulus for the development of bioorganic and medicinal chemistry of boron was provided by revival of interests in boron neutron capture therapy (BNCT) of cancers.[7,8] This is connected to the progress in nuclear research reactor technology and the prospective availability of

suitable clinical sources of neutrons necessary for the treatment of cancers using BNCT. The discovery of polyhedral boron compounds in the 1960s[9] facilitated the quest for new boron carriers for BNCT, containing boron clusters instead of one boron atom per molecule.[10–13] The study of electron-deficient boron clusters has developed into a major area of inorganic–organometallic chemistry with considerable overlap into organic and medicinal chemistry as well. Bioorganic chemistry of polyhedral boranes is a new trend in this field. It emerged in part as a result of a quest for better boron carriers for BNCT of tumors. Among many low-molecular-weight compounds synthesized for BNCT are carborane-containing amino acids, lipids, carbohydrates, porphyrins, nucleic acid bases and nucleosides, and DNA groove binders.[10,13] A new generation of radiosensitizers for BNCT described recently includes biopolymers bearing one or more carboranyl residues. This class of boron trailers includes carboranyl peptides and proteins, carboranyl oligophosphates, and nucleic acids (DNA-oligonucleotides).[14–16] However, the interest in BNCT is characterized by ups and downs and there is still a long way ahead before it will become a useful clinical technology. Nevertheless, basic knowledge about toxicity and pharmacokinetics of particular classes of boron-containing compounds has been obtained during extensive studies on boron carriers for BNCT, and this can help in the development of the other biological applications of boron compounds.

Simultaneously new, previously unknown biological activities of boron cage molecules and their complexes with metals have been discovered, which including anti-HIV activity, anticancer activity, or in the form of conjugates with nucleosides (nucleic acid components) activity as purinergic receptor modulators.

These and other recent findings clearly show that there is a great, still unexplored potential in bioorganic chemistry of boron and medical applications of boron-containing molecules. This account is not meant to be comprehensive but rather focused on developments of new chemistries and avenues. Several aspects of biological applications of boron-containing compounds are discussed in other chapters of this book, therefore, issues such as BNCT, application in radiotherapy, or anti-HIV protease activity will be omitted. Emphasis is laid on molecules bearing or being derivatives of boron clusters. The vast field of compounds were derived from boric acid and their biological functions had to be left out due to the limited scope of the present overview; Research in this area merits focused reviews in its own right.

1.2 SOME PROPERTIES OF BORON CLUSTERS IMPORTANT FOR MEDICAL APPLICATIONS

Polyhedral heteroboranes have been the subject of intense research for over 50 years. A subset of this extensive class of compounds are dicarbadodecaboranes expressed by the general formula $C_2B_{10}H_{12}$.[9,17] Carboranes are a category of caged-boron compounds most widely explored in medicinal chemistry; however, other boron clusters, such as dodecaborate anion and boron cluster-based coordination compounds accommodating boron cages of different sizes and structural features (metallaboranes and metallacarboranes), also focus on growing attention (Figure 1.1).

Carboranes such as icosahedral dicarba-*closo*-dodecacarboranes ($C_2B_{10}H_{12}$) (**1**–**3**) are characterized by rigid geometry, high chemical and biological stability, and an exceptional hydrophobic character. These characteristics support their use in designs based on the hydrophobic nature of carboranes. If increase in water solubility of boron cluster-biomolecule conjugates is required, an ionic and hydrophilic dodecaborate unit type of (**4**) can be used. Metallacarboranes (e.g., types of **5** and **6**) offer opportunities related to the properties of metals being a part of the complex as well as unique structural features of the metallacarborane molecule as a whole.[18,19] Metallacarboranes comprise a vast family of metallocene-type complexes consisting of carborane cage ligand(s) and one or more metal atoms such as Co, Fe, Cr, Nb, Ni, Cu, Au, Pt, Ru, Re, Tc, and many others. Application of metallacarboranes as vehicles for metals for modification of biomolecules is still underexplored.

An additional advantage of boron clusters and their metal complexes is that they are abiotic and therefore chemically and biologically orthogonal to native cellular components (stable in

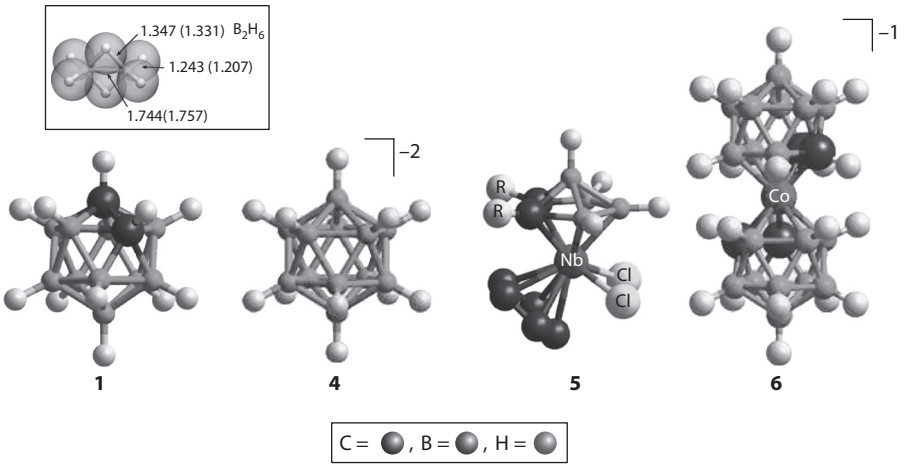


FIGURE 1.1 Example of boron clusters and boron cluster-based coordination compounds used in medicinal chemistry: 1,2-dicarba-*closo*-dodecaborane ($C_2B_{10}H_{12}$) (**1**), *closo*-dodecaborate ($B_{12}H_{12}^{2-}$) (**4**), carbon-substituted cyclopentadienyl-niobium dichloride-dicarbahexaborate [$(C_5H_5)NbCl_2(R_2C_2B_4H_4)$] (**5**), 3-cobalt-bis(1,2-dicarbollide)ate [$Co(C_2B_9H_{12})_2^-$] (**6**). Inset: An example of 3-center-2-electron (3c2e) bonds (B-H-B bridge in diborane).

biological environment) and usually resistant to catabolism, which is a desirable property for biological applications.

1.3 STRUCTURAL FEATURES

General boron cluster chemistry has been the topic of several books and review articles;[9,11,17] therefore, only basic information pertinent to that discussion in this chapter is provided. Polyhedral borane and carborane clusters are characterized by delocalized electron-deficient linkages, meaning that there are too few valence electrons for bonding to be described exclusively in terms of 2-center-2-electron (2c2e) bonds. One characteristic of electron-deficient structures is the aggregation of atoms to form 3-center-2-electron (3c2e) bonds (Figure 1.1), which typically results in the formation of trigonal faces and hypercoordination. The high connectivity of atoms in a cluster compensates for the relatively low electron density in skeletal bonds. The three-dimensional deltahedral shapes are typical of boron and carborane clusters.

The types of polyhedral boron compounds best known and most often used in medicinal chemistry are icosahedral dicarbadodecarboranes ($C_2B_{10}H_{12}$) (**1–3**) in which two BH vertices have been replaced by two CH units. They have nearly spherical geometry with 20 sides and 12 vertices, in which the carbon and boron atoms are hexacoordinated and participate in the heavily delocalized bonding. This, together with undergoing reactions typical for aromatic compounds, leads to the carborane molecule being characterized as a "pseudoaromatic" system. It is remarkable that the aromatic character of carboranes is expressed in three dimensions in contrast to two-dimensional aromaticity in planar polygonal hydrocarbons such as benzene.[20] The space occupied by dicarbadodecaborane is about 50% larger than that of the rotating phenyl group. Dicarba-*closo*-dodecaboranes ($1,X\text{-}C_2B_{10}H_{12}$) exist in three isomeric forms depending on the location of two carbon atoms within the cage, with $X = 2, 7, 12$, as *ortho*-, *meta*-, and *para*-carboranes, respectively (**1–3**). Numbering of boron and carbon atoms is shown in Figure 1.2.

One of the most important features of a carborane system is its ability to enter into substitution reactions at both the carbon and boron atoms without degradation of the carborane cage. The susceptibility for removal of the most electrophilic boron atom in closed-cage carborane such as 1,2-dicarba-*closo*-dodecaborane is an added advantage for its transformation into open cage form

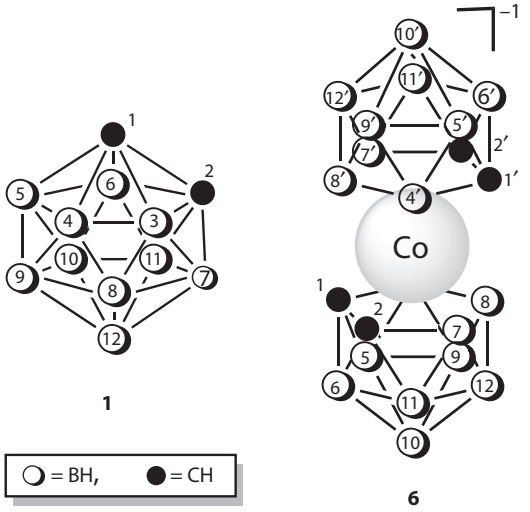


FIGURE 1.2 Numbering of boron and carbon atoms in 1,2-dicarba-*closo*-dodecaborane (*ortho*-carborane) (**1**) and 3-cobalt-bis(1,2-dicarbollide)ate, $[Co(C_2B_9H_{11})_2^-]$ (**6**).

7,8-dicarba-*nido*-undecaborate ion $(C_2B_9H_{12})_{-1}$ under basic conditions, followed by the ability to form "sandwich" type derivatives which are analogs of the transition metal cyclopentadienide derivatives.

1.4 BORON CONTENTS

The boron content per molecule is an important factor for the application of boron compounds as boron carriers for BNCT. For BNCT to be successful, a suitable number of ^{10}B atoms must be localized on or preferably within neoplastic cells, and a sufficient number of thermal neutrons must be delivered to sustain a lethal ^{10}B (n, alpha) lithium-7 reaction. It is estimated that an average of 3–7 alpha-particle traversals through the cell is required to destroy a cell which contains ca. 15 μg ^{10}B/g tumor tissues. Therefore, the development of highly boron loaded, tumor-selective drugs play an important role if BNCT is to evolve into clinically accepted treatment for cancer. At the early stages of the process of development of boron carriers for BNCT, boron compounds consisting of natural boron existing as a 19.9% ^{10}B isotope and 80.1% ^{11}B isotope mixture are used. In clinical practice, boron carriers enriched in ^{10}B isotope are applied due to a much higher neutron capture cross-section (σ) for ^{10}B than for ^{11}B, 3837 and 0.005 barns, respectively.

Boric acid $[B(OH)_3]$ and borane clusters (*closo*-$B_{12}H_{12}^{2-}$) are the only two types of boron entities used so far in the synthesis of carrier molecules for BNCT being a component of two clinically used drugs: L-4-(dihydroxyboryl)phenylalanine (BPA) and the sodium salt of thioborane anion ($Na_2B_{12}H_{11}SH$, BSH). The obvious advantage of polyhedral boron compounds over the derivatives containing one boron atom per molecule as boron donors for BNCT is their much higher boron content. More recently, a growing interest in metallacarboranes containing about 1.5 times as much boron as BSH and 18 times more boron atoms than boric acid, and double-cage boron compounds such as N-substituted bis-decaborate anion a^2-$(B_{10}H_9)(B_{10}H_8)NH_2R$ (**7**) or 1-(1,2-dicarbadode carborane)-oxabutoxy-dodecaborate $(C_2B_{10}H_{11})(CH_2)_4O(B_{12}H_{11})$ (**8**) (Figure 1.3), can be observed.

1.5 HYDROPHOBICITY

Carboranes and numerous metallacarboranes are characterized by exceptional lipophilicity or amphiphilicity. These properties make them particularly suitable for use as hydrophobic components in biologically active molecules, particularly those which interact hydrophobically with

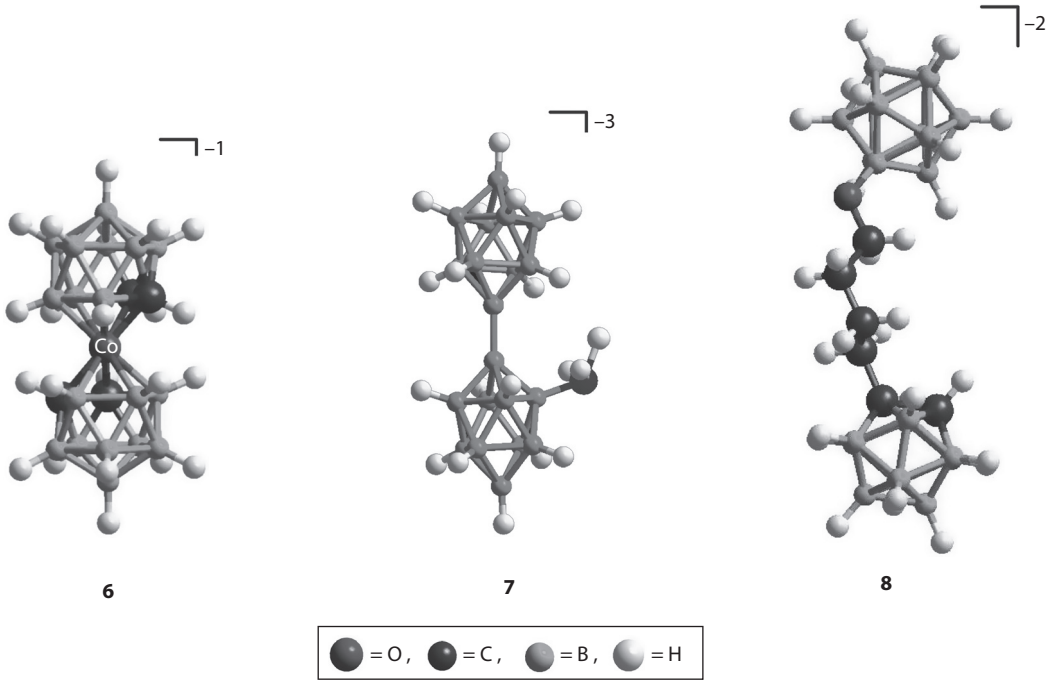


FIGURE 1.3 Examples of double-cage boron compounds for biomedical applications: 3-cobalt-bis(1,2-dicarbollide)ate, $[Co(C_2B_9H_{12})_2^-]$ (**6**); N-substituted bis-decaborate anion a^2-$[(B_{10}H_9)(B_{10}H_8)NH_2R]^{-3}$ (**7**) (a) (Adapted from E. M. Georgiev et al., *Inorg. Chem.*, **1996**, *35*, 5412–5416.) and 1-(1,2-dicarbadodecarborane)-oxabutoxy-dodecaborate $[(C_2B_{10}H_{11})(CH_2)_4O(B_{12}H_{11})]^{-2}$ (**8**) (b) (Adapted from I. B. Sivaev, S. Sjoberg, V. I. Bregadze, *J. Organomet. Chem.*, **2003**, *680*, 106–110.)

molecular targets in the cellular environment. The high hydrophobicity of many boron clusters and their derivatives can be explained by the presence of partial negative charge (density differs for different hydrogens and depends on the type of cluster), located on boron-bound hydrogen atoms in B–H groups and their "hydride-like" character. This prevents them from forming classical hydrogen bonds, which causes a lipophilic/hydrophobic character of the boron clusters (Figure 1.4).

The electronegativity of hydrogens enables boranes to form unconventional hydrogen bonds, namely dihydrogen bonds. Dihydrogen bonds, also called proton–hydride bonds, generally occur between a positively charged hydrogen atom of a proton donor *A*H (*A* = N, O, S, C, halogen) and a bond of an *M*H proton acceptor (*M* = electropositive atom, such as boron, alkali metal, or transition metal).[23] However, the dihydrogen bonds are weaker than classical hydrogen bonds; therefore, repulsive effect toward surrounding water molecules prevails, and the hydrophobic nature of many boron clusters is observed. In boranes, NH···HB, CH···HB, and SH···HB dihydrogen bonds have been found. Another type of interaction was found for CH (carborane)–Y hydrogen-bonded complexes. These complexes were, however, much less stable.[24,25]

The electronic effects of the boron atom in the carborane cage change according to the following sequence: the more remote the boron atom (electronegativity = 2.0) is from the carbon atoms (electronegativity = 2.6) in the cluster, the stronger is its electron-donating effect; consequently, the electron density in 1,2-dicarba-*closo*-dodecaborane (**1**) decreases in the order 9 (12) > 8 (10) > 4 (5,7,11) > 3 (6) > 1 (2). On the other hand, the carborane group as a whole has a strong electron-withdrawing character.

Boron clusters as modifying entities for biomolecules offer rich possibilities of tailoring the hydrophobic property due to different dipole moments and hydrogen-binding sites of the molecule though there is only limited knowledge as to how to reach this in a geometrically predefined manner.

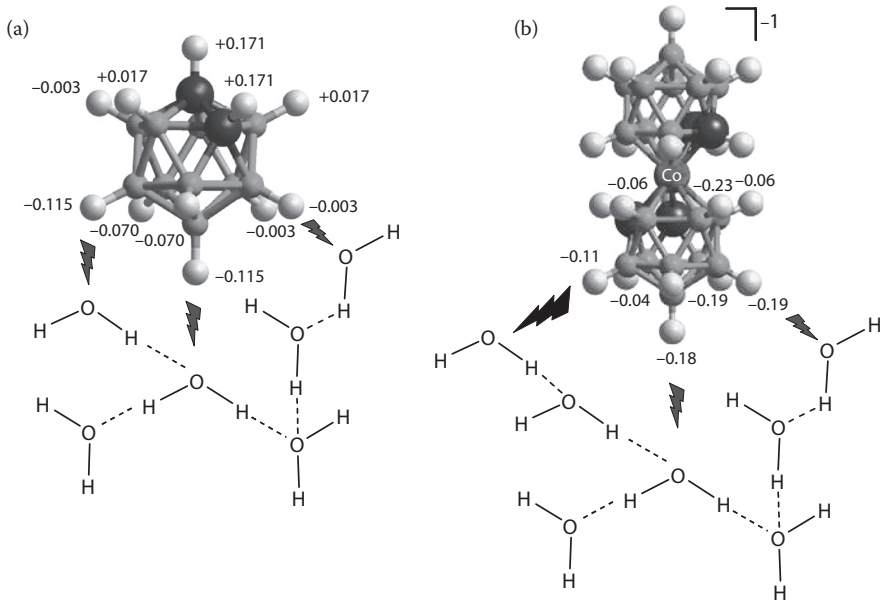


FIGURE 1.4 Hydridic character of boron cage hydrogens causes inability to contribute in hydrogen bonding with water and participates in hydrophobic character of carboranes and metallacarboranes. Charge density distribution for 1: 1 (2) = +0.172; 3 (6) = +0.017; 4 (5, 7, 11) = −0.003; 8 (10) = −0.070; 9 (12) = −0.115 determined from pK_a values of carborancarboxylic acid (a),[26] and 6: 4 (7) = −0.06; 8 = −0.23; 5 (11) = −0.04; 6 = −0.11; 10 = −0.18; 9 (12) = −0.19, calculated according to Two Atom Natural Population Analysis method (b).[27]

The hydrophobicity of dicarbadodecaboranes can be reduced by the presence of a dipole moment, which is strongly dependent on the position of the carbon atoms in the carborane cage.

Consequently, the hydrophobicity of dicarbadodecaborane ($C_2B_{10}H_{12}$) (**1**–**3**) isomers increases in the following order: 1,2-dicarba-*closo*-dodecaborane (*ortho*-carborane) (**1**) <1,7-dicarba-*closo*-dodecaborane (*meta*-carborane) (**2**), 1,12-dicarba-*closo*-dodecaborane (*para*-carborane) (**3**) (Figure 1.5). Removal of the most electrophilic boron atom in hydrophobic, neutral *closo*-carborane results in the formation of more hydrophilic, anionic *nido*-carboranes ($C_2B_9H_{12}^-$).

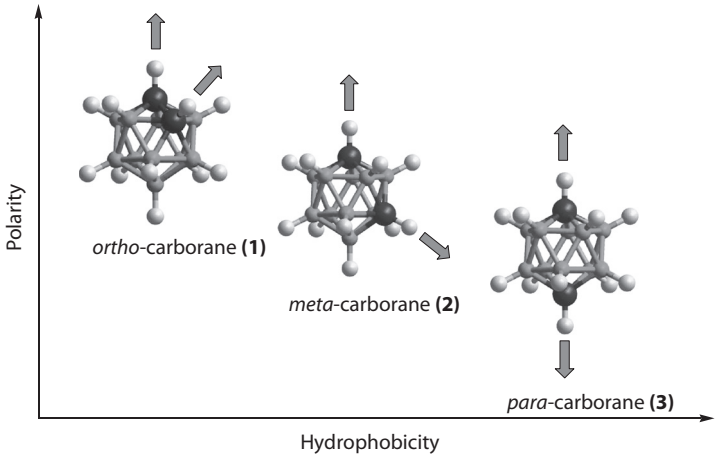


FIGURE 1.5 An effect of dipole moment on hydrophobicity of dicarbadodecaboranes: 1,2-dicarba-*closo*-dodecaborane (*ortho*-carborane) (**1**); 1,7-dicarba-*closo*-dodecaborane (*meta*-carborane) (**2**); 1,12-dicarba-*closo*-dodecaborane (*para*-carborane) (**3**).

1.6 MEDICAL APPLICATIONS OF BORON CLUSTERS

The cage-like, ball-shaped dicarbadodecaborane structure mimics well the dodecahedral volume created by rotation of the planar phenyl ring over 360°, but it is bigger and has a much more hydrophobic moiety. Its higher volume and surface area in comparison with phenyl ring may explain the high-efficacy interactions of carborane-containing biomolecules with hydrophobic domains of proteins such as receptors. These advantages were first exploited for modification of amino acids and peptides. L-Ortho-carboranylalanine and several other carborane-modified amino acids were synthesized in the late seventies. The lipophilicity of L-ortho-carboranylalanine assigned by partition coefficient measurement was much higher than that of the parent L-phenylalanine and higher than that of another lipophilic phenylalanine analog, L-adamantylalanine. Subsequently, several analogs of biologically active peptides, such as enkephalin, angiotensin, bradykinin, substance P, and insect neuropeptide pyrokinin in which the residue Phe and/or Tyr was replaced with carborane-bearing amino acid analog, have been synthesized. Often highly increased biological activity was achieved, for example, the carborane-modified pyrokinin analog exhibited a 30-fold increase in pheromonotropic activity *in vitro* and a 10-fold increase in *in vivo* studies. It was also significantly more stable toward aminopeptidase. Several homopeptides containing carborane-containing amino acid analog for antibody modification and subsequent BNCT studies have also been prepared.[15]

The recent revival of interest in the application of boron clusters in drug design was initiated by extensive studies by Endo and associates on a range of receptor modulators containing carboranes as a hydrophobic pharmacophore, such as analogs of retinoic acid, estradiol, or androgene. Some of these and other examples are briefly discussed below.

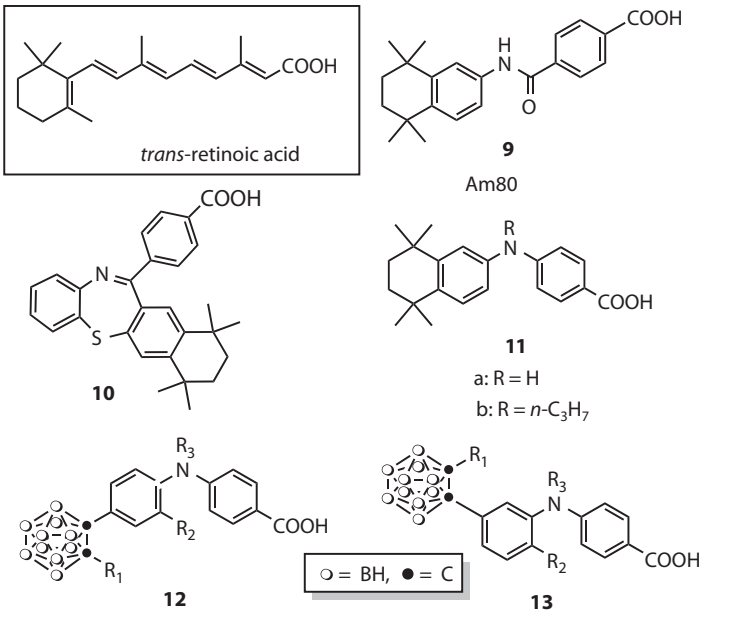
1.6.1 Retinoid Receptor Ligands Having a Dicarba-*closo*-Dodecaborane as a Hydrophobic Moiety

Retinoids and their analogs are of particular interest as chemopreventive and therapeutic agents in the field of dermatology and oncology. The biological activities of retinoids are mediated by binding to and activation of the retinoic acid receptors (RARs), with subsequent modulation of the gene transcription by the complex. High-binding activity requires a carboxylic acid moiety and an appropriate hydrophobic group which interacts with the hydrophobic cavity of the RAR ligand-binding domain.

Numerous diphenylamines bearing a 1,2-dicarba-*closo*-dodecaborane (**1**) moiety have been synthesized and their biological properties were studied. Retinoidal activity was examined in terms of the differentiation-inducing ability toward human promyelocytic leukemia HL-60 cells. 4-[4-(1,2-Dicarba-*closo*-dodecaboran-1-yl)phenylamino]benzoic acids (**12**) and 4-[3-(1,2-dicarba-*closo*-dodecaboran-1-yl)phenylamino]benzoic acids (**13**) (Figure 1.6) showed potent agonistic activity at concentrations of 10^{-8}–10^{-9} M. Among the synthesized compounds 4-[4-(2-propyl-1,2-dicarba-*closo*-dodecaboran-1-yl)phenylamino]benzoic acid (**12d**: R_1=*n*-C_3H_7, R_2=H, R_3=H) exhibited biological activity almost equal to that of the natural ligand. It was also found that the RXR antagonistic activity could be separated from retinoid agonistic activity by introduction of a methyl group on the aromatic ring or alkyl groups on the nitrogen atom. The field of carborane analogs of RAR ligands and modulators is still expanding and provides excellent candidates for a new class of therapeutic agents.[28–30]

1.6.2 Steroid Analogs Bearing Boron Cluster Modification

Steroids are a class of lipids characterized by a sterane core and additional functional groups. Hundreds of distinct steroids are found in plants, animals, and fungi. It is possible to classify steroids based on their chemical composition into cholestanes (e.g., cholesterol), cholanes (e.g., cholic acid), pregnanes (e.g., progesterone), and androstanes (e.g., testosterone and androgen). Steroids play many important biological roles, often as hormones interacting with specific receptors. The hydrophobic



a: $R_1 = H, R_2 = H, R_3 = H$
b: $R_1 = CH_3, R_2 = H, R_3 = H$
c: $R_1 = C_2H_5, R_2 = H, R_3 = H$
d: $R_1 = n\text{-}C_3H_7, R_2 = H, R_3 = H$
e: $R_1 = i\text{-}C_3H_7, R_2 = H, R_3 = H$
f: $R_1 = n\text{-}C_4H_9, R_2 = H, R_3 = H$
g: $R_1 = CH_3, R_2 = H, R_3 = CH_3$
h: $R_1 = CH_3, R_2 = CH_3, R_3 = CH_3$

a: $R_1 = H, R_2 = H, R_3 = H$
b: $R_1 = CH_3, R_2 = H, R_3 = H$
c: $R_1 = C_2H_5, R_2 = H, R_3 = H$
d: $R_1 = n\text{-}C_3H_7, R_2 = H, R_3 = H$
e: $R_1 = i\text{-}C_3H_7, R_2 = H, R_3 = H$
f: $R_1 = n\text{-}C_4H_9, R_2 = H, R_3 = H$
g: $R_1 = CH_3, R_2 = H, R_3 = CH_3$
h: $R_1 = CH_3, R_2 = CH_3, R_3 = CH_3$

FIGURE 1.6 Selected examples of two types of specific nuclear receptor ligands (retinoic acid receptors: RARs and retinoid X receptors: RXRs), unmodified and modified with boron cluster pharmacophore. (Adapted from Y. Endo et al., *Bioorg. Med. Chem. Lett.*, **1999**, *9*, 3313–3318; Y. Endo et al., *Bioorg. Med. Chem. Lett.*, **1999**, *9*, 3387–3392; K. Ohta et al., *Bioorg. Med. Chem. Lett.*, **2004**, *14*, 5913–5918.)

structure of steroids is important for their biological activity, often playing the role of a scaffold, fixing the spatial positions of hydrogen-bonding functional groups. These open attractive opportunities for modification of biologically important steroids with boron cluster lipophilic pharmacophore to modulate essential hydrophobic interaction in receptor–ligand complexation.

1.6.2.1 Estrogen Analogs Having a Dicarba-*closo*-Dodecaborane as a Hydrophobic Moiety

The steroid hormone estrogen influences the growth, differentiation, and functioning of many target tissues. Estrogen plays an important role in the female and male reproductive system and also in bone maintenance, in the central nervous system, and in the cardiovascular system. The first step in the appearance of these activities is mediated by binding of hormonal ligands to the α and β estrogen receptor (ER) monomers resulting in the formation of an ER dimer; hydrophobic interactions play an important role in this process. Several novel carborane-containing estrogenic agonists have been synthesized (Figure 1.7).

The estrogenic activities of the synthesized compounds were examined by the luciferase reporter gene assay in which a rat ERK expression plasmid and a reporter plasmid, containing five copies of estrogen-response elements, were transiently transfected into COS-1 cells. 17β-Estradiol at 1×10^{-10}–1×10^{-8} M induced the expression of luciferase in a dose-dependent manner. Among the

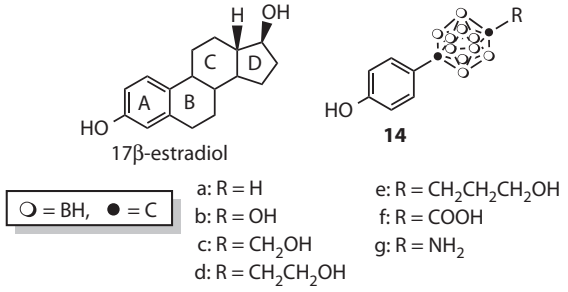


FIGURE 1.7 Example of highly active estrogen receptor (ER) agonists based on carborane structure. (Adapted from Y. Endo et al., *Chem. Biol.,* **2001**, *8*, 341–355.)

compounds studied, 1-hydroxymethyl-12-(4-hydroxyphenyl)-1,12-dicarba-*closo*-dodecaborane (**14c**) appeared 10 times more active than its natural counterpart, 17β-estradiol.[31]

Development of potent carborane-containing estrogenic agonists should yield novel candidates of therapeutic agents, especially selective ER modulators. Furthermore, the suitability of the spherical carborane cage for binding to the cavity of ERαLBD should provide a basis for a similar approach to develop novel ligands for other steroid receptors. In addition, the unique character of biologically active molecules containing a carborane skeleton may give rise to unusual membrane transport characteristics and metabolism compared to conventional active molecules.

1.6.2.2 Androgen Analogs Based on Boron Cluster Structure

The androgen receptor (AR) is a member of the nuclear receptor super family of ligand-regulated transcription factors and plays a key role in the development and maintenance of the male reproductive system. Its functions are initiated by the binding of the steroid hormones, testosterone, and/or 5α-dihydrotestosterone to the AR, and an intricate machinery involving translocation of AR into the nucleus, binding to specific DNA sites, formation of a transcriptional complex, and activation of the expression of specific genes occurs. AR ligands have been applied clinically for the treatment of illnesses such as aplastic anemia and prostate cancer.

Nonsteroidal androgen antagonists with a 1,12-dicarba-*closo*-dodecaborane (**3**) cage in place of the steroidal C, D rings of the testosterone or 5α-dihydrotestosterone have been developed. The second-generation, more potent AR antagonists containing cyanophenyl and nitrophenyl groups, respectively, instead of the cyclohexene ring were also proposed.[32,33]

The biological activity of the synthesized compounds was evaluated by means of a transient transactivation assay. The cotransfection assay was conducted in mouse fibroblast NIH3T3 cells, using an expression plasmid for hAR and reporter plasmids, ARE/Luci (firefly luciferase), and pRL/CMV (Renilla luciferase).

The potency of compounds with the CN and NO_2 groups in meta-position (Figure 1.8) was superior to that of hydroxyflutamide, a nonsteroidal AR antagonist used clinically for the treatment of prostate cancer. It was suggested that hydrophobic interaction of the carborane structure with the hydrophobic region of the AR ligand-binding pocket may account for the high binding affinity to AR, and owing to the bulky carborane cage, the conformation of the AR–ligand complex may not be appropriate for interaction with cellular coregulators, resulting in antagonistic activity.

1.6.2.3 Boron Cluster Bearing Cholesterol Mimics

Cholesterol is an important constituent of the mammalian cell membrane and is a frequently used component of liposomal formulations in drug-delivery technology. Numerous cholesterol derivatives containing boron cluster attached to the cholesterol skeleton as external entities have been synthesized as potential boron carriers for BNCT. In general, two types of cholesterol boron cluster

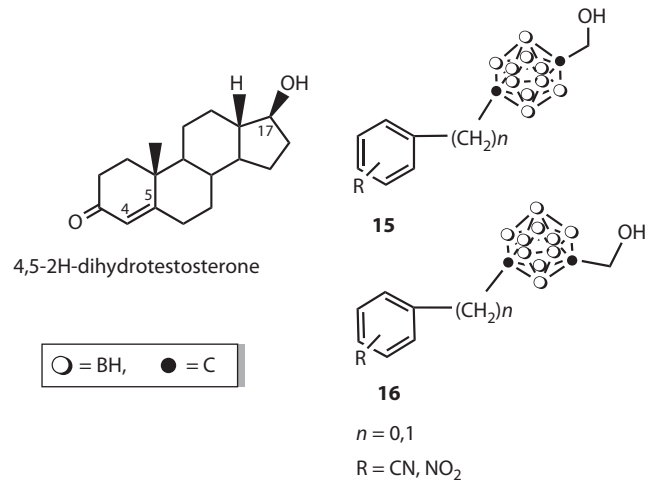


FIGURE 1.8 Selected examples of androgen receptor (AR) ligands based on carborane structure. (Adapted from T. Goto et al., *Bioorg. Med. Chem.*, **2005**, *13*, 6414–6424; S. Fujii et al., *Bioorg. Med. Chem.*, **2009**, *17*, 344–350.)

modification can be defined, the first includes cholesterols conjugated with boron clusters,[34,35] and the second includes cholesterol mimic[36] (Figure 1.9).

Recently, novel cholesterol derivatives containing boron cluster as a pharmacophor were proposed (**19**–**21**). A major structural feature of these boronated cholesterol mimics is replacement of the B and C rings of cholesterol with boron cluster, analogous to estradiol modification proposed earlier.[36]

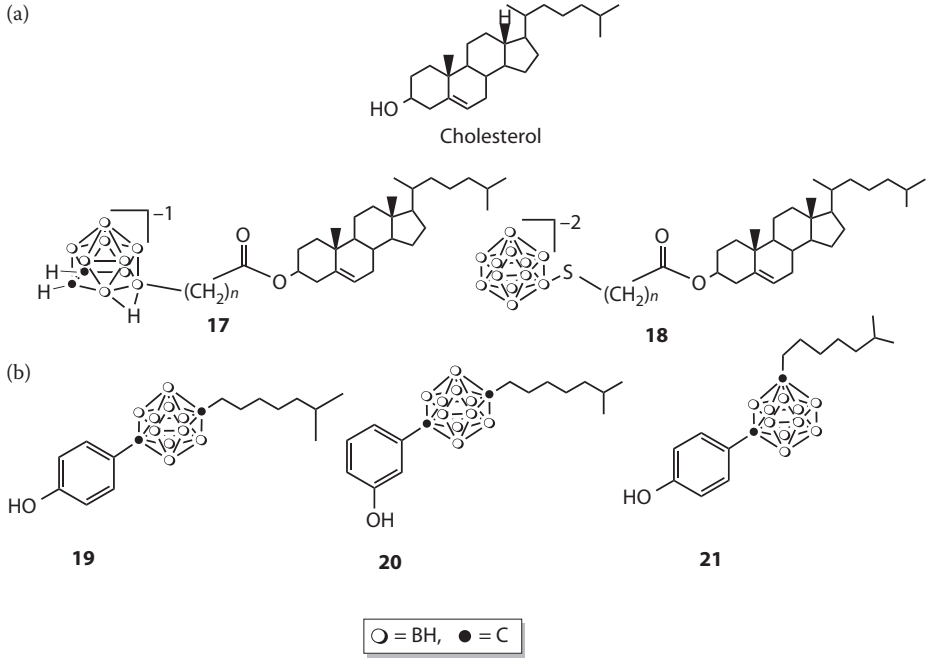


FIGURE 1.9 Boronated cholesterol conjugates (**17**,**18**) (a) (Adapted from D. A. Feakes, J. K. Spinler, F. R. Harris, *Tetrahedron*, **1999**, *55*, 11177–11186; H. Nakamura et al., *Tetrahedron Lett.*, **2007**, *48*, 3151–3154.), and cholesterol mimics (**19**–**21**) (b) (Adapted from B. T. S. Thirumamagal et al., *Bioconjugate Chem.*, **2006**, *17*, 1141–1150.)

Computational analyses indicated that all three boronated compounds have structural features and physicochemical properties that are very similar to those of cholesterol. One of the synthesized boronated cholesterol mimics (**21**) was stably incorporated into nontargeted, folate receptor (FR)-targeted, and vascular endothelial growth factor receptor-2 (VEGFR-2)-targeted liposomes. No major differences were found in appearance, size distribution, and lamellarity between conventional dipalmitoylphosphatidylcholine (DPPC)/cholesterol liposomes, nontargeted, and FR-targeted liposomal formulations of compound **21**. These results demonstrate that the novel carboranyl cholesterol mimics are excellent lipid bilayer components for the construction of nontargeted and receptor-targeted boronated liposomes for BNCT of cancer and for other applications.

1.6.3 Transthyretin Amyloidosis Inhibitors Containing Carborane Pharmacophores

Transthyretin (TTR) is a thyroxine-transport protein found in blood that has been implicated in a variety of amyloid-related diseases. Previous investigation have identified a variety of nonsteroidal anti-inflammatory drugs (NSAIADs), such as flufenamic acid or diflunisal, and structurally related derivatives that instill kinetic stabilization to TTR, thus inhibiting its dissociative fragmentation and subsequent aggregation to form putative toxic amyloid fibrils. The cyclooxygenase (COX) activity associated with these pharmaceuticals may, however, limit their potential as long-term therapeutic agents for TTR amyloid diseases. In efforts to solve this problem, several carborane analogs of NSAIADs have been synthesized and evaluated for inhibition of amyloid fibril formation.[37] Some of them also caused substantial decrease of COX activity, a highly desired property. Inhibitors were evaluated by using a 72 h stagnant fibril-formation assay. During this assay, physiological concentrations of TTR (3.6 μM) are subjected to acid-mediated partial denaturation at pH 4.4 either in the presence or absence of an inhibitor. Fibril formation is measured by optical density at 400 nm, and the results are reported as percent fibril formation (% ff), with TTR in the absence of inhibitor defined as 100% ff. The most promising of these compounds is 1-carboxylic acid-7-[3-fluorophenyl]-1,7-dicarba-*closo*-dodecborane (**28**) with ff 15 +/– 5 at 3.6 μM inhibitor concentration (Figure 1.10).

The obtained results show that hydrophobicity, steric bulk, and lack of π-interactions make the carborane functionality ideal scaffolding for use in the binding channel of TTR. Similarly, these same properties are detrimental when applied to COX inhibitors. Consequently, it has been shown that the substitution of a carborane moiety for a phenyl ring in NSAIDs with known TTR tetramer stabilizing activity retains the TTR potency of the compound while dramatically reducing the

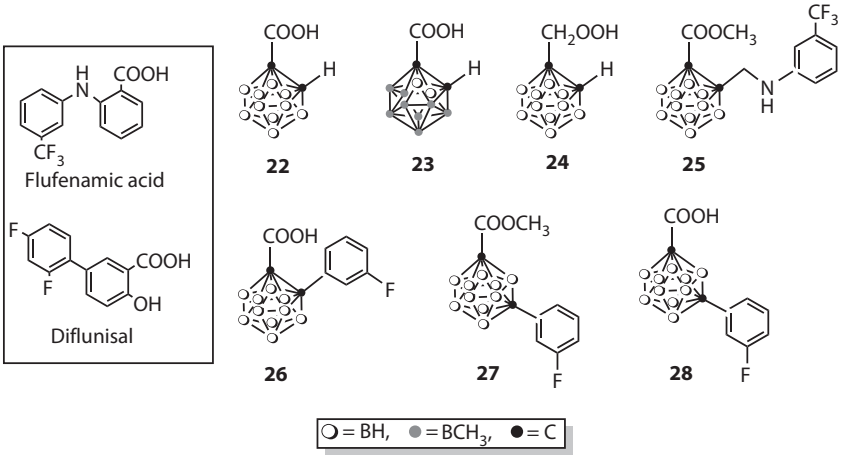


FIGURE 1.10 Transthyretin (TTR) amyloidosis inhibitors, analogs of nonsteroidal anti-inflammatory drugs flufenamic acid and diflunisal, containing carborane pharmacophors. (Adapted from R. L. Julius et al., *Proc. Nat. Acad. Sci. USA*, **2007**, *104*, 4808–4813.)

detrimental COX activity. The unique properties noted above as well as biological and chemical stability make carboranes very attractive pharmacophores in the design and synthesis of a new class of potent and selective NSAIADs and other types of pharmaceuticals.

1.6.4 α-Human Thrombin Inhibitor Containing a Carborane Pharmacophore

α-Human thrombin, a serine protease, is a potent platelet agonist involved in the blood coagulation cascade and is an attractive target for an anticoagulant agent due to its involvement in several debilitating diseases. In recent years, the development of synthetic small-molecules, thrombin and prothrombin activating factor Xa inhibitors have led to a number of potent anticoagulant compounds. These include bicyclic *trans*-lactone **29** isolated from leaves of *Lantana camara* (wild sage) and its synthetic analogs **31** and **32**, more resistant to hydrolysis in plasma. In this direction, a new architecture for size-selective serine protease inhibitors that utilize a fully methylated icosahedral *p*-carborane as a dominating hydrophobic pharmacophore was also proposed recently. Using a computational docking program, flexX, a carborane-containing inhibitor, was designed and synthesized. Computationally, this compound displayed the ability to provide ligand–protein binding interactions throughout the thrombin's main active site (S1–S3), while positioning an acylating group for facile irreversible attack at the Ser^{195} hydroxyl group (Figure 1.11).

It is worth noting that in design of the α-human thrombin inhibitor, the fully methylated *para*-carborane derivative was used instead of the dicarbadodecaborane structure most often utilized as pharmacophore.[38]

1.6.5 Adenosine Modified with Boron Cluster Pharmacophores as a New Human Blood Platelet Function Inhibitor

Adenosine is an endogenous modulator of intercellular signaling that provides homeostatic reduction in cell excitability during tissue stress and trauma. The adenine nucleoside phosphates: adenosine 5′-monophosphate (AMP), adenosine 5′-diphosphate (ADP), adenosine 5′-triphosphate (ATP), which are

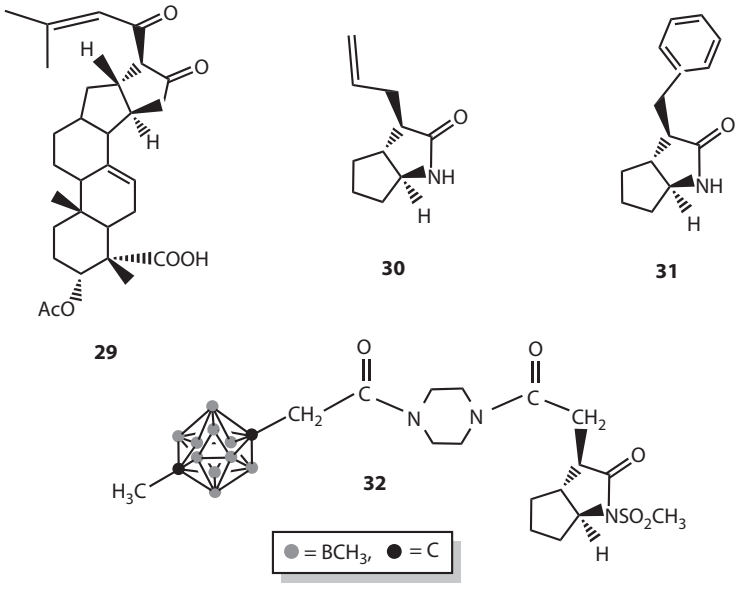


FIGURE 1.11 Naturally occurring [5,5]-*trans*-lactone thrombin inhibitor **29**, its synthetic analogs **30** and **31**, and lead thrombin inhibitor containing hydrophobic carborane pharmacophore **32**. (Adapted from M. F. Z. Page et al., *Synthesis,* 2**008**, 555–563.)

maintained in equilibrium by adenylate kinase (AK), constitute the bulk of the purine nucleotide pool. In addition, ATP is the most important molecule for capturing and transferring free energy in most organisms and it is a substrate for RNA polymerases. Another adenosine phosphate cAMP (cyclic adenosine 3′,5′-monophosphate) is the second messenger for many hormones and plays an important role in the regulation of cellular metabolism. Adenosine is also known as an endogenous antiaggregating substance that inhibits platelet aggregation *in vitro* and acts synergistically with other antithrombotic drugs.

The biological activity of adenosine and its phosphates is manifested through its interaction with purinergic receptors and therefore they are considered as important targets for new drugs based on adenosine structure. Among the disadvantages of using adenosine and its derivatives as chemotherapeutics are their short half-lives in circulation and the often unsatisfactory specificity and affinity for receptors. Alterations in the structure and stereochemistry of synthetic adenosine derivatives result in the modulation of receptor-binding potency, selectivity, and biological activity; therefore, a vast array of adenosine derivatives and analogs has been synthesized and tested. Adenosine–boron cluster conjugates were, however, not available due to the lack of methods for their synthesis. Recently, several general methods for the modification pyrimidine as well as purine nucleosides with a variety of different boron cluster was proposed opening the way for biological screening and evaluation of this new class of bioorganic–inorganic conjugates.[39–41]

A small library of adenosine and 2′-deoxyadenosine conjugates with boron clusters (Figure 1.12) was compared for their effects on the responses of platelets (aggregation, protein release, and P-selectin expression) to stimulation by the agonists, ADP, and thrombin. It was found that the modification of adenosine at the 2′-C position with a *para*-carborane cluster ($C_2B_{10}H_{11}$) (**33**) results in the efficient inhibition of platelet function, including aggregation (Figure 1.13). These preliminary findings, and the new chemistry proposed, form the basis for the development of a new class of adenosine analogs that modulate human blood platelet activities.[42,43]

1.7 SUMMARY

All life is derived ultimately from the element carbon, which lies next to boron in the periodic table of elements. Boron compounds not only share some similarities with carbon but also have important differences. It is the combination of these similarities and differences that give boron its unique potential in medicine. The important similarity is that boron, like carbon, combines with hydrogen to form stable compounds that can participate in biochemical reactions and interactions. The key difference is that these compounds have distinctive geometrical shapes and electronic charge distributions with greater 3D complexity than their carbon-based equivalents. While organic carbon molecules tend to comprise rings and chains, boron hydrides are made up of clusters and cages. This 3D structure makes it possible to design molecules with specific charge distributions by varying their internal structure, and this in turn brings the potential to tune how each part of the structure relates to water molecules—if a component is hydrophobic, it is well placed to enter cells by crossing the membrane and to interact with hydrophobic domains of target proteins. If it is hydrophilic it will naturally be soluble in water.

As decades of research begin to bear fruit, the field of bioorganic and medicinal chemistry of boron is on the verge of providing a new generation of drugs and therapies. Boron clusters can find applications as enhancers of hydrophobic interactions between pharmaceuticals and their receptors and entities can be used to increase *in vivo* stability and bioavailability of compounds that are normally rapidly metabolized. They are attracting fast-growing research interest in the quest for novel drugs potentially overcoming limitations and side effects of current products. Several examples in the area of anticancer drugs, inhibitors of platelet aggregation, and modulators of important hormone receptors have been shown above.

Anti-infectious disease drugs bearing essential boron component forms another area of medicinal chemistry of boron awaiting exploration. The fact that novel boron compounds will be unfamiliar to life has potential advantages for antibiotic drugs, since pathogens will be less able to develop

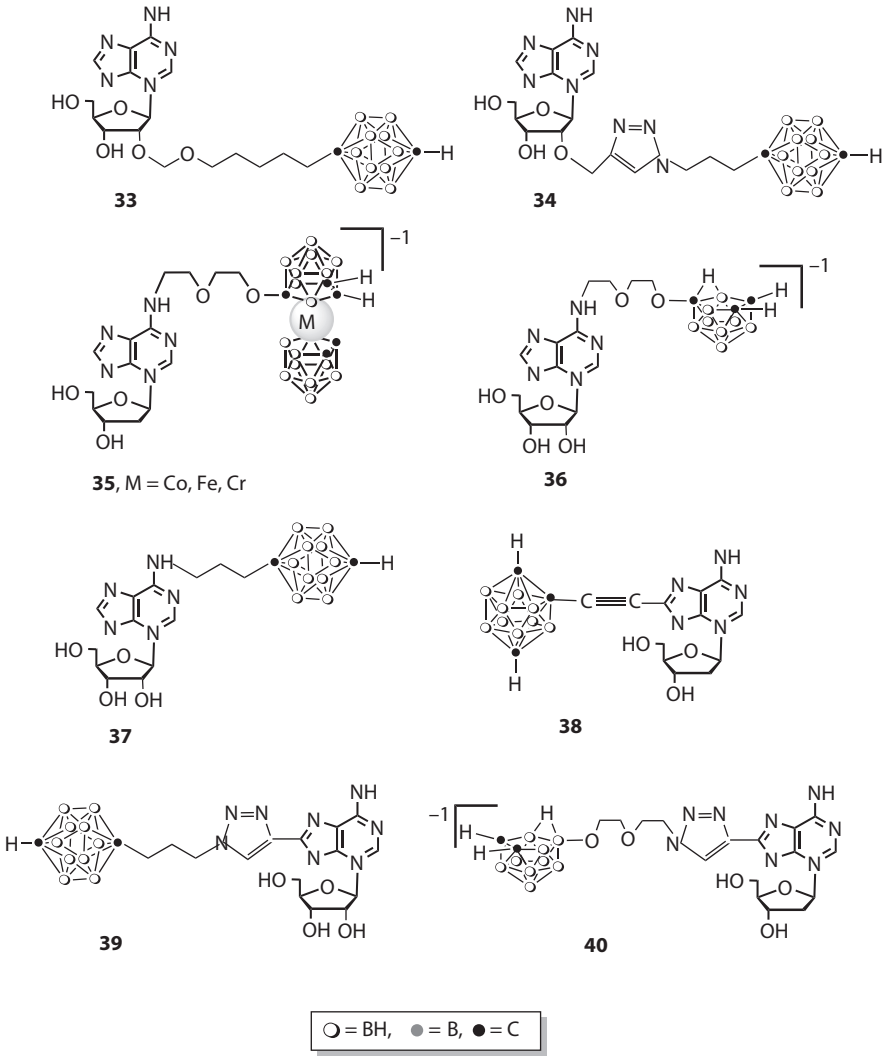


FIGURE 1.12 Selected examples of adenosine and 2′-deoxyadenosine conjugates with boron clusters: 2′-O-(*para*-carboran-1-yl)propyleneoxymethyl]-adenosine (**33**), 2′-O-{[(*para*-carboran-1-yl)-3-propan-1-yl]-1N-1,2,3-triazol-4-yl]methyl}-adenosine (**34**), 6-N-{5-[3-metal bis(1,2-dicarbollide)-8-yl]-3-oxa-pentoxy}-2′-deoxyadenosine (metal: cobalt, iron, chromium) (**35**), 6-N-{5-[7,8-*nido*-carboran-10-yl]-3-oxa-pentoxy}-adenosine (**36**), 6-N-[(7,8-*nido*-carboran-10-yl)-3-propan-1-yl]-adenosine (**37**), 8-(2-*para*-carboranethynyl)-2′-deoxyadenosine (**38**), 8-{[(*para*-carboran-1-yl)-3-propan-1-yl]-1N-1,2,3-triazol-4-yl}adenosine (**39**), 8-{5-[7,8-*nido*-carboran-10-yl]-3-oxa-pentoxy}-1N-1,2,3-triazol-4-yl}adenosine (**40**). (Adapted from A. B. Olejniczak, J. Plesek, Z. J. Leśnikowski, *Chem. Eur. J.*, **2007**, *13*, 311–318; B. A. Wojtczak et al., *Chem. Eur. J.*, **2008**, *14*, 10675–10682; B. A. Wojtczak, A. B. Olejniczak, Z. J. Leśnikowski, *Current Protocols in Nucleic Acid Chemistry*, S. L. Beaucage (Ed.), John Wiley & Sons, Inc., Chapter 4, Unit 4.37, pp. 1–26, **2009.**)

resistance against them. Also the kind of interactions would somehow be different from key–lock systems built up in living cell lines in nature for billions of years. One can thus anticipate that active substances would be less prone to development of resistance. This is an obvious advantage of boron drugs. While eventually pathogens such as bacteria and viruses are capable of evolving resistance against almost any molecule that attacks them, one can believe that it would take longer for this to happen in the case of boron-based compounds, which would therefore make it easier for humans to remain one step ahead rather than struggling to keep pace as at present.

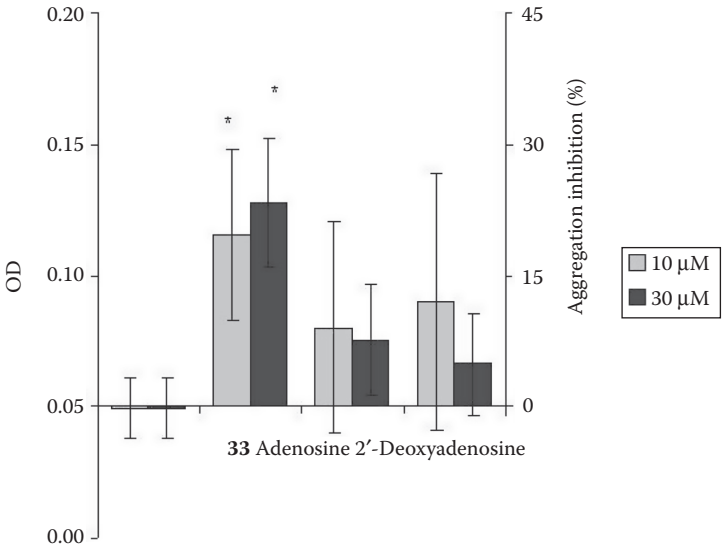


FIGURE 1.13 The effects of compounds **33**, adenosine and 2′-deoxyadenosine (10 and 30 μM) on the extent of platelet aggregation after a long-time (120 min) treatment of platelets with thrombin. Platelets were incubated with the compounds for 5 min at 37°C and then stimulated with thrombin (0.5 U/cm^3) for 120 min. The optical density (OD, wavelength 630 nm) shows the extent of platelet aggregation (left axis); the percentage of platelet aggregation inhibition (right axis). The data are expressed as mean values ± SD for three donors in triplicates; $*p < 0.05$ (compound + thrombin versus thrombin). (Adapted from K. Bednarska et al., *ChemMedChem*., **2010**, *5*, 749–756.)

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FIGURE 1.13 The effects of compounds 33, adenosine and 2′-deoxyadenosine (10 and 30 μM) on the extent

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FIGURE 2.11 Cell viability of HeLa cells exposed to bisphosphonate 72 and bisphosphonothioate 73.

(Adapted from Stadlbauer, S. et al. unpublished results.)

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Part II

Boron for Living: Health and Nutrition

This section, covering nutritional aspects of boron, consists of a single chapter, Chapter 4, by

Samman, Foster and Hunter. Boron has been found to be an essential nutrient for both plants and

animals, including man. Current dif□culties in advancing knowledge of its functions include the

limited availability of boron data in tables of food composition, and challenges in the analysis of

boron in food and in biopsy materials. The focus on a role for phytochemicals in disease prevention

should be expanded to consider the possibility that some of their biological effects are intertwined

with those of boron. In view of the distribution of boron in the food chain, mainly in foods of plant

origin, the reported bene ts of the consumption of vegetables, fruit, and cereals may be contributed

in part by boron. Thus, boron is an integral part of health and nutrition. Accordingly, Chapter 4 assesses the literature on dietary sources and intake of boron in humans,

and evaluates the impact of boron on metabolism in health and disease. It was found that boron was

capable of in uencing steroid hormone metabolism; however, the speci c condition that controls the

nature (and direction) of the response remains to be determined.

4 Chapter 4: The Role of Boron in Human Nutrition and Metabolism

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Part III

Boron for Living: Radioisotope

One major use of radioisotopes is in nuclear medicine. Of the 30 million people who are hospital

ized each year in the United States, one third are treated with nuclear medicine. More than 10 mil

lion nuclear-medicine procedures are performed on patients and more than 100 million

nuclear-medicine tests are performed each year in the United States alone. A comparable number of

such procedures are performed in the rest of the world. What is a radioisotope? When a combination of neutrons and protons, which does not already

exist in nature, is produced arti cially, the atom will be unstable and is called a radioactive isotope

or radioisotope. There are also a number of unstable natural isotopes arising from the decay of pri

mordial uranium and thorium. Overall there are some 1800 radioisotopes. At present there are up to

200 radioisotopes used on a regular basis, and most must be produced arti cially. A very effective role for radioisotopes in nuclear medicine is the use of short-lived positron emit

ters such as 11C, 13N, 15O, or 18F in a process known as positron emission tomography. Incorporated

in chemical compounds that selectively migrate to speci c organs in the body, diagnosis is effected

by detecting annihilation gamma rays–two gamma rays of identical energy emitted when a positron

and an electron annihilate each other. These gamma rays

have the very useful property that they are

emitted in exactly opposite directions. When both are detected, a computer system may be used to

reconstruct where the annihilation occurred. By attaching a positron emitter to a protein or a glu

cose molecule, and allowing the body to metabolize it, we can study the functional aspect of an

organ such as the human brain. Therefore, the radioisotopes play a crucial role in nuclear medicine

that extends the lifespan of living people. Part III consists of two chapters. Chapter 5 by Kabalka discusses the use of boron in the incor

poration of stable and unstable radioisotopes in molecules using organoborane reagents. The iso

topes usually incorporated are those of H, C, N, O, and the halides. The growing need for structurally

complex compounds labeled with such isotopes will continue to be a challenge. It is clear that

organoboration will play an ever-increasing role in this area of research. On the other hand, Chapter

6 by Tjarks, et al. discusses the syntheses and uses of (radio)halogenated boron clusters in tumor

imaging and therapy. The undesired in vivo release of radiohalogens, frequently observed in thera

peutics and diagnostics radiolabeled at carbon atoms, has been a major motivation for the explora

tion of boron clusters as “prosthetic groups” for radiohalogens in radiopharmaceuticals. Not only

are the halogen–boron bonds stronger than carbon–halogen bonds, the boron–halogen bonds are

less susceptible to enzymatic and hydrolytic cleavage than the carbon–halogen bonds; no enzymatic

system has yet been reported for the in vivo cleavage of the boron–halogen bond. The fact that novel

boron compounds, especially those based on the polyhedral boron hydride design, are unfamiliar to

life gives them an advantage in living systems. Since pathogens develop less or no resistance against

those boron-based drugs, enzymatic systems will be less able to metabolize them. Also, the kind of

interactions would be somewhat different from that of the natural key-lock systems that have been

developed over billions of years.

5 Chapter 5: Isotope Incorporation Using Organoboranes

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Part IV

Boron for Living: Boron Neutron

Capture Therapy

Part IV discusses boron neutron capture therapy (BNCT) that is divided into six chapters. BNCT is

a binary form of cancer therapy that is based on the preferential localization of B-10-containing

compounds in cancer cells and then irradiating the cells with thermal neutrons. Boron-10 has an

extremely high tendency of absorb neutron, giving an excited B-11 that immediately undergoes a

fission reaction producing high-energy alpha particles 4 He 22+ and recoil 7 Li 3 ions. These particles

deposit their energies at distances of essentially a cell diameter in a biological medium. Thus, cell

death will occur within the cell containing the B-10, sparing those cells not containing boron. The

discovery of polyhedral boron compounds added new dimensions to the medicinal chemistry of

boron, facilitating the quest for biologically active molecules containing boron clusters rather than

only a single boron atom per molecule. The major dif▯culties to be overcome in BNCT are the

design and syntheses of tumor-seeking boron drugs and the development of ef▯cient methods for

drug delivery; the chapters in this section address these points. Chapter 7 (by Zhu, Maguire & Hosmane) and Chapter 10 (by Sibrian-Vazquez and Vicente) discuss

the use of macromolecules in boron delivery. While Chapter 7 presents a general review of the use of

liposomes, dendrimers, polymers, magnetic nanoparticles and carbon, boron nitride and boron nano

tubes as boron delivery agents, Chapter 10 extends the discussion to include porphyrins, nucleosides,

antibodies, and liposomes. Chapter 8 (by Nakamura) and Chapter 12 (by Feakes) concentrate the use

of liposomes in boron delivery. Liposomal delivery is a method of supplying large amounts of boron

to cells and may well prove to be the most ef▯cient drug delivery method. Chapter 9 (by Bregadze and

Sivaev) describes the syntheses of various polyhedral boron compounds that show promise as boron

delivery drugs. Chapter 11 discusses a companion therapy that uses gadolinium neutron capture as a

cancer therapy (GdNCT). Gadolinium-157 has a thermal-neutron-capture cross section of 255,000

barn, which is 65 times greater than that of B-10. The neutron-capture reaction, 157Gd(n,γ)158Gd,

releases Auger electrons, internal conversion electrons, γ-rays, and x-rays. The reaction releases a total

kinetic energy of 7.7 MeV, almost double that released by 10B(n,α)7Li. The disadvantage of GdNCT

is that, to be cytotoxic, the metal must be next to the DNA in the cell nucleus. Gadolinium is exten

sively used as a magnetic resonance image enhancement agent, and the combination of both elements

in compounds could results in potent diagnostic and therapeutic compounds.

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FIGURE 7.14 TEM image of a multiwalled BNNT containing a Fe particle at one tip. (Adapted from

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FIGURE 8.6 Structures of cholesterol-boron cluster conjugates (42 and 44) and ortho-carboranyl phenol 43.

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11 Chapter 11: Future Applications of Boron and Gadolinium Neutron Capture Therapy

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FIGURE 11.43 Inhibition by GdNCT of intimal hyperplasia (left) and thrombus formation (right) after rat

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12 Chapter 12: Design and Development of Polyhedral Borane Anions for Liposomal Delivery

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Part V

Boron for Electronics: Optoelectronics

INTRODUCTION

Boron for electronics is the highlight of the chapters in this section, with contributions from Andrea

Vöge, Detlef Gabel, Piotr Kaszynski, and Paul A. Jelliss. Boron compounds in the ﬁeld of nonlinear

optics, liquid crystals, and photoluminescence are the major part of discussions in this section. The

“structure–property relationship” is a commonly used phrase because the structural features of

certain compounds dictate their properties. Evidently, the structure–property relationship of boron

based materials plays a vital role in the ﬁeld of electronics, as described in the following chapters. Nonlinear optics is one of the rapidly growing ﬁelds of science that describes a branch of optics

where matter responds in a nonlinear fashion to incident light beams. Nonlinear optical materials

have gained tremendous importance lately due to their possible applications in information storage

and optical communications. Although organic molecules, with their diverse structural variations,

are effective as nonlinear optical materials, more studies are now being performed on polyhedral

boron cluster compounds as nonlinear optical materials. Carboranes have long been known for their

nonlinear optical behavior, while numerous substituted carboranes are now emerging as candidates

for this kind of behavior. In addition, photoluminescence properties of polyhedral boron cluster com

pounds are equally important in the field of electronics. Boranes, carboranes, and metallacarboranes,

by virtue of their structural features, are steadily making ground in the field of optoelectronics. Liquid crystals are also an important class of compounds; they have become an inseparable part

of our day-to-day lives through their presence in almost all display devices. They are mainly com

posed of an anisotropic rigid core and a terminal alkyl substituent. Several derivatives of closo

boranes, along with a metallacarbollide, form liquid crystals, and many more clusters are under

investigation. Ongoing research in this field should provide us with a better understanding of the

structure–property relationships of similar type of materials.

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Part VI

Boron for Energy: Energy Storage,

Space, and Other Applications

INTRODUCTION

From electronics we will now enter the realm of energy. This part includes a thorough review on the

usefulness of boron compounds in the eld of energy. A wide variety of materials composed of

boron that are particularly useful for energy-related applications will be discussed in terms of their

properties and syntheses in the chapters of this part. The contributing authors are David M. Schubert,

Michael J. Greenhill-Hooper, Amitabha Mitra, David A. Atwood, Bohumir Gru˝ner, Jir˘í Rais, Pavel

Selucký, Mária Luc˘aníková, Amartya Chakrabarti, Lauren M. Kuta, Kate J. Krise, John A. Maguire,

and Narayan S. Hosmane. Hydrogen is considered to be one of the most valuable and “green” energy sources in the near

future. The major problem associated with its use as an energy source is the hazards related to its

storage and transportation. Extensive research efforts have been initiated worldwide to get a feasible

solution; they are being supported by a number of governmental and nongovernmental funding

agencies. Among many hydrides and other hydrogen-containing materials being tested as possible

sources of hydrogen, the metal borohydrides, by virtue of their lightweight and stabilities, have been

a unique choice. Even, some boranes, for example, ammonia borane, are also currently being inves

tigated as hydrogen storage materials. Thus, boron compounds are going to dominate the ﬁeld of

energy production in the near future. The electron-deﬁcient nature of boron contributes to several interesting applications of boron

based materials; one of them is in the oilﬁeld technology. Borates and perborates are important

classes of boron compounds that play a crucial role as additives in several oilﬁeld operations. While

borate acts as a polymer crosslinker or a set retarder for the prevention of early setting of cement on

the borehole walls, perborates help to degrade and remove the polymer residues. Another useful

application of boron compounds is as additives in the aluminum industries. Boron additives act as

preventive agents to avoid the oxidation of aluminum

metals, thus saving substantial energy loss

caused by the oxidation of aluminum and magnesium metals. Boron compounds, besides being

energy producers, have proven to be a great savior of energy as well. Cobalt bis(dicarbollide), commonly known as “CoSan”, is an example of a boron compound

which serves the role of a scavenger for the extremely biotoxic Cs-137 ion produced from the nuclear

wastes. Although it has long been synthesized, the importance of this particular compound has

developed only recently. Cobalt bis(dicarbollide) anion and its chloroprotected form have now being

used as extractants for high-level liquid nuclear wastes. The properties of materials in their nanodimensions vary from those in their bulk form. These

variations open up several new applications. A variety of boron and boron-based nanomaterials

designed and prepared to date have been found to be useful in energy, space, and other applications.

Boron nitride nanotubes (BNNTs) are useful for hydrogen storage and space applications, while

boron nanorods (BNRs) are considered to be useful as rocket fuels. In the following chapters,

detailed discussions are made on these versatile aspects of boron compounds in different fields of

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Borates have been proposed for use in different ways to reduce the permeability of zones in

the reservoir in order to control the path or pro□le taken by injected §uids in water □ooding.

In one approach, borates are used to form cross-linked polymer gels that reduce permeabil

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in borate salt solubility at low temperatures to cause a hot nearly saturated solution to form

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Part VII

Boron for Chemistry and Catalysis:

Catalysis and Organic Transformations

INTRODUCTION

The final section of this book focuses on another perspective of boron-based materials, that is,

boron for chemistry and catalysis. It highlights the syntheses, properties, and applications of boron

compounds, including titanacarborane monoamides, phosphorus-substituted carboranes, boron and

organoboron halides, polyhedral boron hydrides, organoboranes, borates, carborane, and boron

cluster compounds. The crucial roles of boron compounds in various organic syntheses, along with

their catalytic activities, are portrayed in the following chapters by Hao Shen, Zuowei Xie, Sebastian

Bauer, Evamarie Hey-Hawkins, Min-Liang Yao, George W. Kabalka, Igor B. Sivaev, Vladimir I.

Bregadze, Subash Jonnalagadda, J. Sravan Kumar, Anthony Cirri, Venkatram R. Mereddy, Barada

Prasanna Dash, Rashmirekha Satapathy, John A. Maguire, Narayan S. Hosmane, Rosario Núñez,

Francesc Teixidor, Clara Viñas, Michael A. Corsello, Brandon R. Hetzell, Andrea Vöge, and Detlef

Gabel. Catalysts are an inevitable part of the modern world of chemistry. They are known to be useful

in increasing the reaction rates, but today they are increasingly being used in asymmetric synthe

ses, specifically in the pharmaceutical industries, to impart chirality in the desired product.

Phosphorus-substituted carborane compounds have an advantage in reactivity due to the presence

of electron-de cient boron in their structure and a phosphorus atom that is either directly linked to

the carborane cage or linked through a spacer moiety. They exhibit pronounced catalytic activities

for hydrogenation, hydroformylation, polymerizations, and several coupling and cross-coupling

reactions, including Sonogashira coupling. A different class of boron compounds, the titanacarbo

rane monoamides with constrained geometry, has recently been synthesized and tested for catalytic

activities on C–N bond formation/cleavage reactions. The positive outcome of such a compound’s

activity with amines and many unsaturated organic molecules should surely trigger more research

endeavors in this direction. Boron compounds play an essential part in many organic syntheses, from C–O bond breaking in

a variety of ethers, esters, and acetals, to asymmetric allylation of carbonyl compounds. Boron

halides are useful tools for C–O bond breaking reactions, and they also act as coupling agents for

reactions of aromatic aldehydes with alkynes, allylmetals, etc. While boron halides have proven to

be effective as halogen transfer reagents for many reactions, organoboron halides act as reagents to

form enol borinates and many other reaction intermediates for several boron derivatives. Chiral

organoboranes, on the other hand, help in asymmetric allylation of carbonyl compounds. The ver

satility of organoboron reagents has been successfully utilized in Suzuki–Miyaura cross-coupling

reactions, which are one of the most effective and popular

carbon–carbon bond forming reactions

developed recently. Polyhedral boron cluster compounds are useful in many ways. They have found applications

ranging from medicinal fields to the area of materials chemistry, where they can be used as building

blocks for many dendritic structured species. These dendritic macromolecules, based on polyhedral

boron hydrides, besides being very promising boron delivery agents for boron neutron capture ther

apy (BNCT), can find their way into several other applications, including catalysis, optoelectronics,

ionic liquids, and optical sensors. The fascinating chemistry of carborane cage-appended dendri

meric structures has been reported recently. Moreover, the oxonium derivatives of polyhedral boron

hydrides have also been successfully synthesized and can act as a starting material for many excit

ing, yet useful, macromolecules. Another interesting application of boron compounds is in syntheses involving ionic liquids, one

of the fastest-growing fields in chemistry. Ionic liquids are basically salts with low melting points.

These ions are weakly coordinating and thus can act as solvents for many chemical reactions. The

high thermal stability and low vapor pressures of ionic liquids make them even more attractive as

solvents. Boron clusters, along with tetravalent boron anions, are now being used as anions for ionic

liquids. Although there are not many examples of boron-based ionic liquids, some excellent features

of the cluster compounds of boron may lead many researchers to explore more in the field of ionic

liquids.

21 Chapter 21: Constrained-Geometry Titanacarborane Monoamides : From Synthesis and Reactivity to Catalytic Applications

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24 Chapter 24: Cyclic Oxonium Derivatives as an Efficient Synthetic Tool for the Modification of Polyhedral Boron Hydrides

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FIGURE 24.19 3,3′-cobalta bis(1,2-dicarbollide) derivatives of tert-butyl-calix[4]arenes. Co Co R O O O O N + R′ – –

FIGURE 24.20 3,3′-cobalta bis(1,2-dicarbollide)-based HIV protease inhibitors.

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25 Chapter 25: Asymmetric Allylation of Carbonyl Compounds via Organoboranes

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SCHEME 25.44 Propargylboration. OH OH OO O O OH OH OH Mycolactone core S S O B SiMe 3 S S OH 264 265 266 247

SCHEME 25.45 Application of B-allyl-10-TMS-BBD for the synthesis of mycolactone core.

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FIGURE 26.30 Para-carborane dicarboxylic acid dianion.

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27 Chapter 27: Large Molecules Containing Icosahedral Boron Clusters Designed for Potential Applications

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FIGURE 27.24 X-ray crystal structure of the dianionic platform derived of tert-Butylcalix[4]arenes with two

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29 Chapter 29: Boron in Weakly Coordinating Anions and Ionic Liquids

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FIGURE 29.15 Bis- and tris-alkylated derivatives of ammonioundecahydro-closo-dodecaborate. (Adapted

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FIGURE 3.2 Three-dimensional structure of HIV protease (HIV PR) in open and closed conformation.

(a) Overall structure of the apo-form of HIV PR. One monomer is colored blue and the second in pink. Two

catalytic aspartates are represented by sticks with carbon color corresponding to the chain color and oxygen

atoms colored red. Flaps (residues 43–58) in open conformation are highlighted in darker colors. (b) Overall

structure of HIV PR in complex with the FDA-approved drug darunavir bound in the active site. Active site

bound darunavir is shown as a stick model (carbon atoms in green, sulfur in yellow, oxygens and nitrogens in

red and blue, respectively) with its solvent accessible surface in semitransparent green. The figure was gener

ated with PyMol (DeLano, 2002) using the structure of free HIV-1 PR [PDB code 1HHP (Spinelli, 1991)] and

the structure of a highly mutated patient-derived HIV-1 PR [PDB code 3GGU (Saskova, 2009)].

FIGURE 3.3 HIV PR resistance-associated mutations. The three-dimensional crystal structure of the HIV

PR dimer depicting mutations associated with resistance to clinically available protease inhibitors (Johnson,

2008). Mutated residues are represented by their Cα atoms (spheres) and colored in red and yellow for major

and minor mutations, respectively. For major mutations in residues affecting substrate and/or inhibitor bind

ing, the transparent solvent accessible surface is also shown in red. Active site aspartates are represented in

stick models; the inhibitor bound in the enzyme active site is omitted from the gure for clarity. The gure was

generated from the structure of highly mutated patient-derived HIV-1 PR [PDB code 3GGU (Saskova, 2009)]

with the program PyMol (DeLano, 2002). 150 HIV PR-resistant mutants 1: D30N/N88D 2: M46I/A71V/V82T/I84V 3: A71V/V82T/I84V 4: V32I/I47A 5: L10I/I15V/E35D/N37S/R41K/ I62V/L63P/A71V/G73S/L90M 6: L10I/L24I/L33F/M46L/I54V/ L63P/A71V/V82A/I84V 7: L10F/L19I/K20R/L33F/E35D/M36I/ R41K/F53L/I54V/L63P/H69K/ A71V/T74P/I84V/L89M/L90M/I93L 125 100 75 V i t a l i t y 50 25 0 S a q u i n a v i r I n d i n a v i r N e l f i n a v i r L o p i n a v i r A m p r e n a v i r A t a z a n a v i r D a r u n a v i r G B 1 8 G B 2 1 G B 4 8 G B 8 0 G B 7 1 G B 1 0 5 G B 1 0 6 HIV PR 1 2 3 4 5 6 7

FIGURE 3.5 Metallacarboranes inhibit resistant HIV PR variants. Vitality values of seven clinical inhibi

tors and seven cobaltacarborane compounds analyzed with the panel of HIV-1 PR-resistant species (Kozisek,

2008; Rˇezácˇovaˇ, 2009). Mutations in the HIV-1 PR variants are shown in the gure inset. The vitality is a

measure of the enzymatic tness of a particular mutant in the presence of a given inhibitor and is de ned as

(K i k cat /K m) MUT /(K i k cat /K m) WT , where K i is inhibition constant, K cat and K m are enzymatic constants and MUT

and WT is mutated and wild-type enzyme variant, respectively (Gulnik, 1995). HIV-1PR:GB-18 [PDB code 1ZTZ] HIV-1PR:GB-80 [PDB code 3/8W] Ile54 Gly48 Ile47 Thr82 Val82 Ile84 3.5 6.5 Ile84′ Gly48′ Pro81′ Thr82′ (a) (b) (c) (d)

FIGURE 3.6 Metallacarborane binding to HIV PR. Crystal

structures of wild-type HIV-1 PR in complex

with the parent cobalt bis(1,2-dicarbollide) ion (GB-18) and compound GB-80 containing two parent clus

ters connected with a linker. (a) Overall structure depicting the asymmetric binding of two cobalt bis(1,2-di

carbollide) clusters of GB-18 into the symmetric HIV PR dimer. The enzyme is shown by means of animation

with two catalytic aspartates shown in sticks. The metallacarborane atoms are depicted as spheres. (b) Detail

of the GB-18 inhibitor:enzyme binding. The cluster occupies a hydrophobic pocket formed by enzyme resi

dues Pro81, Val82, and Ile84 and is covered by the §ap residues Ile47, Gly48, and Ile54. This site corresponds

approximately to the S3 and S3′ substrate-binding subsites. Interacting residues are highlighted in sticks with

their van der Waals surfaces. (c) Overall structure depicting the symmetric binding of two cobalt bis(1,2-dicar

bollide) clusters of GB-80. Representation corresponds to panel A. (d) Detail of the GB-80:enzyme interaction.

Models of the four most probable conformers of the linker are shown. The dashed lines and numbers represent

distances to catalytic aspartates in Å. The ﬀgure was generated using the program PyMol (DeLano, 2002).

FIGURE 3.7 Comparison of metallacarborane and darunavir binding to HIV PR. Superposition of HIV

PR–compound GB-18 complex with HIV PR–darunavir complex structure. Protease complex with daruna

vir [PDB code 3GGU (Saskova, 2009)] is represented in orange with darunavir shown as a stick model, and

color coding for PR–GB-18 complex is the same as in Figure 3.6. The ﬀgure was generated using the program

PyMol (DeLano, 2002).

FIGURE 3.8 Comparison of the GB-18 and GB-80:HIV-1 PR

complex structures. (a) Close-up top view

into the enzyme active site showing differences in the HIV PR:GB-18 (green) and HIV PR:GB-80 (gray)

structures. Carbon and boron atoms in cobaltacarboranes are shown as sticks with the central cobalt atom

represented by a sphere. (b) Top view into the enzyme active. Representation and color coding are analogous

to panel A. The figure was generated using the program PyMol (DeLano, 2002). −0.15 +0.34 2.27 2.25 +0.34 −0.15

FIGURE 3.10 Interaction between CB H 11 12 − with glycine via two dihydrogen bonds. Partial charges on

the interacting hydrogens as well as distances in Å are shown. Color coding: boron–purple, carbon–green,

nitrogen–blue, oxygen–red, hydrogen–white.

FIGURE 3.11 Aggregation of cobalt dicarbollides in aqueous solutions. (a) Typical cryo-TEM micrograph

of sodium cobalt bis(dicarbollide) GB-18 in aqueous solution. (J. Ruokolainen, Helsinki, unpublished work.)

(b) Typical fluorescence lifetime imaging (FLIM) picture of fluorescein-cobalt bis(dicarbollide) conjugate

(GB-179) aggregates deposited on the bottom of an aqueous solution in which the diameter of the aggregates

is roughly 400 nm. (P. Jurkiewicz, Prague, unpublished work; Uchman, 2010a.)