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 CR1CR2rCR3CR4r 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'éspace' 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'.

Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis. Edited by Helena Dodziuk

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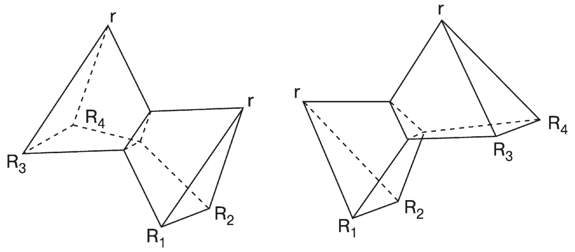


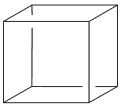
Figure 1.1 The representation of two stereoisomers of a tetrasubstituted ethane molecule CR1CR2rCR3CR4r, as published 100 years ago in van't Hoff's book [197].

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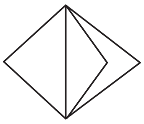
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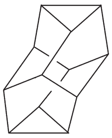
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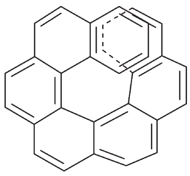
We are experiencing such a rapid development of this science that it is not possible to discuss all the unusual hydrocarbons. Therefore, a selection, by no means considered to be exhaustive, of interesting molecules which did not find a place in other chapters is presented in Section 1.4.

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 cycloproparenes like **5** are presented in Sections 4.2 to 4.4, respectively.



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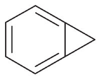

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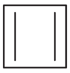
As discussed earlier fullerenes, to which the longest Chapter 5 is devoted, are actually not hydrocarbons but their extended closed nonplanar conjugated aromatic systems deserve to be discussed in this book. After a short introduction in Section 5.1 their chemistry is presented in Section 5.2, and physicochemical 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 carcenogenicity 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



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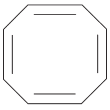

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presented in some detail from both theoretical and experimental (mainly NMR, IR) points of view.

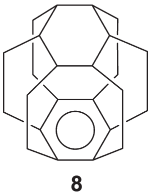
Hydrocarbons with nonplanar graphs, discussed in Chapter 9, conform to van't Hoff and Le Bel stereochemistry but they are so unusual that they were considered to fit into this monograph. Such molecules having distinct topological properties represent an exciting border area between chemistry and mathematics. 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



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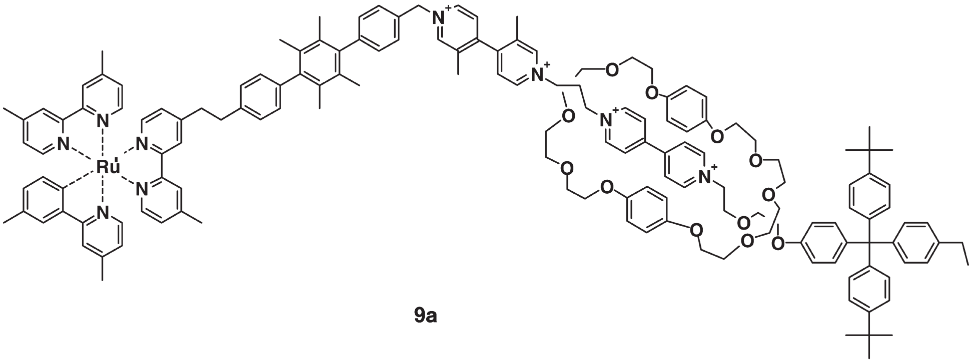
imaging, etc., http://plc.cwru.edu/tutorial/enhanced/files/textbook.htm) are foreseen for them. Discovered in 1888 by a botanist, Reinitzer [26], they were for almost 100 years considered to be the physicists' toys. In 1966, an article entitled 'Liquid crystals – an area of research of little use?' appeared 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′-bipydidinium 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



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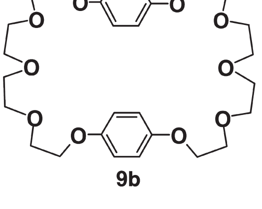

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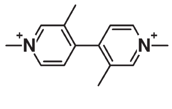

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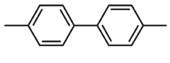

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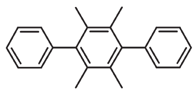
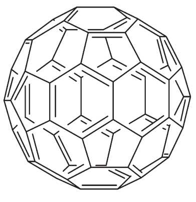


9e



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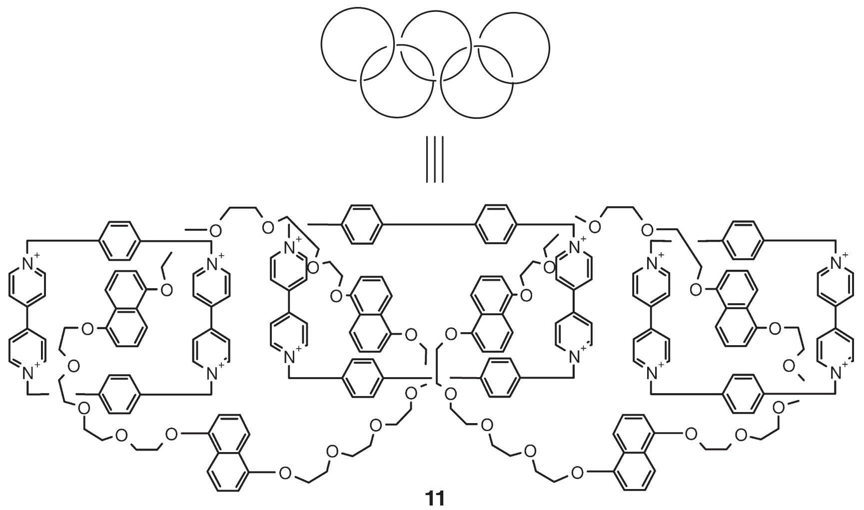

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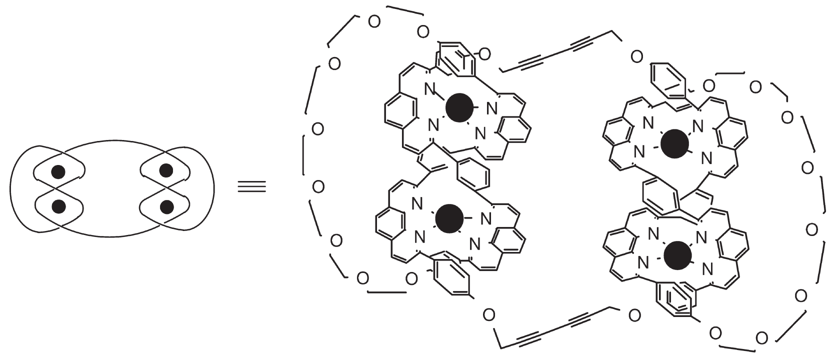

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research is driven by curiosity not practicality but somehow in the long run it pays off. No-one thought about chemical applications when the foundations of a new branch of mathematics – topology – were formulated in the 1820s, long before such abstract concepts as links (catenanes) like olympiadane **11**, Möbius strip, and knots, like double knot **12,** were shown to be of use in chemistry [31] (some hydrocarbons with distinct topological properties are presented in Chapter 9).

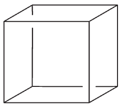
Moreover, the discovery in the 1990s that circular DNAs in the living organisms [32–34] form links, knots and other systems with nontrivial topological properties, will have consequences which cannot be anticipated today. We begin to understand the mechanism of their formation but the role they play in nature is still unclear. Similarly, Einstein's work on the photoelectric effect published in 1905, for which he was awarded the Nobel prize, certainly did not seem to have any practical significance at that time. Nor were cosmic studies carried out to develop kevlar and teflon! These materials were spin-offs of the space journeys.

For examples closer to chemistry let us look at the fullerene **10** applications, much praised in the 1990s [35]. The Krätschmer method [36] which produces a significant amount of the substances spurred numerous proposals for their application. They were thought to exhibit superconductivity, serve as a drug carrier, its derivative $C_{60}F_{60}$ was anticipated to be an ideal lubricant, etc [35].

None of these promises was fulfilled. Superconductivity of fullerene derivatives is exhibited only at very low temperatures [37]; $C_{60}F_{60}$ was synthesized but it turned out to decompose in air with the HF formation [38]; and, in spite of promising reports, to our best knowledge no drug involving fullerene is on market. One of few fullerene applications today consists in their use as AFM tips (http://www.foresight.org/Updates/Update27/Update27.3.html). Few other are presented in Section 5.0 while those discussed in Section 5.7 still await marketable applications. This does not mean that fullerenes should not be intensively studied and that they will not finally be of practical use. At present these elegant-looking, highly symmetrical molecules are exciting and worth studying simply because of their unusual properties. They (1) form the nonplanar system of conjugated bonds; (2) have a hollow space inside that can accommodate other, smaller molecules, ions or even an elementary particle [39]; (3) with cations inside they form unusual salts since the fullerene cage assumes the negative charge, thus the salt can be dissociated only by its destruction; and, last but not least, (4) their formula merely look beautiful or, in other words, they are aesthetically appealing.

The last point, that is the beauty of molecular formulae as the driving force for studying a molecule, was strongly denied by Jansen and Schön in their essay provocatively entitled 'Design in chemical synthesis – an illusion?' [40]. Their argument, which deserves much longer comment, contraposes purely aesthetical Gropius' teapot designs (apparently not constrained by the properties of materials from which the objects were to be made) to the design of molecules whose structure is unequivocally defined by the energy hypersurface. No objection: molecular structure must obey the basic rules of chemistry and physics. However, within these limits there is plenty of room for designing molecules with predefined desirable properties. In addition to the complicated and not always successful field of drug design, hydrocarbons with unusual spatial structure present numerous examples of molecular design which was not usually aimed at marketability.

For instance, let us look at cubane **1** (discussed in Sections 2.3 and 2.4) synthesized almost 50 years ago. The molecule was obtained by Eaton [41] not because of its immediate applicability. Its synthesis presented a considerable challenge and **1** was aesthetically pleasing (the aspect denied by Jansen and Schön [40]). The molecule turned out to have untypical properties, due to its nonstandard structure, e.g. **1** exhibits unusual rearrangement reactions such as the rearrangement of cubane to cuneane **13**. In addition, NMR spectra of cubane allow one to explore the Karplus dependence of the ^3J coupling constants [42]. And as for the cubane applications not looked for by Eaton? For more than 30 years secret studies were carried out by the American Army on nitro-derivatives of **1** because the high energy content of the cubane core magnified by the nitro-substituents suggested that these materials might have extraordinary explosive properties. (The synthesis of octanitrocubane **14** was eventually reported a few years ago [43].) There were also attempts to use cubane derivatives as therapeutic agents [44, 45].



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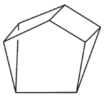

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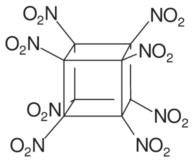

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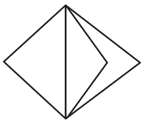
However, the emerging applications of some hydrocarbons with unusual spatial structure should not deceive us. The main goal of studying them is not their marketing but to deepen our understanding of the chemical bond. Interestingly, until recently this very fruitful concept, on which all chemistry is based, was not anchored in quantum chemistry. We could carry out calculations on the molecule as a whole but, without using artificial approximate constructs, were unable to analyze properties of specific bonds within it. In particular, studying molecules with bonds which are very different from the standard is indispensable to understand the limits of the very concept of the chemical bond. The question as to what extent a chemical bond can be distorted without breaking is thought provoking. Moreover, in certain cases even the mere existence of a bond between two carbon atoms has been questioned. This was the case encountered in [1.1.1]propellane **2** (discussed in some detail in Sections 1.3 and 2.1) [46]. The synthesis of this exciting molecule, preceded by the calculations supporting its feasibility and predicting the propellane properties, serves as a fascinating example of a mutually fruitful interaction of theoretical and experimental studies [47]. **2** represents one of the most amazing examples from the point of view of organic stereochemistry since, contrary to van't Hoff [48] and Le Bel [49] hypothesis, all four substituents on its bridgehead atoms lie in one hemisphere. Such atoms bearing the name 'inverted carbons', are also present in other small-ring propellanes (discussed in detail in Section 2.1) such as a derivative of [4.1.1]propellane **15** and that of [1.1.1]propellane **16** [50]. The discussion of the existence of the bridgehead–bridgehead bond in small-ring propellanes is remarkable [51]. The distance between the atoms in these molecules is about 1.6 Å [52], which is significantly longer than the typical C–C bond of 1.54 Å (some authors [50] consider this difference small but the energy required for such bond lengthening is considerable). However, 1.6 Å or even longer bonds have been encountered in several hydrocarbons [53]. In spite of the reliable bond length of the former bond in small ring propellanes, the differential electron density maps for **15** [54] and **16** [50] measured in X-ray studies have not shown any build-up of the differential electron density between the bridgehead propellane atoms which should accompany the bond between them. The former finding and the possibility of a biradical structure for **14** without the central bond triggered a discussion on the reliability of the maps as the criterion of the bonding. On the one hand, the formulation of the limitations of this criterion resulted, stating that the lack of the build-up of the differential electron density is an artifact of the promolecule density distribution not reflecting the relative properties of the charge distributions [47]. The quantum calculations for **2** carried by Wiberg, Bader and Lau [47] showed that there is the bond-critical point along the line connecting bridgehead atoms in this molecule, thus proving the existence of the bond between the atoms. These calculations also revealed that the exceptional stability of this molecule is not due to the typical two-center integrals describing chemical bonds but is the result of the operation of the three-center integrals. In addition, other criteria for the existence of the central bond in **2** modeling [1.1.1] propellane have been checked [50].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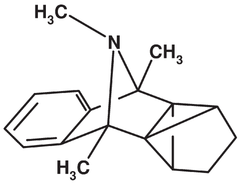

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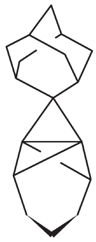
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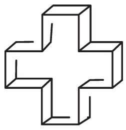
Helvetane **17** and israelane **18** appeared as a joke in a 1st April issue of *Nouveau Journal de Chimie* [55]. These highly strained hypothetical molecules belong to a very interesting class of $(CH)_{2n}$ cage compounds to which cubane **1**, dodecahedrane $C_{20}H_{20}$ **19** and hypothetical perhydrogenated fullerene $C_{60}H_{60}$ [56] (discussed in Sections 2.3 and 2.4) belong. These molecules were shown to be of much higher energies than other members of the $C_{20}H_{20}$ family [57] which should be much more easy to synthesize. Nevertheless, they have been calculated by several theoreticians who pointed out than removing symmetry constraints would significantly lower the energy of **17** and **18**. Then such molecules being members of a large group of isomers without interesting properties would seem to be of no specific interest.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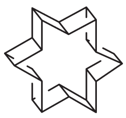
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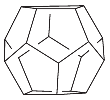
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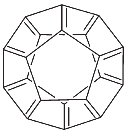
It should be stressed that a molecule dismissed as purely hypothetical today can be a plausible synthetic target tomorrow. Herzberg, later awarded Nobel Prize, stated in his seminal 'Infrared and Raman Spectra of Polyatomic Molecules' in 1945 that it is not likely that molecules of I_h symmetry will ever be found [58]. It took several years of hard work for the Paquette group to synthesize the first molecule of such a high symmetry, aforementioned dodecahedrane **19**, about 40 years later [59]. (In our opinion this synthesis deserves the name molecular design vigorously discredited by Jansen and Schön [40].) Today, the best known such molecules are fullerene **10** (discussed in Chapter 10), parent fullerene C_{20} **20** [60] and perfluorinated fullerane $C_{60}F_{60}$ (which, as discussed in Chapter 10, similar to other short-lived species could be stabilized in molecular flasks) as well as the most symmetrical isomers of their higher homologs, like C_{240}, C_{540}, C_{960}, etc and some nested fullerenes formed by carbon cage compounds [61] belonging to the latter group.



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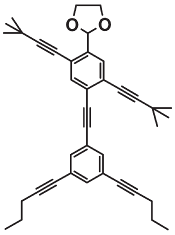
A kind of laborious play, that seems not to promise serious consequences but bears all the attributes of a standard synthetic work, has been reported by Chanteau and Tour [62]. They described the syntheses of nanoputanes, like **21**, the anthropomorphic molecules named after the Jonathan Swift lilliputanes. With meticulously described syntheses, the authors showed not only the way to obtain the nanokid **21** but also got a 'dancing' nanoputanes layer on a surface **22**.



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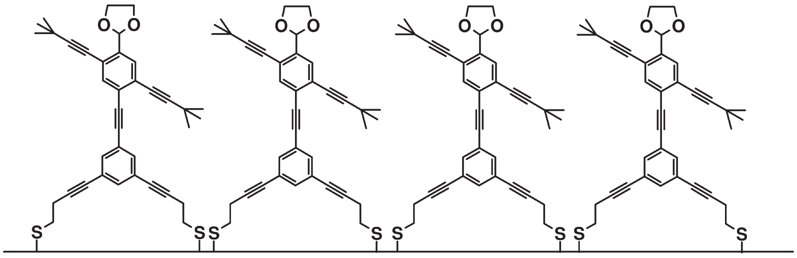

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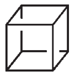
To summarize, the choice of a molecule for studies is not simple. Most standard systems are trivial and unworthy of serious consideration in basic research. Other untypical molecules can also have their pitfalls. Keeping in mind that what is impossible to synthesize today can be realizable tomorrow, one should nevertheless exhibit caution when choosing an object to study which should be of a serious scientific interest. However, it should be stressed once more that immediate applications should not be the reason for financing basic research.

1.3
Computations on Strained Hydrocarbons

Andrey A. Fokin and Peter R. Schreiner

Despite some potential applications as high-energy materials and specialty polymers, highly strained compounds mostly play a conceptual and educational role. Over 10 000 chemical papers contain the key words 'strained hydrocarbon' and more than 18 000 ACS papers alone the terms 'strain energy.' Despite the fact that our rationalistic and thrifty ages leave lesser space for exotic molecules, the aesthetic beauty of the cages such as cubane **1**, tetrahedrane **23**, octahedrane **24** or dodecahedrane **25** still fascinate organic chemists and represent the artistry of organic synthesis. Nature also uses highly strained compounds: The recent discovery of ladderanes **26** and **27** as membrane lipids of certain anaerobic bacteria [63] and natural antifungal oligocyclopropane antibiotic **28** [64] underline the importance of such structures (Scheme 1.1).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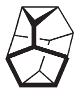
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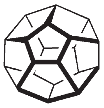
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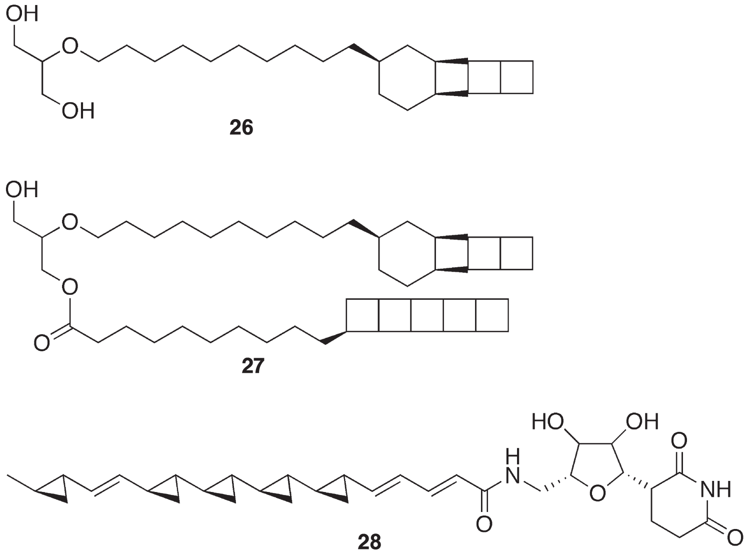
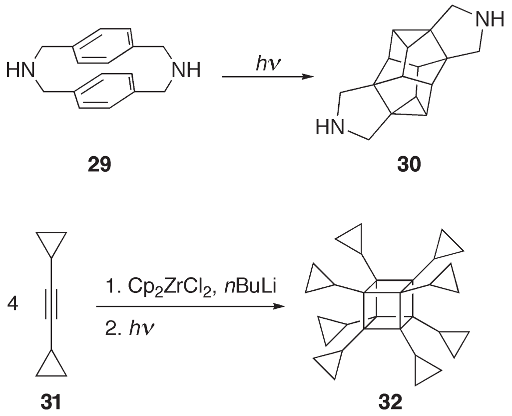
It is generally considered that highly strained compounds are difficult and expensive to make and, sometimes, also to store. However, once a challenging molecule has been prepared, the development of a simpler way for its synthesis is impending. The most recent example is highly strained octahedrane **24**, which was first prepared in 1993 by an expensive and elaborate procedure [65, 66]. Now some octahedrane derivatives such as **30** can be prepared by one-step photochemical dimerization of readily available aromatic cyclophane **29** [67]. A simple preparation of octacyclopropylcubane **32** by an effective two-step condensation of four dicyclopropylacetylenes **31** is another remarkable example (Scheme 1.2) [68]. The stability of strained compounds is not necessarily a concern: cubane and its derivatives are stable even at high temperatures because the strain is uniformly distributed throughout the molecule and orbital symmetry forbids the cleavage of two C–C bonds at the same time. Some unstable and highly strained hydro-



Scheme 1.1 Highly strained hydrocarbons and some natural compounds containing strained moieties.



Scheme 1.2 Highly strained derivatives of octahedrane and cubane prepared recently through short and simple procedures.

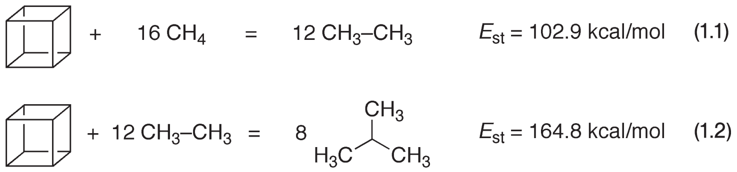
carbons have been successfully encapsulated and stored at room temperature as guest molecules in hemicarceplexes [69].

The chemistry of strained organic molecules probably began with the realization of cyclopropane derivatives by Perkin [70] that was almost immediately followed by the development of strain theory [71]. It was soon recognized that Baeyer's angular strain is the main contributor to the potential energies of organic molecules. The quantitative description of strain was first proposed in the mid

1940s by Hill [72] and was developed further by Westheimer into molecular mechanics [73]. As with many other useful chemistry concepts like conjugation, aromaticity, chemical bonding, etc., strain itself is not defined exactly, but can be expressed well quantitatively by 'strain energy,' which is, however, not measurable experimentally. Its value is calculated as the difference between the experimental enthalpy of formation of the molecule of interest and that of a *hypothetically* strain-free structure. The enthalpies of formation of strain-free reference compounds are calculated through group additivity schemes [74] based on the 'averaged' contributions of groups (CH_3, CH_2, CH, etc.) from the straight-chain hydrocarbons. The group's contributions are derived from thermochemical measurements for which, however, equilibrium conformer distributions are difficult to take into account. Group equivalent schemes also require experimental thermochemical data on the molecule of interest but these are equally error-prone. The most recent example is the heat of formation of cubane that was reinterpreted based on the corrected value of its sublimation enthalpy [75]. Unluckily, cubane has already been used for the parameterization of some molecular mechanical methods [76] that now require re-parameterization. New additivity schemes [77, 78] demonstrate excellent accuracy, but only for moderately strained hydrocarbons.

The computations of ΔH_f° through atomization energies and bond/group separation reactions are more trustworthy; atomization energies are more useful for computation of the enthalpies of formation of small molecules [79–81]. Bond separation (isodesmic) equations proposed by Pople [82] for which the bonds between the non-hydrogen atoms are separated into strain-free reference molecules, give the strain energy directly (cf. Equation 1.1 for the evaluation of the strain energy of cubane). Alternatively, homodesmotic [83] equations (such as Equation 1.2), that contain an equal number of groups and bonds on both sides of the same type, largely cancel systematic computational errors. These two approaches lead to different strain energies (Scheme 1.3).

The choice of strain-free reference compounds is problematic. The generally accepted strain energy of cubane (164.8 kcal mol^{-1}, without the newest correction for its enthalpy of sublimation) was computed through homodesmotic Equation 1.2. However, the strain energy evaluation in Equation 1.2 is not properly balanced because the eight isobutane molecules are stabilized by twelve additional 1,3-interactions (protobranching) [84] relative to cubane. Thus, isoalkanes have 'negative strain' relative to *n*-alkanes, and cannot be used as references for strain energy evaluations: using branched alkanes artificially increases the strain



Scheme 1.3 Isodesmic (1.1) and homodesmotic (1.2) equations to determine the strain energy (E_{st}) of cubane.

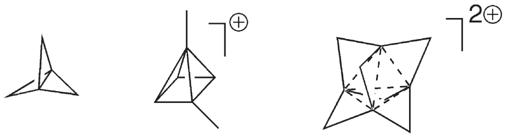
of the molecules of interest. On the other hand, Equation 1.1 is properly balanced because it is based only on strain-free molecules – methane and ethane. The strain energy of cubane calculated via Equation 1.1 is 102.9 kcal mol^{-1} [85] and this value should be used. Equally, other strained hydrocarbons appear to be less strained than originally assumed. Concerning the validity of isodesmic Equation 1.1, one can argue that ethane is also not a strain-free molecule because of van der Waals' contacts while methane is destabilized by Pauli repulsions. As these effects are present in all organic molecules these two hydrocarbons are still the best candidates as strain-free reference hydrocarbons; there is no conformational problem either.

Computations are the only way to evaluate the strain energies of molecules for which the experimental thermochemistry is not available. Chemically accurate computations for small molecules nowadays are inexpensive, fast, and they can be used with ease. However, there are *many* sources of systematic as well as non-systematic errors in computational chemistry modeling. Some of them are of general character, others are typical only for strain energy evaluations. For instance, due to the large number of reference molecules used in the above equations, the errors in zero-point vibrational energy (ZPVE) corrections, which are usually derived from a crude harmonic approximation model, do not effectively cancel.

The choice of a *proper computational method* especially for 'unusual' strained molecules is critical. Computational chemistry estimates the contributions of angular strain well, even at the level of molecular mechanics. Another source of strain, nonbonding attractions/repulsions, is more challenging to compute correctly as only very expensive state-of-the-art computational methods are able to describe them accurately. Popular density functional theory (DFT) methods offer numerous functionals with different empiric exchange-correlation terms. While some of them are especially designed to describe certain types of interactions properly, virtually all of them systematically underestimate or completely neglect weak interactions [86]. DFT methods, such as the most popular B3LYP functional, give rise to various unsystematic errors and, worse, these increase dramatically with the size of the molecules [87, 88]. DFT methods may also exhibit some artifacts like electron self-exchange, which affects the electron energies considerably. Medium-range electron correlation, which contributes to the energies of saturated systems significantly, is poorly described both by local and hybrid functionals [89]. All of the above problems lead to unacceptable DFT errors for unstrained [86, 89] and, especially, strained [88, 90] molecules with more than ten heavy (= non-hydrogen) atoms – *the ones for which DFT methods currently are used most often* [91]. The use of new DFT formulations [92, 93] or a posteriori corrections (MP2 or coupled cluster) together with accurate thermochemical methods (G*n* [94], W*n* [95], or CBS [96]) significantly improves the quality of strain energy evaluations [79]. Nevertheless, most of the computational errors in strain energy evaluations are smaller than the discrepancies resulting from the arbitrary choice of strain-free reference states.

Chemists targeting the preparation of a potentially strained compound are faced with the problem of predicting its stability and reactivity. The 'strain energy per heavy atom’ or ‘per bond’ is a good starting point but it reveals little about the kinetic stability of a molecule. If an appreciable reaction pathway for lowering the potential energy does not exist, the molecule may be stable despite being highly strained. The extraordinary thermal stabilities of prismane and cubane are associated with the feature that breaking just one C–C bond causes only minimal changes in the remaining part of the molecular structure. Stabilization of tetrahedrane with bulky groups, which hinder rearrangements due to the ‘corset effect,’ is another example [97, 98].

Computational chemistry can help predict the behavior of strained compounds, and there are many inspiring examples (for selection see Scheme 1.4). The unusual stability of highly strained [1.1.1]propellane **2** [99–101] (discussed in Section 2.1) protonated pyramidane derivatives **33** [102, 103], and the T_{d}-1,2-dehydro-5,7-adamantanediyl dication **34** [104] first predicted computationally, initiated successful attempts to prepare these highly strained systems.



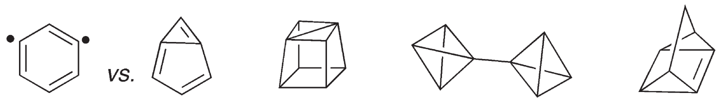
2 **33** **34**

Scheme 1.4 Some highly strained molecules, whose anomalous stability was predicted computationally before preparation.

The prediction of the thermal stabilities of strained compounds is a routine, albeit elaborate, procedure now and involves computations on the barriers of the crucial bond breaking pathway (see, for instance, a recent study on the kinetic stability of tetrahedrane) [98]. As the kinetic stability is a relative value, i.e. it depends on the reaction partner and the conditions, the barriers for the attack of radicals on strained compounds not only allow one to analyze their potential stability, but also to choose a proper reagent for their derivatization. For instance, cubane [105] and octahedrane [66] were found to be highly sensitive to the nature of the attacking radicals and they follow either C–C addition or C–H substitution paths. Computations on the reactions of strained compounds with electrophiles are more difficult, because the carbocationic species that form after primary electrophilic attack are largely prone to rearrangements to release the strain. Even reproducing experimental proton affinities is difficult, especially for a system as strained as cubane [106]. Cyclopropane is an exception because the edge-protonated form is a minimum and the downhill ring-opening path has a relatively high barrier [107].

Highly strained compounds quite often represent intriguing bonding situations, which modern computational methods are able to describe well. They offer not only accurate energies and geometries of strained compounds, but also provide information about electron density distributions, molecular orbitals, bond critical points and so forth [108]. One of the examples is the unusual bonding situation between inverted carbons of [1.1.1]propellane **2**. Twenty years ago theory predicted

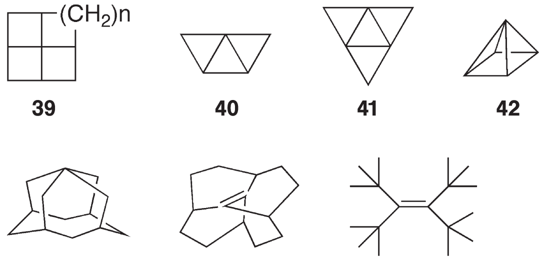
[109] that there is a bond critical point between the central carbon atoms of **2** despite the fact that the electron density does not accumulate in this region. Recent synchrotron experiments on derivatives of **2** confirmed that this remarkable computational description indeed is correct [110]. The examples of *m*-benzyne **35** and *m*-dehydrocubane **36** demonstrate the borderline between proper C–C bonding and open-shell singlet biradical states (Scheme 1.5). The latter is favored for *m*-benzyne if dynamic electron correlation is included exhaustively: the fundamental frequencies of the *m*-benzyne singlet biradical computed at CCSD(T) [111] perfectly agree with the experimental IR spectra [112]. *m*-Dehydrocubane forms a singlet state and is predicted to exhibit an extremely long C–C bond (1.844 Å from REKS-B3LYP/6-31G* data) [113]. Unusually short bonds were found for the dimers of strained compounds. In 1989 the shortest single C–C bond (1.438 Å) was computed [114] for *bis*-tetrahedrane **37**; recently this value was confirmed experimentally [115]. The properties of highly pyramidalized alkenes are difficult to study experimentally as only some matrix IR-spectra are available [116] and computational results are difficult to validate. A real breakthrough in this area was achieved recently when it was found that the computed proton affinities and heats of hydrogenation of 1,5-dehydroquadricyclane **38** agreed well with experiment [117].



35 **36** **37** **38**

Scheme 1.5 Selected strained molecules that represent unusual C–C bonding situations.

Most importantly, computational chemistry can not only predict the properties of molecules, but also help to discover new classes of strained compounds that may challenge experimentalists (Scheme 1.6). Molecules with planar tetracoordinated carbon: fenestranes **39** [118], tricyclo[2.1.0.0^{1,3}]pentane **40** [119, 120], and tetracyclo[3.1.0.0^{1,3}.0^{3,5}]hexane **41** [121]; with inverted geometries around the carbon atoms: pyramidane **42** [122] and bowlane **43** [123]; as well as with highly twisted double bonds: orthogonene **44** [124] and tetra-*t*-butyl ethylene **45** [125],



39 **40** **41** **42**

43 **44** **45**

Scheme 1.6 Highly strained molecules computationally predicted to be isolable.

were computationally predicted to be isolable and thus represent challenging yet realistic synthetic targets.

The development of the chemistry of strained compounds has been closely connected to the progress of computational chemistry for the last three decades. We have finally reached a situation where geometries, electronic and thermodynamic properties as well as the reactivity of highly strained and 'unusual' small molecules may be estimated computationally with chemical accuracy.

1.4
Gallery of Molecules That Could Have Been Included in This Book

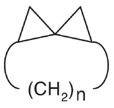
Helena Dodziuk

1.4.1
Introductory Remarks

The aim of this monograph is to present the richness of the domain of hydrocarbons with unusual spatial structure, not only in chemistry but also in their physicochemical properties, and not only in experimental studies but also in model calculations that play an increasingly important role in this domain. Clearly, such a broad scope, to be understood as a protest against the narrow specialization from which we all suffer, could not be fully covered in this limited volume. Thus, for various reasons, not all molecules deserving incorporation in this book could even be mentioned. To counteract this situation, in this chapter several fascinating molecules that have not been presented in other chapters will simply be listed with short notes showing why they are of interest. This is of particular importance since at least some of them merit further, more detailed studies.

1.4.2
Saturated Hydrocarbons

Of the family of bridged spiropentanes **46**, the known [4.1.0.0^{1,6}]tricycloheptane ($n = 2$) **46a** is stable and exhibits a considerable widening of the C2C1C7 angle up to about 160° [126, 127]. There is NMR evidence of [2.1.0.0^{1,3}]tricyclopentane **46b** for which ab initio calculations yielded a pyramidal configuration on the central carbon atom [128, 129]. On the basis of ab initio quantum chemical calculations, QC, exciting tricyclo[3.1.0^{1,3}]hexane **46c** has been found to exhibit almost linear arrangement of the formally Csp^3–Csp^3 bonds with the <C1C2C3 angle value of



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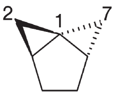
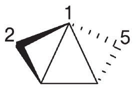
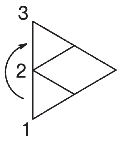


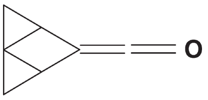
46a



46b



46c



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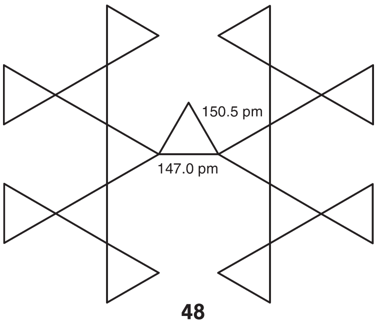
178° [130]. Wiberg and Snoonian [131] reported the synthesis of the derivative **47** observed at 10 K having the highly reactive ketene group. Thus, until now the highly unusual spatial structure of **46c** could not be proven.

One of the largest member of the trangulane family is branched C_{2v}-[15]triangulene **48**. A shortening of the central C–C bond in this molecule has been interpreted in terms of a considerable change in hybridization of the two central spirocarbon atoms due to severe steric strain [132]. Smaller, but also overcrowded, triangulanes also studied by the de Meijere group exhibited some unusual reactivity [133].



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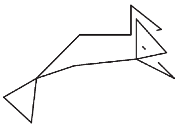
As shown by boat–twist conformation of the central C_6 ring in trispirocyclopropanated cyclohexane **49** [134–136] and by the boat conformation of these rings in tetraasterane **50** [137, 138] discussed in Section 2.3, the cyclohexane ring does not necessarily have to assume the chair conformation.

Recently synthesized octacyclopropylcubane **51** is not very stable: it has a half-life of 3 h at 250 °C and has ‘tremendous overall strain’ of 390 kcal mol^{-1} [139]. In the crystal it exhibits quite rare C_{4h} symmetry. The average length of C–C bonds in the cubane core of 158.3 pm have been found to be slightly but distinctly longer than that in cubane (156.5 pm in the gas phase and 155.1 in the crystal).



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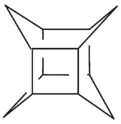

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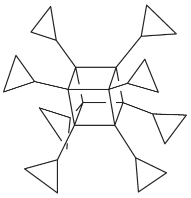

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Three examples of interesting stereochemical and/or structural phenomena will be given at the end of this subchapter.

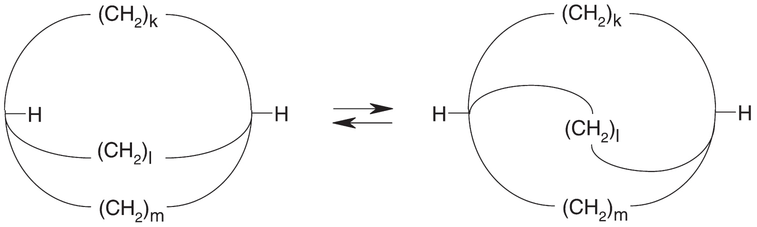
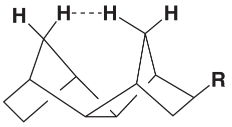


Figure 1.2 Bicyclic hydrocarbons.

A rare but interesting observation, i.e. *in, out* isomerism in bicyclic hydrocarbons (Figure 1.2) [140–142], has also been noticed in several natural products [143]. For larger values of *k*, *l* and *m* the molecules exhibit dynamic equilibrium.

Steric strain may also cause 'squeezing' a molecule leading to a very close distance between the nonbonded atoms. Since X-ray analysis is not the most reliable tool for the determination of H atoms' position, indirect arguments are sometimes used for their estimation as was done for **52** [144].



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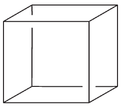
As found for cubane **1** [145] and C_{60} **53**, highly symmetrical structures may exhibit interesting dynamic behavior in the solid state [146, 147]. In the latter case, it also leads to the structural diversity of host–guest and intercalation complexes of the fullerene as studied by X-ray technique [148].

It took more than 20 years to synthesize dodecahedron **54** [149] which, due to its strain, exhibits quite unusual rearrangement reactions. Remarkably, both **53** and **54** are of I_h symmetry, that is every carbon atom (and hydrogen, respectively) in these molecules is identical with the other.



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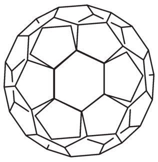

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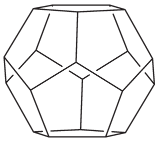

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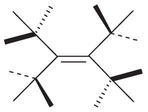
1.4.3
Distorted Double Bonds

A detailed discussion of several routes that were expected to lead to highly strained tetrakis-*t*-butylethene **55** but were unsuccessful is given in detail in Ref. [150].



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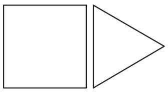
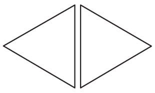
Hypothetical bicyclo[1.1.0]-1(4)-pentene **56a** and bicyclo[1.1.0]-1(3)-butene **56b** remain unknown but according to ab initio calculations such molecules should have considerably pyramidalized formally C_{sp2} carbon atoms [151, 152].

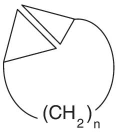


56a



56b

Pyramidalized carbon atoms should be exhibited in known bridged bicyclobutane **57** (*n* = 3) [153–156] and **58** which has probably been observed [157].



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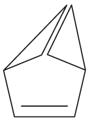
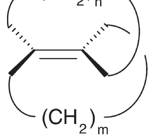


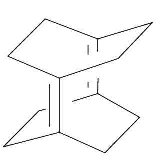
58

The smallest synthesized [*m*][*n*]betweenanene **59** has *m* = *n* = 8 [158, 159]. To the best of our knowledge, no X-ray structure determination exists but simple MM modeling indicates significant distortions from standard geometry [160]. The larger (*m* = 22, *n* = 10) not highly strained betweenanenes have been expected to exhibit interesting dynamic effects involving 'a jumping of the longer chain' around [161].



59

Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene **60** [162] and its tetraaryl-substituted derivative **61** [163, 164], both with strongly pyramidalized C_{sp2} carbon atoms, are known, while diene **62**, also with very close distance between double bonds, is still unknown [165]. Noteworthy, the aromatic rings in **61** are planar.



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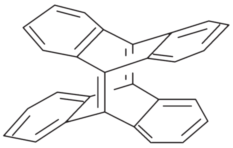

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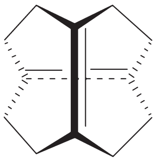
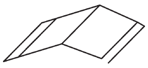


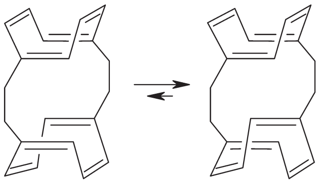
62

The name Dewar benzene of **63** is thought to have no sound basis [166]. The system is stable in the form of its tri-*t*-butyl [167, 168] or hexamethyl [169, 170] derivatives. Although the highly reactive **63** was obtained more than 40 years ago and attracted the attention of several theoreticians [171], the reactivity of this molecule and/or its derivatives is still the subject of studies today [172].



63

Out of two possible **64a** and **64b** diastereomers of [2.2]cyclooctatetraenophane, which are present as a (*d,l*) mixture, the former was synthesized and found to isomerize to the latter [173].

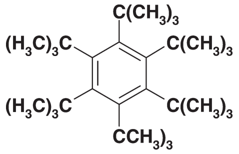


64a **64b**

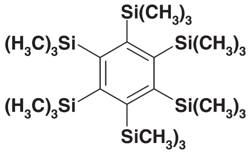
1.4.4

Benzene Rings with Nontypical Spatial Structures

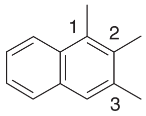
Typical structure of aromatic systems consists in the planarity of the aromatic ring and its substituents and in close to 120° value of all bond angles. Steric hindrance can force another spatial structure. To the best of our knowledge, highly strained hexa-*t*-butylbenzene **65** (X = C) is not known. However, a less strained derivative (due to longer C–Si than C–C bonds), hexakis(trimethylsilyl) derivative **65**, exhibits an unusual distorted chair conformation [174]. Another, less symmetrical type of nonplanar distortion of the aromatic ring is provided by 1,2,3-*tri-t*-butylnaphthalene **66** [175]. Considerable strain in the latter molecule allowed for the freezing of internal rotations of the methyl groups in 1- and 2-positions at 193 K. Interestingly, in disagreement with molecular mechanics [176], modeling the barrier for the rotation of the groups at the 3-position was the smallest. It is also noteworthy that due to its large size, **66** did not form the inclusion complex with γ-cyclodextrin but rather 'sat' on top of the macrocyclic sugar.



65a

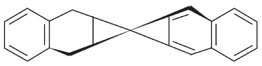


65b



66

Twisted acenes are schematically presented in formula **67** [177]. Additional phenyl groups as in **68** stabilize the molecule and have allowed Pascal to achieve a formidable twist of 144° between the planes of terminal aromatic rings [178]. Interestingly, **68** has been resolved into enantiomers. Such highly twisted aromatic systems can find an application as porous solids. They are also expected to have chiroptical properties and have been incorporated into light emitting diodes (www.cnsi.ucla.edu/arr/paper?paper_id=193298). According to DFT calculations, **68** is a disjointed radical exhibiting exciting electronic structure [179].



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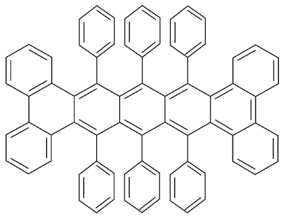
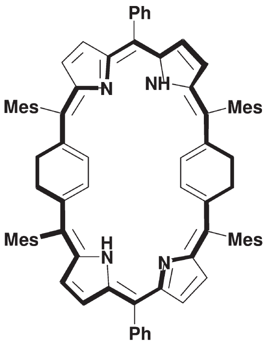
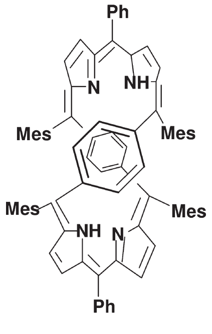


68

Latos–Grazynski group reported the synthesis of di-*p*-benzhexaphyrin that is in dynamic equilibrium of two forms: 'standard' **69a** and **69b** representing a topologically nontrivial Möbius strip [180]. (Other topological nontrivial molecules are presented in Chapter 9.) In the solid state, only the latter was found to exist.



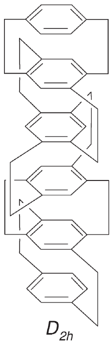
69a



69b

Cyclophanes [181] (covered in Section 4.2) have been studied mainly because of their non-standard structure and a strong π–π interaction between close-lying aromatic rings [182] manifesting itself in UV/Vis [183] and NMR spectra [184].

Syntheses of impressive layered *para*-cyclophanes called cochins having up to six aromatic rings as in **70** and **71** were reported by Otsubo and coworkers [185–187] while those of three isomers of four-layered [2.2]metacyclophanes **72**–**74** were published by Umemoto [188, 189]. In analogy with the smaller [2.2]*meta*-cyclophane **75** discussed in detail in Section 4.2, protons of C–H bonds situated between two bridges exhibit very unusual values of chemical shifts since they lie above (or below) the plane of the neighboring aromatic ring.



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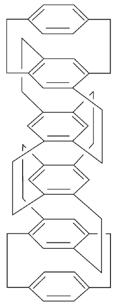

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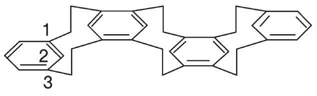

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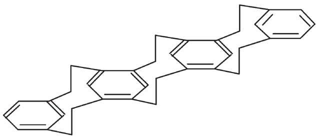

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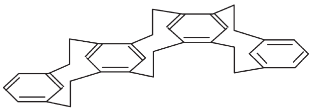

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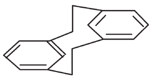
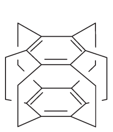


75

In spite of its high strain, superphane **76** [190, 191] is relatively stable, even $[2_6]$(1,2,3,4,5,6)cyclophane-1-ene **77** with an additional double bond has been reported [191]. The benzene C_{sp2} carbon atoms in **76** all lie in the respective planes but its spatial structure is untypical since not all substituents on the aromatic rings lie in the plane of the rings [192]. **78** and **79** still await their syntheses [190].



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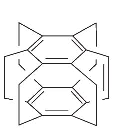

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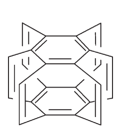

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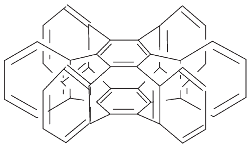
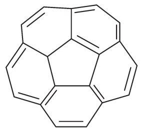


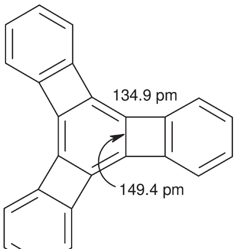
79

Corannulene **80** has the shape of a bowl because it includes a five-membered ring, and is known to invert rapidly [193]. In addition to its nonstandard geometry and dynamic behavior, the molecule attracted a lot of interest since it has been considered as an important building block that should enable the organic chemistry synthesis of C_{60} **53**. Corrannulene derivatives also exhibit interesting packing behavior in the solid state [193]. As discussed in detail in Kawase and Kurata review [194] not only bowl-shaped but also ball- and belt-shaped aromatic systems provide an exciting opportunity to explore the concave–convex π–π interactions by studying their complexation.



80

Another type of revealing distortion in aromatic rings consists in differentiation of their bond lengths achieved by fusing cyclobutane or cyclopentane rings to them, resulting in the remarkable differences in the C–C bond lengths for **81** [195] and **82** [196]. Such systems are indispensable for studying the limits of aromaticity.



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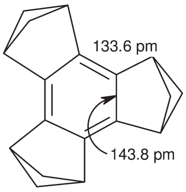
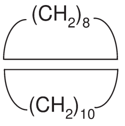


82

1.4.5
Cumulenes

Interestingly, the cumulenes' structure was predicted by van't Hoff [197] who stated that in cumulenes with an even number of double bonds the four substituents must be placed in two perpendicular planes while for the odd-numbered series the substituents must lie in one plane with the double bonds. The cumulenes discussed in Section 3.3 are distorted from such arrangements. No X-ray structure of bicyclic allene **83** [198] and triene **84** [199] have been published but, according to MM modeling, the planes of respective bonds are at angles different from zero and 180° [160]. Similarly, to the best of our knowledge no structural data for hexaene **85** [200] and pentaene **86** [201] have been published but the molecules, with *t*-butyl groups added to increase stability, definitely do not have the standard structure.



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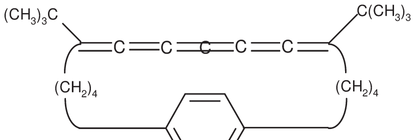

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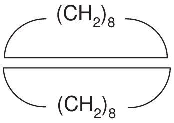

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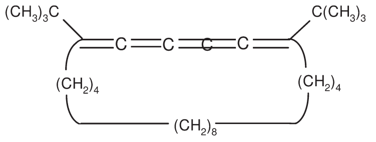
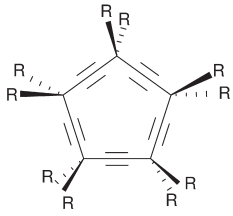


86

1.4.6
Acetylenes

Permethylated [5]pericyclyne **87** (R = Me) and larger analogs are known [202, 203]. Interestingly, in analogy with cyclopentane the central ring in **87** adopts the envelop conformation even in the solid state while model calculations indicate that in permethylated [6]pericyclyne the central ring [204] can adopt either the most stable chair conformation or boat or twist-boat ones. Aromaticity and the role of conjugation in **88** and other analogous carbocycles have been studied by Lepetit [205]. X-ray spectra of an octaphenyl derivative of **89** [206] reveal the planar structure of the bicyclic core with considerable bond angle distortions.



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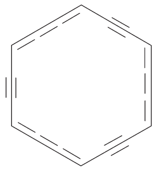
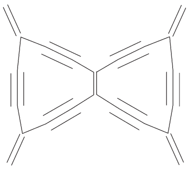
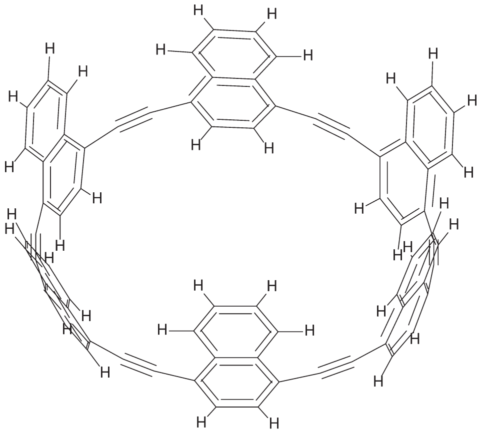


88



89

Only a few of many exciting distorted hydrocarbons could be mentioned in this chapter. It should be stressed, however, that with a new domain of macrocyclic host molecules rapidly developing this area will expand further since not all large macrocycles are strain-free. For instance, **90** can host C_{60} **53** into its cavity assuming C_{6v} symmetry [194, 207].



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