

Boronic Acids in Saccharide Recognition

Monographs in Supramolecular Chemistry

Series Editor

J Fraser Stoddard, FRS, *University of California at Los Angeles, USA*

This series has been designed to reveal the challenges, rewards, fascination and excitement in this new branch of molecular science to a wide audience and to popularize it among the scientific community at large.

Titles in this series:

Anion Receptor Chemistry

Jonathan L. Sessler, *University of Texas, Austin, Texas, USA*, Philip A. Gale, *University of Southampton, Southampton, UK* and Won-Seob Cho, *University of Texas, Austin, Texas, USA*

Boronic Acids in Saccharide Recognition

Tony D. James, *Department of Chemistry, University of Bath, Bath, UK*, Marcus D. Phillips, *Department of Chemistry, University of Bath, Bath, UK* and Seiji Shinkai, *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan*

Calixarenes

C. David Gutsche, *Washington University, St Louis, USA*

Calixarenes Revisited

C. David Gutsche, *Texas Christian University, Fort Worth, USA*

Container Molecules and Their Guests

Donald J. Cram and Jane M. Cram, *University of California at Los Angeles, USA*

Crown Ethers and Cryptands

George W. Gokel, *University of Miami, USA*

Cyclophanes

François Diederich, *University of California at Los Angeles, USA*

Membranes and Molecular Assemblies: The Synkinetic Approach

Jürgen-Hinrich Fuhrhop and Jürgen Köning, *Freie Universität Berlin, Germany*

Self-Assembly in Supramolecular Systems

Len Lindoy, *The University of Sydney, Australia* and Ian Atkinson, *James Cook University, Townsville, Australia*

Visit our website at www.rsc.org/Publishing/Books/MOSC

How to obtain future titles on publication

A standing order plan is available for this series. A standing order will bring delivery of each new volume immediately on publication.

For further information please contact:

Sales and Customer Care, Royal Society of Chemistry, Thomas Graham House
Science Park, Milton Road, Cambridge, CB4 0WF, UK

Telephone: +44 (0)1223 432360, Fax: +44 (0)1223 426017, Email: sales@rsc.org

Boronic Acids in Saccharide Recognition

Tony D. James

Department of Chemistry, University of Bath, Bath, UK

Marcus D. Phillips

Department of Chemistry, University of Bath, Bath, UK

Seiji Shinkai

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

RSC Publishing

ISBN-10: 0-85404-537-6
ISBN-13: 978-0-85404-537-2

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

© The Royal Society of Chemistry 2006

All rights reserved

Apart from fair dealing for the purposes of research for non-commercial purposes or for private study, criticism or review, as permitted under the Copyright, Designs and Patents Act 1988 and the Copyright and Related Rights Regulations 2003, this publication may not be reproduced, stored or transmitted, in any form or by any means, without the prior permission in writing of The Royal Society of Chemistry, or in the case of reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency in the UK, or in accordance with the terms of the licences issued by the appropriate Reproduction Rights Organization outside the UK. Enquiries concerning reproduction outside the terms stated here should be sent to The Royal Society of Chemistry at the address printed on this page.

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Typeset by Macmillan India Ltd, Bangalore, India
Printed by Henry Lings Ltd, Dorchester, Dorset, UK

Preface

The ability to monitor the presence of analytes within physiological, environmental and industrial systems is of crucial importance. However, owing to the scale that recognition events occur at on the molecular level, gathering this information poses a non-trivial challenge. It is therefore the case that robust chemical molecular sensors with the capacity to detect chosen molecules selectively and signal this presence have attracted considerable attention over recent years.

Of particular interest is the real-time monitoring of saccharides in aqueous systems, such as D-glucose in blood. To this end, the covalent pair-wise interaction between boronic acids and saccharides has been exploited.

This book documents research into the design of novel boronic acid-based receptors with selectivity for saccharides.

There is so much to do. You can wander off in space or in time, set out for Tierra del Fuego or for King Midas's court . . . You can build castles in Spain, steal the Golden Fleece, discover Atlantis, realise your childhood dreams and adult ambitions.

Jean-Dominique Bauby
The Diving-bell and the Butterfly

Contents

Chapter 1	Introduction	1
Chapter 2	The Molecular Recognition of Saccharides	3
2.1	Molecular Recognition	3
2.2	The Importance of Saccharides	4
2.2.1	Saccharides and Carbohydrates	4
2.2.2	Diabetes Mellitus	5
2.2.3	Structure of Saccharides	5
2.2.4	Home Blood Glucose Monitoring	7
2.3	Non-Boronic Acid Appended Synthetic Sensors for Saccharides	9
Chapter 3	Complexation of Boronic Acids with Saccharides	13
3.1	A Brief History	13
3.1.1	Early Work	13
3.1.2	Boronic Acid – Diol Complexation	14
3.2	Acidity and the O–B–O Bond Angle	17
3.2.1	O–B–O Bond Angle Contraction	17
3.2.2	Orbital Interpretation	20
3.2.3	Computational Analysis	20
3.3	Complex Formation and Dependence on pH	21
3.3.1	Empirical Data	21
3.3.2	Proton Transfer	22
3.3.3	Effect of Altering the Ligand	24
3.3.4	Effect of Altering the Boron Acid	24
3.3.5	Deuterium Isotope Effect	25
3.3.6	Computational Analysis	25

3.3.7	Reactions with Tetrahedral Borates	27
3.3.8	Pentavalent Coordination at Boron	29
3.3.9	Complex Formation and B-O Bond Length Dependence	29
3.3.10	B–O Bond Length and Acidification	30
3.4	Binding Constants and the Influence of Lewis Bases	31
Chapter 4	Fluorescent Sensors	34
4.1	The Application of Fluorescence in Sensing	34
4.2	Photoexcitation and Subsequent Relaxation	35
4.3	Excited State Internal Charge Transfer (ICT)	36
4.3.1	Solvent Relaxation	36
4.3.2	Dual Fluorescence	37
4.3.3	Excited State Twisted Internal Charge Transfer (TICT)	38
4.4	Fluorescent Internal Charge Transfer (ICT) Sensory Systems	40
4.4.1	Early Fluorescent Sensors for Saccharides	40
4.4.2	Fluorescent Internal Charge Transfer Sensors Incorporating the ortho-(Aminomethyl)phenylboronic Acid Fragment	48
4.5	Excited State Photoinduced Electron Transfer (PET)	50
4.5.1	Electron Transfer (ET)	50
4.5.2	The Mechanistic Interpretation of PET	52
4.6	Photoinduced Electron Transfer (PET) Sensory Systems	53
4.6.1	Diboronic Acid Sensory Systems with Selectivity for Specific Saccharides	55
4.7	Ditopic Sensors	62
4.8	Other Fluorescent Sensors	67
4.9	Amine–Boron (N–B) Interactions	72
4.10	The Importance of Pyranose to Furanose Interconversion	75
4.10.1	Pyranose to Furanose Interconversion as a Function of Time and Water	75
4.10.2	The Preference of Monoboronic Acids for D-Fructose.	77
4.10.3	Disaccharides	79
4.11	Summary	82
Chapter 5	Modular Fluorescent Sensors	84
5.1	The Design Rationale	84
5.2	Modular Systems	87
5.2.1	Linker Dependence	87

<i>Contents</i>	ix
5.2.2 Linker Dependence and Disaccharides	91
5.3 Energy Transfer Systems	95
5.4 Fluorophore Dependence in Modular Systems	98
5.4.1 Inference	102
5.5 Other Approaches	107
5.5.1 Wang and Co-workers	107
5.5.2 Hall and Co-workers	108
5.6 Summary	110
Chapter 6 Other Types of Sensor	111
6.1 Colorimetric Sensors	111
6.2 Electrochemical Sensors	118
6.3 Assay Systems	119
6.4 Polymer and Surface Bound Sensors	125
6.5 Odds and Ends	129
Chapter 7 Other Systems for Saccharide Recognition	130
7.1 Receptors at the Air–Water Interface	130
7.2 Transport and Extraction	131
7.3 CD Receptors	134
7.3.1 Homogeneous Systems	135
7.3.2 Heterogeneous and Polymeric Systems	142
7.4 Molecular Imprinting	145
Conclusion	149
References	151
Subject Index	168
Author Biographies	173

