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The Nature of the Mechanical Bond: From Molecules to Machines. By Carson J. Bruns & J. Fraser Stoddart. Wiley, 2016. Hardback, Pp. 786. Price GBP 180.00, EUR 216.00. ISBN 978-1-119-04400-0

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This book is a monumental review of the area of chemistry embracing the fascinating world of mechanically interlocked molecules (MIM). This field emerged about fifty years ago and the recognition of its achievements culminated by the attribution of the Nobel prize for chemistry to Jean-Pierre Sauvage, J. Fraser Stoddart (one of the authors of this book) and Bernard L. Feringa in 2016. Starting in the mid-1980s, this field developed rapidly thanks to the efforts of numerous researchers. This book is a tribute to the work of all these chemists.

The first chapter of *The Nature of the Mechanical Bond: From Molecules to Machines* clearly defines the concepts. It introduces the mechanical bond (interlocked molecules which cannot be separated without breaking a chemical bond) and presents the two main types of mechanically interlocked molecules, namely catenane (interlocked rings) and rotaxane (a ring around a rod with two big stoppers at its ends). The chapter presents an historical perspective of the mechanical bond and makes fascinating connections with patterns analogous to chemical bonds in nature, ancient and modern civilizations, and art. This opening chapter can be read with pleasure and interest not only by chemists but also by any curious person.

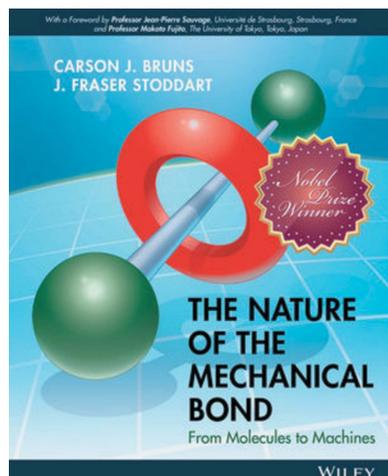
Chapter 2 reviews the different synthesis strategies used to build molecular structures containing mechanical bonds under kinetic control with a specific emphasis on template-directed synthesis (noncovalent bonding interactions serve as templates instead of covalent bonds) and active template synthesis (a species – usually a transition metal centre – acts as a template and a catalyst). These template strategies have proven to be very efficient for obtaining catenanes and rotaxanes.

Chapter 3 presents the strategies used to make mechanical bonds under thermodynamical control, which rely on reversible bond breaking–bond forming steps. Techniques such as slippage, self-assembling of metallo-organic MIMs, condensation, olefin metathesis and reversible nucleophilic reactions are described and illustrated by many examples.

Chapter 4 is devoted to the analysis of catenane topologies and rotaxane architectures. Topological isomerism concerns molecular ensembles containing the same atoms and chemical bonds which cannot be interconverted by any deformations that do not involve the breaking and forming of chemical bonds. In topology, rotaxanes differ from catenanes in the sense that they are topologically trivial (components can be separated without any bond breaking). This chapter describes numerous catenane and rotaxane structures with potentially interesting chemical and physicochemical properties.

Chapter 5 explains and illustrates the concepts of stereochemistry in mechano-molecules. Mechanostereoisomers are isomers which have the same interlocked component parts, but their positions in space differ. The ability of mechanostereoisomers to interconvert through a dynamical process distinguishes the dynamical mechanostereoisomers from the static ones which generally cannot be interconverted without the breaking and making of bonds.

The last chapter of the book describes the molecular switches (systems changing their conformation in response to a stimulus) and molecular machines (systems performing mechanical work) which can be designed from mechanostereoisomers interconverting through a dynamical process driven by a chemical reaction (acid–base, redox or covalent), light, solvation effect, molecular recognition, heat, pressure, and so on.



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The book contains numerous schemes and illustrations of high quality. These facilitate the visualization of the molecular structures and of the chemical and dynamical processes. Each chapter contains approximately 500 to 1500 references and the book presents a total of 3400 unique references which corresponds to the main publications in this research domain. Undoubtedly, the book will be a most useful tool for all researchers interested in mechanically interlocked molecules.

This book contains a limited number of equations and can therefore be appreciated by chemists who are not particularly interested in the theoretical aspects of the subject. However, the equations are sometimes inaccurate or insufficiently explained. In equation 3.1, which gives the expression of the rate constant within the transition state theory (TST), it would be useful to specify that ΔG^\ddagger is not exactly the activation free energy, but that one degree of freedom (the reaction coordinate) of the transition state is removed in that calculation and that the contribution of this degree of freedom is incorporated in the prefactor $k_B T/h$ summarizing different contributions. Equations 5.1 and 5.2 are inconsistent with the Tables containing equilibrium constant K_{eq} and the standard Gibbs free energy of reactions, ΔG° . As stated in equation 5.2, $K_{\text{eq}} = e^{-\Delta G^\circ/RT}$, so when ΔG° is negative $K_{\text{eq}} > 1$ and when ΔG° is positive $K_{\text{eq}} < 1$. For example, Table 5.1 reports positive values when ΔG° and K_{eq} are larger than 1, which is somewhat surprising. Moreover, K_{eq} is a dimensionless quantity and it is

often tabulated with a specified unit (for example, M^{-1}). There is a problem with the dimensions in equation 5.10. If $\tau = k/2$ (with k being the rate constant), as stated in the text, τ has the dimension of inverse time, but in the denominator of equation 5.10, it must have the dimension of time. In equation 6.2, the excluded volume is noted as ' ω ' and as ' w ' in the text, and the grafting density σ is noted as ' s ' in the text. σ is defined as A/n (surface area divided by the number of polymer chains, n). In equation 6.2, however, σ must have the dimension of length^{-2} . Such inaccuracies and misprints can be troublesome for students and the equations should be carefully checked for future reprinting.

The amount of information gathered in this book and the amount of work done to write it is impressive. This book will be a reference for researchers and students interested in building mechanically interlocked molecular systems or seeking applications of molecular switches and molecular machines.

The authors dedicate the book to the memory of Linus Pauling, author of *The Nature of the Chemical Bond*, and Ernest Eliel, author of *The Stereochemistry of Carbon Compounds*. According to the authors, these two books have changed the way chemists think about chemistry. One can anticipate, I believe, that *The Nature of the Mechanical Bond* will open new horizons for generations of readers and will stimulate the creativity of many architects of matter who wish to design more and more fascinating molecular systems.