

Strained Hydrocarbons

Beyond the van't Hoff and Le Bel Hypothesis

Edited by Helena Dodziuk



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Foreword

Chemistry is the truly anthropic science. The molecules we make can heal us, and they can hurt us, because they are on the scale of the molecules that make up our bodies. And our synthetic creations interact, even react, with the molecules that nature – our enzymes, the environment – put into us.

Molecular science is also anthropic (male and female, of course) because it presents a challenge to human intelligence that is just right, commensurate with our intellect. The exciting story this book develops bears testimony on every page to that anthropic cognitive nature of organic chemistry.

Let me explain: our remarkable neural system is steered by a complex brain. That brain has prejudices for sure; it tends to simplify things, falling at every proffered opportunity for beautiful equations, simple mechanisms, Platonic solids and the honeyed simplicities of politicians. But when challenged, we can deal with substantial complexity. Indeed, the brain relishes being stretched: by rich sensual inputs, by patterns, by puzzles.

Along comes a science, our chemistry. It offers in its molecular structures, a game that is at first sight deceptively simple. Take hydrocarbons (most of the molecules in this book are in this category) – what could be simpler? Two elements, C and H, that by a transparent rule of intercombination form four bonds, and one bond, respectively. You are well aware of the manifestation of these rules and combinatorics – a chemical universe of incredible diversity.

These molecules can not only be thought up, they can also be synthesized in a human span – roughly the time it takes for a graduate student to get a Ph.D. We are not making a ladybug, nor a spiral galaxy; we are making a paracyclophane. The complexity of the challenge is on the human scale. And so are the possibilities: What can I do to string eight carbons across the *para* positions of a benzene? Can I reduce the bridging carbons to seven? Will I make it easier if the eight carbons are partially in a benzene ring themselves? The questions just flow one after the other; it takes no talent to ask them, just a normal curious human being, privy to the structural codes of chemistry.

So the game itself, the game of chemical structure, is exciting. Chess pales by comparison. Add to that ludic challenge potential utility, and also the natural human desire to probe limits (just how far can I distort that double bond out of its planar normalcy?), and you have all the makings of intense interaction, part

intellectual, part emotional, between a human being and an object of his or her creation.

The object of our intense contemplation – a compound macroscopically, a molecule microscopically – is complex enough not to be boring, yet not unpredictably chaotic. The strained molecule is just right for some of us to exercise our creativity in thinking up these strange beasts, others in coming up with ingenious ways of making them (for molecules are real!), all of us admiring the complexity, simplicity and function all rolled into one.

Enjoy reading this book!

Roald Hoffmann

Preface

Strained hydrocarbons represent an amazing domain. About 80 years after the formulation of van't Hoff and Le Bel's hypothesis new, exciting molecules representing in Hoffmann and Hopf formulation (R. Hoffmann, H. Hopf, *Angewandte Chemie*, submitted), what is probably too much of anthropomorphization, 'molecular sadism' were synthesized. Paraphrasing D. J. Cram, one could say that such molecules elicit wonder, stimulate the imagination and challenge both synthetic talents and interpretive instincts. Up to the early 1990s the field of strained hydrocarbons was a kind of elitist area in which only the best synthetic and theoretical chemists were active. It was a playground of few, characterized by vivid interactions between synthetic and theoretical chemistry allowing one to propose plausible synthetic targets on the basis of model calculations. On the other hand, it allowed Bader, Wiberg and their followers to refine the definition of the chemical bond. The situation in the domain of distorted molecules changed after the discovery of fullerenes and nanotubes which attracted numerous researchers. These molecules, having nonplanar systems of conjugated bonds, are not hydrocarbons but their derivatives are numerous. Thus, they have been included into this volume in view of the rapid development of these areas and, still largely unfulfilled, prospects of their applications.

Several researchers helped me in this project. First of all, I would like to thank all contributors to this volume. I would like also to acknowledge the support I have obtained from Professors T. Marek Krygowski, Jay S. Siegel and Henning Hopf in the initial stage. Finding contributors was sometimes a difficult task. The help of Professors A. de Meijere, E. Osawa, F. Diederich, C. Thilgen, W. T. Borden, J. Cioslowski and H. Kuzmany in the search for coauthors is gratefully acknowledged. I am deeply obliged to my colleague, Dr. K. S. Nowinski, for designing the cover picture. On the other hand, I owe a deep apology to the authors of many interesting papers on strained hydrocarbons which could not be presented in this book or were insufficiently covered due to space limitations.

The question: 'To what extent can a bond be distorted without being broken?' is fascinating. This book is devoted to the presentation of distorted hydrocarbons. It is an effort to counteract, in this limited volume, overspecialization by showing not only syntheses, physicochemical studies and theoretical calculations of these molecules, but also the prospects of their applications. Strained molecules are

exciting objects for studies *per se*. With several novel hypothetical molecules waiting to be synthesized on the one hand, and with the possibility of obtaining fascinating supramolecular complexes with distorted hydrocarbons as building blocks on the other, this domain will remain enthralling.

Warsaw, January 2009

Helena Dodziuk

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1 Introduction

1.1 Initial Remarks

Helena Dodziuk

Let us start with a bit of history. Today, it is hard to imagine how difficult it was to develop basic concepts and ideas of chemistry in the second half of the 19th century. The story about Kekulé's fight for his benzene structure shows that not all the arguments he used in its favor are valid today [1]. His idea could not be supported by the poor experimental instrumentation of that time. There was no X-ray analysis, no modern spectroscopic techniques and no calorimetry. The idea of the constitution of molecules, that is building them from a certain number of different types of atoms, was established, as well as several experimental findings which demanded rationalization. Among them were optical activity and the existence of a number of different molecules with the same constitution. Pasteur foresaw that the former phenomenon could be related to the positioning of atoms in space but only the van't Hoff [2] and Le Bel [3] hypotheses on the tetrahedral arrangement of substituents on the tetravalent carbon atom explained most observations known at that time. Interestingly, the independently proposed models differed slightly: that of van't Hoff was based on a regular tetrahedron, while in the second one used an irregular tetrahedron to represent the carbon atom. This difference was not significant but, remarkably, the more idealized van't Hoff approach was generally accepted. An illustration from the 1908 German edition of van't Hoff's book, showing two stereoisomers of the tetrasubstituted ethane molecule $\text{CR}_1\text{CR}_2\text{rCR}_3\text{CR}_4\text{r}$ shows the way in which molecules were depicted at that time (Figure 1.1).

The van't Hoff and Le Bel hypothesis was met with strong criticism, not always expressed in impartial scientific language. The renowned chemist and editor of the German *Journal für praktische Chemie*, Prof. Adolf Kolbe wrote: 'A Dr. H. van 't Hoff of the Veterinary School at Utrecht has no liking, apparently, for exact chemical investigation. He has considered it more comfortable to mount Pegasus (apparently borrowed from the Veterinary School) and to proclaim in his 'La chimie dans l'espace' how the atoms appear to him to be arranged in space, when he is on the chemical Mt. Parnassus which he has reached by bold fly'.

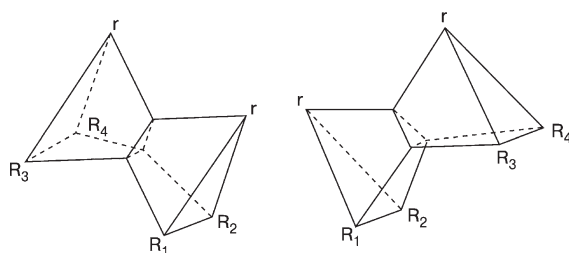


Figure 1.1 The representation of two stereoisomers of a tetrasubstituted ethane molecule $\text{CR}_1\text{CR}_2\text{rCR}_3\text{CR}_4\text{r}$, as published 100 years ago in van't Hoff's book [197].

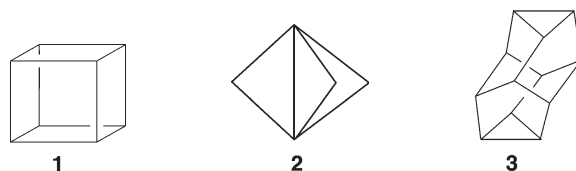
In spite of such a strong attack and the difficulties associated with the lack of modern physicochemical methods, the idea of the tetrahedral arrangement of substituents around a tetravalent carbon atom was generally accepted and van't Hoff became a first recipient of the Nobel prize for Chemistry in 1901, interestingly not for his stereochemical ideas but 'in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions'.

Remarkably, an early idea of Sachse on the cyclohexane conformations (today known under the names chair and twist-boat) [4, 5] could not be proved at that time and was not accepted. Then, it took almost 80 years to understand all the consequences of the van't Hoff and Le Bel concepts which not always were based on justified assumptions. For instance, the van't Hoff understanding of the C–C bond implied free rotation around it. This assumption was only shown to be invalid by Pitzer's work [6, 7] on the hindering of the rotation and preferred orientations of substituents on the C–C bond, started in 1936, which marked an important step in development of stereochemistry [8]. The combination of the ideas on tetrahedral orientation of substituents on a tetravalent carbon atom and of the hindered rotation around the C–C bond resulted in rationalization of the cyclohexane conformations and the number of isomers of its derivatives summarized in the Hassel [9, 10] and Barton [11] studies which were also honored by a Nobel Prize 'for their contributions to the development of the concept of conformation and its application in chemistry'. Analogous studies of the spatial structure of alkenes, alkynes and aromatic compounds followed.

With these achievements, the basis of the organic stereochemistry seemed to be laid, and models could be built, of spatial structures of molecules from well-defined rigid fragments. Eaton's report on the synthesis of cubane **1** in 1964 [12] and especially the Wiberg synthesis of [1.1.1]propellane **2** [13] have shown that, in addition to the small-ring cycloalkanes, well-known since the second half of the 19th century, that exhibit Bayer strain [14], hydrocarbons having structures strongly departing from that suggested by van't Hoff and Le Bel can exist. This book is devoted to such nonstandard structures. Let us first define what the standard hydrocarbons are: first, these are saturated hydrocarbons with the arrangement of substituents on the carbon atoms close to tetrahedral; then, double bonds and aromatic rings lying in a plane with its substituents and, last but not least, linear

acetylenes. Also of interest are bond lengths that depart far from the standard value of 154 pm. Of course, fullerenes and carbon nanotubes in their idealized form are not hydrocarbons, but these conjugated aromatic systems are nonplanar and they are definitely the most widely studied distorted aromatic systems today. They also offer a unique possibility of investigating the effect of nonplanarity on structure, physicochemical properties and reactivity. Actually, this book should also be understood as part of my private campaign against too deep specialization, from which we all suffer. Thus, showing the influence exerted by molecular distortions on various physicochemical properties using fullerenes as an example seemed to be of importance.

Highly distorted hydrocarbons are sometimes considered to be of no importance in view of their lack of practical applications. The significance of investigating such systems is discussed in Section 1.2. They are studied by both experimental and theoretical methods that, as discussed in Section 1.3, are of special significance in this domain. As shown by several examples (among other 1 [15] and heptacyclo[6.4.0.0^{2,4}.0^{3,7}.0^{5,12}.0^{6,10}.0^{9,11}]dodecane 3 [16, 17] which have first been studied theoretically then synthesized [13, 18]), to propose novel plausible synthetic targets on the basis of molecular modeling is a reliable aim of calculations.

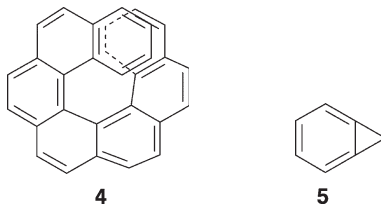


We are experiencing such a rapid development of this science that it is not possible to discuss all the unusual hydrocarbons. Therefore, a selection, by no means considered to be exhaustive, of interesting molecules which did not find a place in other chapters is presented in Section 1.4.

Simple strained saturated hydrocarbons are presented in Chapter 2. Both known, such as [1.1.1]propellane 2, and hypothetical molecules having inverted carbon atoms are discussed in Section 2.1. The importance of these molecules is emphasized by the discussion of the existence of the central bond in 2 which permitted precise definition of a bond in quantum chemistry [19]. The fascinating Hoffmann idea of planar carbon atom lying in a plane with its four substituents [20] was only realized *in silico* [21] and, as described in Section 2.2, still awaits realization. Prismanes (one of which is cubane 1) and asteranes are discussed mainly from the theoretical point of view in Section 2.3 but the influence of molecular distortions on the properties of the known systems is presented there, too. Saturated hydrocarbon cages and planar cyclohexanes (Section 2.4) as well as molecules with ultralong (Section 2.5) and ultrashort (Section 2.6) C–C bonds are also discussed in Chapter 2.

In Chapter 3 which is devoted to alkenes, energetic aspects of distorted double bonds are presented in Section 3.1, small cage alkenes are discussed in Section 3.2 while Section 3.3 is devoted to strained cumulenes.

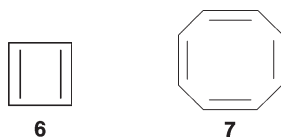
Analogously, in Chapter 4 energetical considerations concerning strained aromatic systems are discussed in Section 4.1, while bridged aromatic rings (i.e. cyclophanes), helicenes like **4**, and cyclopropanes like **5** are presented in Sections 4.2 to 4.4, respectively.



As discussed earlier fullerenes, to which the longest Chapter 5 is devoted, are actually not hydrocarbons but their extended closed nonplanar conjugated aromatic systems deserve to be discussed in this book. After a short introduction in Section 5.1 their chemistry is presented in Section 5.2, and physicochemical properties reflecting their distorted structure (X-ray in Section 5.3.1, UV/Vis spectra in Section 5.3.2, NMR spectra in Section 5.3.3 and electrochemistry in Section 5.3.4) are shown. Next, fullerene films (Section 5.4), endohedral fullerene complexes (Section 5.5), an exciting application of NMR to study the structure of hydrogenated fullerenes (Section 5.6) and, mostly prospective, fullerene applications (Section 5.7). Unfortunately, I did not succeed in finding a specialist willing to present theoretical fullerene studies and their limitations due to the size of these huge cage molecules. This a serious drawback in spite of the inclusion of some fullerene calculations in other chapters.

The inclusion of nanotubes into this monograph was based on similar arguments as those advocating the inclusion of fullerenes. In Chapter 6, structure, chemistry and also mostly prospective applications are shown (Sections 6.1–6.3, respectively). There has been a fascinating development in the financing of carbon nanotubes: people expected to get really big money from investing in CNTs about five years ago and then realized that the returns do not come immediately. Some of the applications introduced or expected to be introduced soon in large-scale manufacturing have not been successful. For instance, using polymer nanocomposites containing small amount of CNTs for electropainting of cars has been abandoned by General Motors, and Korean plans to build a factory for displays involving CNTs few years ago have not been fulfilled. Moreover, a recent observation on the carcinogenicity of multiwalled nanotubes may further slow down the development of CNT applications [22]. Even if we cannot see their rapid introduction, I am sure they will be important in the longer run.

Cyclic alkynes with nonlinear triple bonds are discussed in Chapter 7, while molecules with labile bonds are presented in Chapter 8. They include rigid cyclobutadiene **6**, highly mobile molecules like cyclooctatetraene **7** and short-lived species that could only be trapped at very low temperature in matrices. The fascinating discussion of interconversions between some of these species is



presented in some detail from both theoretical and experimental (mainly NMR, IR) points of view.

Hydrocarbons with nonplanar graphs, discussed in Chapter 9, conform to van't Hoff and Le Bel stereochemistry but they are so unusual that they were considered to fit into this monograph. Such molecules having distinct topological properties represent an exciting border area between chemistry and mathematics. The molecules presented in this chapter have been obtained using elegant methods of traditional organic chemistry, while other systems exhibiting nontrivial topological properties (catenanes, rotaxanes, knots, etc.) could mostly be obtained by taking advantage of methods typical of supramolecular chemistry [23].

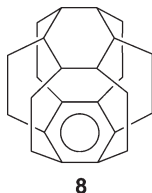
In the last Chapter 10, novel ways of obtaining and stabilizing unstable highly strained species in 'molecular flasks' are presented. The latter method makes use of supramolecular chemistry enabling, for instance, storage of the highly unstable cyclobutadiene **6** for a month at room temperature [24].

1.2

Hydrocarbons with Unusual Spatial Structure: the Need to Finance Basic Research

Helena Dodziuk

By reporting the results on hypothetical hexahydrosuperphane **8** [25], a highly strained molecule with a planar cyclohexane ring, we have been confronted with the question as to whether this molecule had been chosen for study because of its future practical applications. The question was posed by a computer scientist who had no knowledge of stereochemistry, but it corresponds to a general attitude governed by grant funding for scientific research. Namely, any grant application has to show its immediate usefulness. However, in reality hardly any grants that use such justification will bring marketable results at all. For the applications of others we will probably wait 10 or more years and only a few of such grants will find their way to industry soon. Let's inspect some examples in some detail. Liquid crystals today are commonly applied in displays but several other uses (as surface thermometers showing temperature distribution over a body, in optical



imaging, etc., <http://plc.cwru.edu/tutorial/enhanced/files/textbook.htm>) are foreseen for them. Discovered in 1888 by a botanist, Reinitzer [26], they were for almost 100 years considered to be the physicists' toys. In 1966, an article entitled 'Liquid crystals – an area of research of little use?' appeared in the German journal *Nachrichten für Chemie, Technik und Labor* [27]. Then in 1972 the first liquid crystal display was built giving birth to a thriving branch of industry.

Exciting results reported in a series of works carried out by the Stoddart group on so-called molecular machines show that there is a long path from a concept to a marketable device [28]. By using rotaxane systems like **9a** [29] a family of versatile systems has been created which can be used as sensor, switches, 'molecular abacus' or nanomotor. In addition to the spacer **9e**, the axle consists of the π -electron acceptor groups **9c**, **9d** which, upon the imposed conditions, can selectively bind the π -electron-donating macrocycle **9e** shuttling it between the position shown in the formula **9a** and that around the 3,3'-dimethyl-4,4'-bipyridinium unit **9c**. These studies, combining sophisticated syntheses with physicochemical methods, certainly provide an example of an important direction for nanotechnology research in the next few years. However, it is questionable whether they will bring marketable results within this time. This does not mean that such studies are not worth pursuing. Impractical studies elucidating the wave or corpuscular character of light and matter have been carried out since the famous dispute between Newton and Huygens for almost 300 years and, as the diffraction experiments on fullerene C_{60} **10** (this group of molecules is discussed in detail in Chapter 5) from the Zeilinger group show [30], this topic is still vivid. Of course, choosing objects for a project out of more than 27 500 000 known molecules is a hard task, but its expeditious applicability should not be decisive. Most basic

