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Organic molecules with abnormal geometric parameters

I V Komarov

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Abstract. Organic molecules, the structural parameters of which (carbon – carbon bond lengths, bond and torsion angles) differ appreciably from the typical most frequently encountered values, are discussed. Using many examples of 'record-breaking' molecules, the limits of structural distortions in carbon compounds and their unusual chemical properties are demonstrated. Particular attention is devoted to strained compounds not yet synthesised whose properties have been predicted using quantum-chemical calculations. Factors that ensure the stability of such compounds are outlined. The bibliography includes 358 references.

I. Introduction

The experimentally determined lengths of carbon – carbon bonds of one type in the molecules of various organic compounds are usually very close. Thus the lengths of single and multiple carbon – carbon bonds usually deviate only slightly (as a rule, by less than 0.01 – 0.02 Å) from the values obtained by averaging over a large number of experimentally determined bond lengths. These values are often referred to as 'typical' or 'standard' geometric parameters. Some standard lengths of carbon – carbon bonds determined by X-ray diffraction analysis are listed in Table 1.[1–4] The same is true, although to a lesser extent (due to the smaller values of the corresponding force constants), for the bond angles the departure of which from the standard values is normally several degrees. The torsion angles usually vary over broader limits than bond angles; however, in some cases, in particular, for fragments with multiple bonds, these angles are also characteristic parameters.

The standard molecular geometric parameters are fundamental values used in stereochemistry.[5] The invariance of these parameters underlies various types of molecular models and various methods for structure calculation, in particular, molecular mechanics methods.[6]

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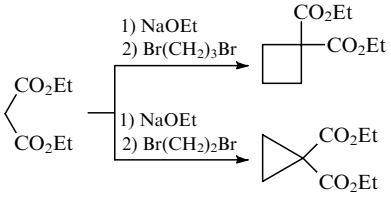
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Table 1. Typical (averaged) lengths of some carbon – carbon bonds.

Type of bond	Length /Å
Single bond	
$C(sp^3)-C(sp^3)$	1.53
$C(sp^3)-C(sp^2)$	1.51
$C(sp^3)-C(sp)$	1.47
$C(sp^2)-C(sp^2)$	1.48
$C(sp)-C(sp)$	1.38
Double bond	
$C(sp^2)=C(sp^2)$	1.32
$C(sp^2)=C(sp)$	1.31
$C(sp)=C(sp)$	1.28
Triple bond [a]	
$C(sp)\equiv C(sp)$	1.186

[a] The data of Ref. 4.

Meanwhile, in the molecules of some compounds, the bond (or torsion) angles and the bond lengths sharply deviate from the typical values. The synthesis of such compounds is often stimulated by a chemist's desire to overstep the limits of the existing theoretical views and concepts. A vivid example is the synthesis of four- and three-membered carbocyclic compounds performed successfully by W H Perkin at the end of the XIX century,[7,8] despite the opinion of scholars of authority in those days who considered the synthesis of small rings to be impossible.[9]



A different tendency has been observed in recent years: one can name a number of compounds with appreciably distorted molecular geometry the successful synthesis of which was pre-

ceded by theoretical predictions of their possible existence and calculations of their spectral properties. In any case, synthesis and study of these compounds were favourable for the accumulation of knowledge on the nature of the chemical bond and mechanistic details for reactions of organic compounds.[10] Research along this line has resulted in the development of new original methods of synthesis and experimental techniques which made an invaluable contribution to modern synthetic organic chemistry.[11,12] The non-trivial syntheses of highly deformed molecules, together with many total syntheses of natural compounds,[13] can be regarded as classical achievements of modern chemical science.

What properties are inherent in substances the molecules of which have highly distorted bond lengths and angles? What is the degree of distortion of the molecular geometry of organic compounds that results in a qualitative (discontinuous) change in their properties? What is the maximum attainable degree of distortion of bond lengths and bond (torsion) angles and do calculations reproduce the observed structural characteristics? In this review, we consider the recent publications concerned with these problems.†

The literature on the synthesis and structural studies of compounds with distorted geometric parameters of molecules is very extensive. This review does not claim to be an exhaustive analysis of all these studies; the author's goal was to illustrate the limits of the possible geometric distortions of organic molecules using a number of interesting examples. Among the vast material, studies devoted to 'record-holder' molecules with the greatest distortions of bond lengths and bond and torsion angles either observed experimentally or calculated are discussed. However, structural chemistry is so rapidly developing that any unusual molecule soon loses the record-breaker title.[18]

The review discusses compounds the molecules of which are stable despite substantial distortions of the molecular geometry. The structures of these compounds are studied by physical methods, most often by X-ray diffraction analysis. Therefore, first, it is pertinent to discuss the specific features of the structures of strained molecules which allow them to reach the stability needed to study them by physical methods.

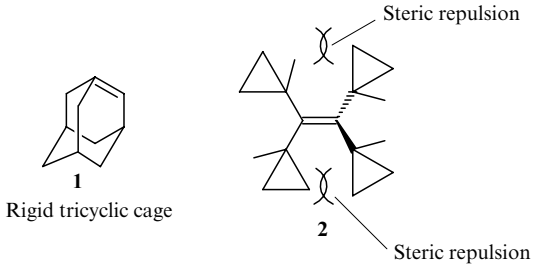
II. Stability of strained molecules

Organic molecules with abnormal geometric parameters possess increased energy. A usual quantitative characteristic of these molecules is strain energy, which is defined as the difference between the experimental standard enthalpy of formation of the molecule and the enthalpy calculated for the 'strainless' (often hypothetical) molecule containing the same number of atoms and the same sequence of bonds between them but no distortion of bond lengths or bond angles and no non-valence intramolecular interactions (for example, steric repulsion).[19] The concept of molecular strain is widely used in chemistry, although it is not exact because the calculation schemes for the enthalpies of formation of strain-free molecules are arbitrary and often different.[20] Therefore, when comparing strain energies, one has to be sure that they have been calculated by the same methods. Normally, calculations involve summation of the strain increments known for the structural fragments present in the molecule.[19]

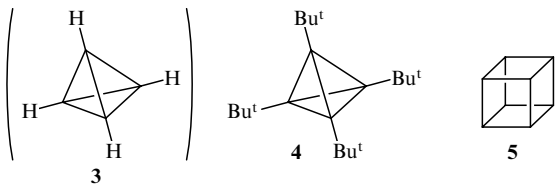
Molecules for which this enthalpy difference is great are referred to as strained. It should be noted that the criteria for regarding one or another structure as strained are quite arbitrary. Even the adamantane molecule with a strain energy of 7.6 kcal mol^{-1} can be regarded as 'strained', although its molecular model seems misleadingly unstrained.[14,15] We shall discuss molecules with strain energies many times exceeding that of adamantane. Such molecules are often reactive and susceptible to intra- and intermolecular reactions which are not typical of strainless analogues. The combination of these properties is associated with the qualitative notion of 'instability', while the factors due to which the chemical transformations of strained molecules can be retarded or entirely avoided are associated with 'stability' of the molecules.

Most highly strained 'record-breaker' compounds known to date exist owing to kinetic stability. Despite the substantial strain energy of the molecules of these compounds, their structures correspond to minima on potential energy surfaces (PES),[21] indicating the possibility of preventing decomposition and relaxation of the geometrically distorted fragments to the unstrained state.

The stability against structural changes that bring a fragment with distorted bonds and angles to the 'normal' state is provided most often by the fact that this fragment is incorporated into a ring or a rigid polycyclic cage. Alternatively, steric repulsion of bulky groups, especially *tert*-butyl substituents, also helps to avoid relaxation of a distorted fragment to an unstrained state.[22] The molecules of compounds **1** and **2** with a twisted double bond can serve as examples of strained molecules having a distorted fragment within a polycycle or bulky groups.



To attain stability of strained molecules, it is necessary to prevent them from entering reactions either with one another (oligomerisation, polymerisation) or with other potential reactants (solvents, oxygen, moisture, *etc.*). These reactions can be prevented by creating steric restrictions around the reaction centres. For example, tetrahedrane **3** is so reactive that it has not been prepared until now, in spite of considerable effort,‡ whereas tetra-*tert*-butyltetrahedrane (**4**), in which the strained C_4 core is shielded, has been isolated and studied, in particular, by X-ray diffraction analysis.



The instability of strained molecules is also related to their tendency to undergo intramolecular rearrangements. Kinetic stability due to electronic factors is an effective method for preventing these rearrangements. A classical example is cubane (**5**) in which the possible rearrangement pathways are forbidden by the orbital symmetry rules. The strain energy of molecule **5** is very high (157 kcal mol^{-1}; determined using data on the heat of

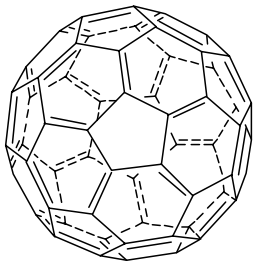
† This review covers studies published before the beginning of 2001. Analysis of publications on this topic up to mid-1970s was carried out by Greenberg and Liebman.[14,15] The publications for this review were collected using the STN electronic databases (Scientific Technical Network,[16] first of all, the REGISTRY database, which contains information on more than 18 000 000 organic and inorganic compounds), *Chemical Abstracts* and *Beilstein* as well as the Cambridge Structural Database (CSDB; the version of April 2001 presents structural information on more than 233 000 compounds).[17]

‡ From here on, the formulae of compounds not obtained experimentally are drawn in parentheses.

combustion of cubane [23]);§ however, cubane does not decompose even at temperatures above the melting point (130–131 °C).[26]

The strain energy of compound **5**, as well as that for other molecules described below, is markedly higher than that required for rupture of the C–C bond. However, the stability of cubane is secured by even distribution of the steric strain over the whole carbon skeleton.

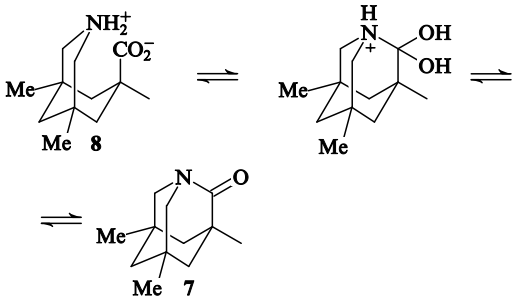
The exceptionally stable C_{60} fullerene (**6**) in the molecule of which strain is uniformly distributed over all the 90 carbon–carbon bonds can serve as yet another example of stable but very strained molecules. The heats of combustion of C_{60} and C_{70} fullerenes and their standard enthalpies of formation, which can be used to estimate the strain energy, have been determined experimentally.[27]



6

In some cases, the concept of thermodynamic stability of strained molecules is discussed but this term is often used improperly. For example, it has been claimed [28] that coordination of a metal atom to a distorted fragment can ensure 'thermodynamic stability' of strained ligands, in particular, *trans*-cycloalkenes. The overlap of molecular π orbitals of a strained alkene with the vacant orbitals of the transition metal and interaction of the occupied *d* orbitals of the metal with the π* orbital of the double bond (dative bond) finally stabilise the complex. However, in our opinion, this is a case of kinetic stability. Thermodynamic stability implies reversible transformations, for example, those between a complex with a ligand containing a distorted structural fragment and a complex with a strain-free analogue of the same ligand. Most transformations of strained molecules are irreversible; therefore, their thermodynamic stability is seldom encountered.

An example is provided by compound **7**, stable in methanol.[29] The driving force of the spontaneous formation of compound **7**, the molecule of which contains a strained twisted amide fragment, in equilibrium with zwitter-ion **8** is the steric strain in the bicyclic system, which decreases upon cyclisation.



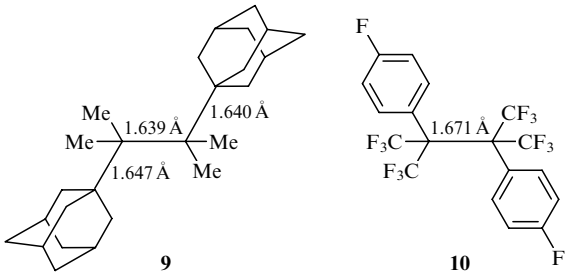
It makes sense to discuss the stability of a compound when conditions for its isolation or investigation are known. For example, a large number of compounds unstable at room temperature have been studied in inert matrices at 4–77 K.[30] Low-temperature isolation in solid matrices of inert gases prevents diffusion and, hence, excludes intermolecular reactions of the compounds under study. Moreover, intramolecular transformations, even those having an energy barrier of only several calories per mole are also retarded.[31]

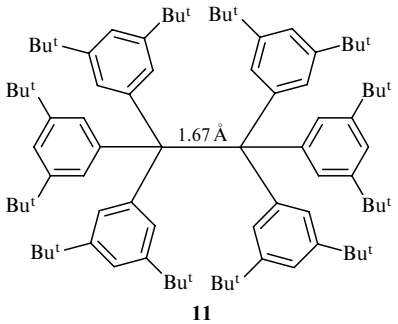
One more method that provides a sufficient (in particular, for spectroscopic studies at room temperature) lifetime of reactive species should also be mentioned, namely, preparation of these species inside cavities of large macromolecules — carcerands and hemicarcerands. In recent years, several studies have been published (see below) devoted to spectroscopic and chemical properties of compounds the isolation and investigation of which at room temperature could not even be discussed before the advent of this method, for example, cyclobutadiene and dehydrobenzene.[32]

III. Abnormally long and short C–C bonds

The characteristic lengths of C–C, C=C and C≡C bonds (see Table 1) can be regarded as fundamental parameters in chemistry. Deviations from 'normal' values are seldom encountered, and they serve as an indicator for the occurrence of steric or electronic effects.

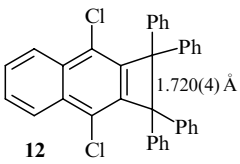
The quest for the longest $C(sp^3)-C(sp^3)$ bond has been called a 'real Odyssey.' [33] Considerable attention was devoted to hexaalkyl- and hexaarylethanes such as **9**–**11**,[34–36] in the molecules of which the central C–C bond is longer than 1.64 Å.

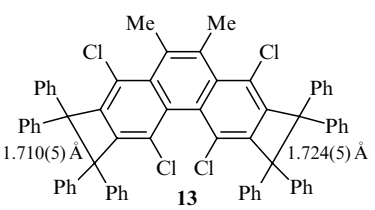




The main cause for bond elongation is steric repulsion between bulky groups. The elongated bonds are weakened, which accounts for the thermal instability of these hydrocarbons.[34] In the case of compound **9**, molecular mechanics (MM2) calculations¶ for the molecular geometry were carried out and good agreement between experimental and calculated values was obtained.

In 1996, Toda *et al.*[37] have reported exceptionally long C–C bonds in two benzocyclobutane derivatives, **12** (1.720 Å) and **13** (1.710 and 1.724 Å).

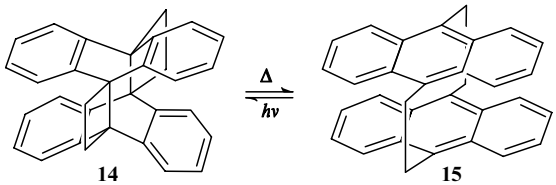




§ These data are somewhat outdated; however, more precise values have not yet been reported. The strain energy of the cubane molecule presented here is consistent with rough values determined from the heats of combustion of various cubane derivatives and with calculated values.[24, 25]

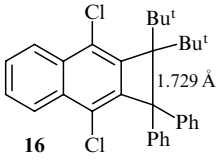
¶ Most of the calculation methods mentioned in the review are described in a book by Jensen.[21]

These values are almost 0.18 Å greater than the standard length of a single carbon–carbon bond; therefore, it is not surprising that some doubts have been cast upon the X-ray diffraction data published. Before the study by Toda *et al.*,[37] examples of compounds with even longer C–C bonds had been reported; however, a thorough verification showed the results of structural studies of these compounds to be incorrect. Thus the lengths of the central bonds in the molecule of compound **14**, a photoisomer of [2.2]tetrabenzoparacyclophane **15**, have been reported [38] to be 1.77 Å. Later, it was found that the measurements were carried out for a mixture of the photoisomers **14** and **15** rather than for a crystal of pure **14**.[39] In subsequent studies of a pure sample of **14** at 170 K, the lengths of the central bonds were found to be 1.648 Å.[40]



14 **15**

Repeated studies [41] of the compound **12** have confirmed, nevertheless, the validity of the previously obtained data,[37] and quantum-chemical calculations (B3LYP/6-31G*) reproduced them satisfactorily.[42] Model calculations [B3LYP/DZ(2d,p)] for the 1,1,2,2-tetraphenylbenzocyclobutene molecule also provided a Ph_2C-CPh_2 bond length consistent with the value found experimentally [37] in compound **12**. These calculations demonstrated the importance of taking into account the electron correlation in order to obtain correct values for geometric parameters of the strained molecules. It was also shown [41] that satisfactory interpretation of the observed elongation of the C–C bond requires that only steric effects (repulsion between bulky groups) be taken into account without considering hyperconjugation effects.[43] This conclusion is also confirmed by recently published data on the synthesis and X-ray diffraction analysis of the even more sterically hindered compound **16**.[44,45] The C–C bond length in the four-membered ring of **16** equals 1.729 Å, *i.e.*, it is longer than those in the molecules **12** and **13**.

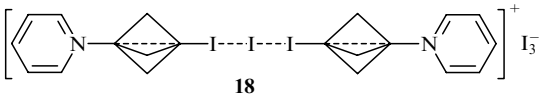


16

The distance between the carbon atoms formally not bound to each other in bicyclo[1.1.1]pentane (**17**) and its derivatives is close to the lengths of the 'stretched' C–C bonds given above. The C(1)–C(3) distance in this simple hydrocarbon measured by electron diffraction [46] is 1.874 Å (or 1.845 Å according to another publication [47]). The search through the CSDB for the shortest C(1)–C(3) distance among the bicyclo[1.1.1]pentane derivatives gave a value of 1.80 Å in bis(3-iodobicyclo[1.1.1]pentan-1-ylpyridinium)iodide triiodide **18**.[48] In this case, the X-ray diffraction data can best be interpreted by assuming that structures containing [1.1.1]propellane contribute to the resonance hybrid. In the molecules of bicyclo[1.1.1]pentane derivatives, the non-bonded bridging carbon atoms are so close to each other that the 'through-space' electronic interaction is clearly identified.[49]



17

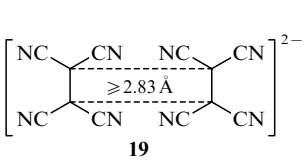


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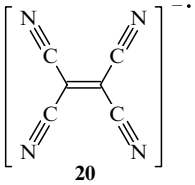
The above-mentioned studies raise the question of what is the longest distance between carbon atoms in a molecule that enable the existence of a chemical bond between them.

Proceeding from the empirical definition of the chemical bond † proposed by Pauling [50] without restricting the consideration to saturated systems, one can find examples of structures with formal C–C bonds longer than 1.729 Å, which is the value established for molecule **16**.

For example, a distance between carbon atoms equal to 2.83 Å has been found recently in the crystal of dimer **19**, formed by two tetracyanoethylene radical anions (**20**). Nevertheless, the results of structural, magnetic, and spectroscopic studies are consistent with the existence of a chemical bond between them.[51] This two-electron four-centre bond results from the π–π binding interaction between the radical anions **20** and the Coulomb repulsion between them. It was shown that the dimers are metastable species, *i.e.*, their formation is an endothermic process; in the solid phase, they can be stabilised upon interaction with metal cations.



19



20

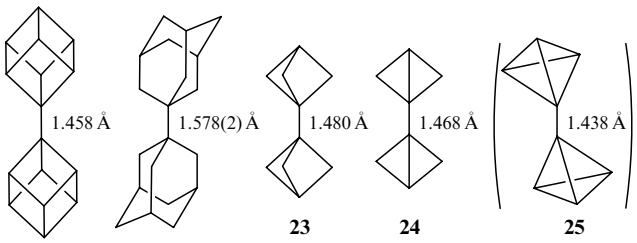
Apparently, it is impossible to establish the limiting bond length of any type on the basis of merely geometric criteria such as 'longer (or shorter) than..'; it is necessary to invoke conceptual models of chemical binding including new ones. Some new approaches to the determination of the nature of the chemical bond could be provided by Bader's theory.[52] This theory is based on the mathematical analysis of topological characteristics of the total molecular electron density function either found experimentally or calculated. In terms of this theory, it is possible to give strict criteria for the occurrence of a bonding interaction between a pair of atoms, irrespective of the distance between them.

A number of studies have been devoted to the search for strained molecules with short carbon – carbon single bonds. For example, the length of the exocyclic bond in bicubane **21** was found to be 1.458 Å,[53] which was explained by rehybridisation of the carbon orbitals. The exocyclic bonds in cubane have a greater *s*-character and, therefore, they are shorter than the standard $C(sp^3)-C(sp^3)$ bonds. The steric strain that could result in elongation of the central C–C bond in compound **21** is insignificant, unlike that in the molecule of 1,1′-biadamantane **22** (the length of the central bond in **22** is 1.578 Å [54]).

The central bond in bicubane can be compared with that in butadiene, the length of which is 1.383 Å, according to electron diffraction data;[55] however, in the latter compound, this bond is further shortened due to conjugation.

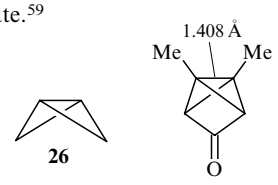
Schleyer and Bremer [56] not only compared the experimental and calculated (MNDO, MP2/3-21G, 6-31G*) lengths of the central bonds in molecules **23**–**25**, similar to the bicubane molecule, but also carried out model calculations for ethane (MP2/3-21G) with variation of the C–C–H bond angle. It was shown that an increase in this angle to 150° entails energy redistribution between molecular orbitals, resulting in strengthening of the C–C bond. The calculated (MP2/6-31G*) length of the C–C central bond in bitetrahedrane **25** is 1.438 Å. The compound **25** has not yet been synthesised; however, Ermer *et al.*[57] believe that the hexa-*tert*-butyl derivative of this compound could be prepared.

† According to Pauling, '... there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species.'



21 **22** **23** **24** **25**

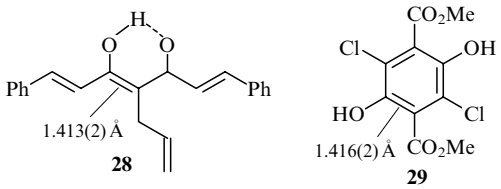
The angle strain in the cyclopropane molecule is known to result in shortening of the formally single C–C bonds (1.499 Å).[58] In the bicyclobutane (**26**) molecule, which is the smallest one among the molecules of bicyclic hydrocarbons, two cyclopropane rings are fused; the central C–C bond exhibits properties of the double bond (for example, electrophilic reagents readily add at this bond to give cyclobutane derivatives) and is abnormally short (1.497 Å). X-Ray diffraction study of bicyclobutane derivatives showed that the length of the central bond depends on the angle between the planes of the three-membered rings. In the compound **26**, this angle is ~122.7°, while in its derivatives **27**, this angle is much smaller (~87°) and the C(1)–C(3) bond is much shortened (1.408 Å), *i.e.*, this is one of the shortest single bonds known to date.[59]



26 **27**

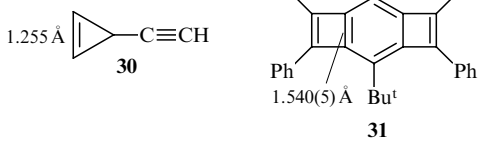
IV. Elongated and shortened C=C bonds

Analysis of the structures deposited in the CSDB shows that abnormally long formally double C=C bonds are found in systems containing long chains of conjugation (see, for example, compound **28**).[60] In aromatic derivatives (see, for example, compound **29**),[61] the C=C bonds can also be elongated. The shortest formally double carbon – carbon bonds have been found in a number of strained molecules (for example, in molecule **30**).[62] Exceptionally long carbon – carbon double bonds have also been found in twisted alkenes. The elongation of these bonds is due to a decrease in the degree of π-bonding.



28 **29**

Let us consider the compounds the molecules of which incorporate the shortest (**30**) and the longest (**31**)[63] C(sp^2)=C(sp^2) bonds known to date.

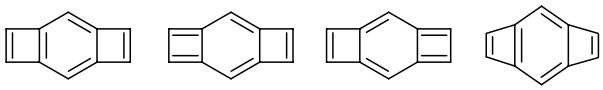


30

31

The length of the double bond in ethynylcyclopropene **30** is approximately an average between the bond lengths found in strain-free alkene and alkyne molecules — 1.255 Å. Even very high-level calculations provide overestimated lengths for the C=C bond in this molecule.[62]

Ab initio (HF/3-21G, 6-31G*) calculations for benzo[1,2:4,5]-dicyclobutene **32** predicted[64] two types of isomerism, one type being due to different bond lengths (**32a** and **32b**, **32c**) and the other type being due to different positions of the double bonds (**32b** and **32c**). X-Ray diffraction analysis[63] of the compound **31** did not confirm the results of calculations reported earlier.[64] The structural parameters found experimentally for **31** and those determined by quantum-chemical calculations for the hydrocarbon **32** (B3LYP/6-31G*, MP2/6-31G*) correspond to the structure **32d** with elongated bonds in the benzene ring. However, it should be emphasised that in this case, we are dealing with aromatic bonds rather than purely double bonds (as in alkenes).



32a **32b** **32c** **32d**

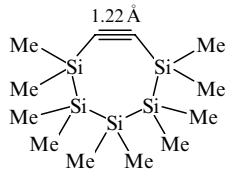
V. Variations of the triple carbon – carbon bond lengths in organic compounds

The deviations of the lengths of triple carbon – carbon bonds in organic compounds from typical values are less pronounced than similar deviations in the case of single or double bonds. For example, according to analysis of the CSDB data,[4] the difference in the C≡C bond lengths in acetylene and its alkyl derivatives is less than 0.05 Å.

It is noteworthy that triple bond lengths determined by electron or neutron diffraction are often greater than those found by the conventional X-ray diffraction technique for the same compound (the difference can reach 0.02 Å or even more). This is due to the fact that X-rays are scattered by the electron density of the object and the electron density maxima (centroids) identified as 'atoms' in the X-ray diffraction method do not always coincide with the positions of the atomic nuclei. The electron density maxima can be displaced towards each other in the case of high concentration of the electron density in the interatomic space, which is often the case for multiple bonds including triple bonds. However, in modern X-ray diffraction software packages, this effect can easily be taken into account. Nevertheless, statistic analysis covering only those parameters in the CSDB which have been determined by electron diffraction in the gas phase results in an even smaller scatter of the C≡C bond lengths, namely, 0.012 Å.[4]

As a rule, elongation or shortening of triple bonds is mainly due to electronic factors. For example, this bond is shorter in the molecules of acetylene derivatives containing electron-withdrawing substituents at the triple bond.[65] (Note that this is equally true for double carbon – carbon bonds.) Elongated C≡C bonds have been found in conjugated systems, for example, in butadiyne[55] [1.2176(6) Å], although the lengths of these bonds in vinylacetylene and propynal molecules exceed only slightly the average value. The steric factors in linear alkynes in which substituents at the C≡C bond are far from each other are minimised.

It can be suggested that the loss of π-bonding caused by bending of the X–C≡C–X fragment (X is any substituent) in cycloalkynes would result in elongation of the triple bond. Nevertheless, in most of the known strained molecules of cycloalkynes, the length of the triple bond is close to the typical value. For example, in compound **33**, despite the substantial bending of the Si–C≡C–Si fragment, the C≡C bond length is equal to 1.22 Å, which virtually coincides with the average value (1.201 Å) for silyl-substituted alkynes.[66]



33

VI. Distortions of bond angles at the tetrahedral carbon atom

The modern theory of the structure of carbon compounds is underlain by the hypothesis advanced independently by Van't Hoff [67] and LeBel [68] in 1874 stating that a tetracoordinated carbon atom has a tetrahedral or a nearly tetrahedral configuration. Later, the results of numerous studies including X-ray diffraction analysis have confirmed Van't Hoff's and LeBel's hypothesis based on empirical data, and the sp^3-hybridisation concept has explained simply and conveniently the stability of the tetrahedral configuration. However, as soon as somewhat more than a decade after the publication,[67, 68] Baeyer, who considered distortions of the tetrahedral configuration of the carbon atom, stated the foundations of strain theory.[69]

The types of distortion of bond angles at the sp^3-hybridised carbon atom are illustrated in Fig. 1. First of all, this is a decrease/increase in one bond angle (the angle between the other two bonds usually correspondingly increases/decreases; this is the so-called scissors distortion) as well as distortions leading to flattening of the carbon configuration, *i.e.*, tetrahedral compression and digonal twist. Special mention should be made of configurations in which all atoms attached to a given carbon atom are located on one side of the plane passing through it, namely, inverted and pyramidal configurations to which an umbrella-type distortion leads. Rigorous mathematical analysis of the disortions of the CX_4 fragment has been reported.[70–72]

It should be noted that in experimental or theoretical study of the electron density distribution in the molecules characterised by highly distorted bond angles at carbon atoms, the regions of increased electron density between the atoms ‡ do not lie on the straight lines connecting the atomic nuclei but are displaced from these lines. These bonds have been referred to as curved (banana) bonds; a classic example of these bonds is found in the cyclopropane molecule. The displacement of the maxima of DED (covalent electron density) outwards the ring in cyclopropane derivatives reaches 0.2 Å or more. An even greater shift of the DED maxima away from the internuclear lines, up to 0.5 Å, was found in tetrahedrane derivatives. Banana bonds are found not only in the molecules with small rings but also in highly strained cage systems.[74]

Subsequently, in particular in the analysis of structural data for cyclic and strained cage molecules, the notion of bond path was defined as the interatomic line along which the total electron density is a maximum relative to any 'lateral' displacement and has a minimum in the so-called saddle point.[52, 73–75] A bond path is not necessarily a straight line; the presence of this line implies a chemical bond between the given atoms.[76] These and some other definitions constitute the foundation of the modern quantum theory of interatomic interactions and chemical bonding, developed by Bader.[52]

In Bader's theory, the bond path angle at an atom is determined by the angle between the tangents to two neighbouring bond paths. In strained molecules, the bond paths are curved, as indicated above. In particular, in a cyclopropane molecule, the bond path angle is ~78.8° rather than 60°, which has been confirmed by a number of X-ray diffraction studies of the electron density distribution in this type of system. Therefore, in the case of strained molecules, it would be more appropriate to discuss the bond path angles.

‡ Normally, this is so-called deformation electron density (DED), which characterises the difference between the electron density of the molecule and that calculated as a sum of the electron densities of isolated spherical atoms located at the same distance from each other.[73]

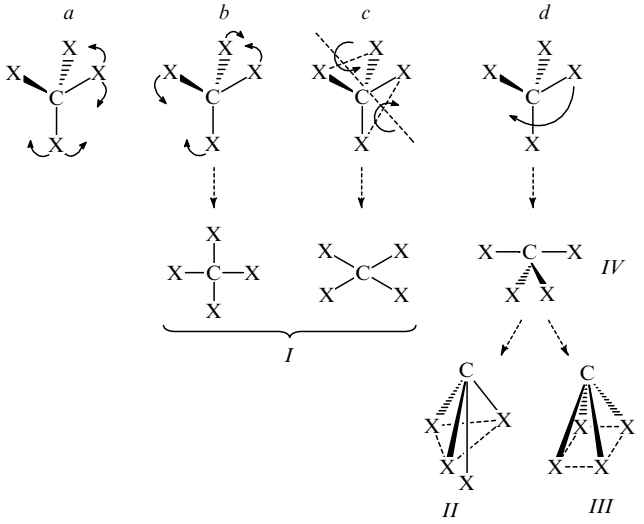


Figure 1. Distortions of bond angles at the tetrahedral carbon atom: scissors (*a*), tetrahedral compression (*b*), digonal twist (*c*), umbrella (*d*). Carbon atom configuration: (*I*) planar, (*II*) inverted, (*III*) pyramidal, (*IV*) intermediate between the tetrahedral and pyramidal.

A number of publications have been devoted to the study of electron density distribution in organic molecules. In these studies, the term 'bond angle' is used to imply the angle between the bond paths and not between the straight lines connecting the atomic nuclei. However, the vast majority of structural studies discuss the angles between the internuclear straight lines. Therefore, in this review, we also consider the latter type of angle unless otherwise indicated.

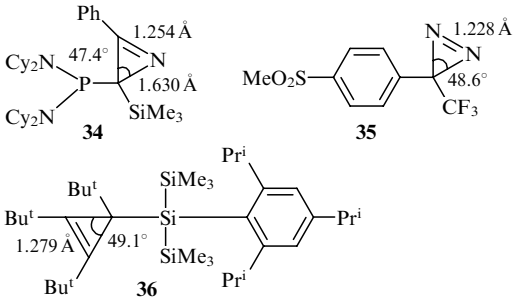
It should be noted that the Bader's topological approach and definition, in terms of its rigorous theory, of the bond path and some other key concepts of the molecular structure theory are drawing increasing attention of researchers. In particular, the classical term 'bond length' (the distance between the nuclei) is replaced in this theory by the notion of 'bond path length.' In the case of a strained molecule, the bond path length would naturally be longer than the internuclear distance. For example, in the cyclopropane molecule, the distance between the carbon nuclei (bond length) is 1.499 Å,[77] and the bond path length between them is ~1.53 Å, *i.e.*, it is nearly equal to the typical C–C bond length (see Table 1). An even greater inconsistency between the internuclear distances and the bond path lengths is found for cage systems, in particular, for icosahedral carboranes.[78]

1. Scissors type distortion: a decrease in the C–C–C bond angle

A considerable decrease in the C–C–C bond angle is found in molecules of cyclic compounds with small rings. A lot of information on the methods of synthesis and properties of these compounds has been accumulated to date. Many fundamental theoretical concepts, for example, the concept of steric strain and banana bonds, have been developed upon investigations of molecules with three- or four-membered carbocycles.[14, 26, 79–81] We shall consider several prominent examples of research along this line.

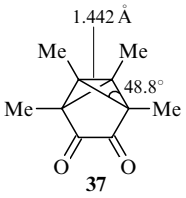
In the CSDB, we found eighteen structures with a bond angle at a saturated carbon atom smaller than 50°. The molecules of these compounds contain three-membered rings, and most of them contain multiple bonds in the rings. The smallest A–C–A angles (A is any atom) are typical of compounds with C=N and

N=N bonds in the three-membered rings. In compounds **34**[82] and **35**,[83] the angle at the saturated carbon atom is somewhat smaller than that in cyclopropene derivatives (for example, in compound **36**).[84] This is due to the fact that the C=N or N=N double bonds are shorter than the C=C bond, and the C−N single bonds are longer than the C−C bonds in cyclopropane (the C−C bond length in cyclopropane is 1.499 Å).[77] Both factors result in a decrease in the angle between the single bonds in unsaturated three-membered heterocycles.



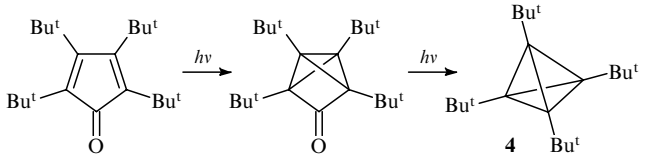
Cy is cyclohexyl.

Among the compounds containing saturated three-membered carbon rings with reduced C−C−C angles, bicyclobutane derivative **37** should be mentioned.[85] In the molecule of this compound, the bond between the bridging carbon atoms is shortened and, therefore, the opposing C−C−C angle in the three-membered rings is reduced.



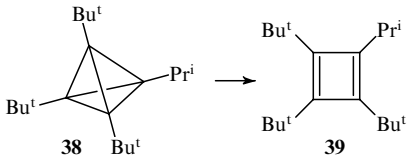
Compounds with reduced bond angles at saturated carbon atoms exhibit unusual reactivity due to the strain in their molecules. As an example, we shall consider derivatives of a hydrocarbon which has not yet been synthesised, tetrahedrane **3**.

Ab initio quantum-chemical calculations of different levels (SCF/4-31G,[86] G2 [87]) give a strain energy of 129–137 kcal mol^{-1} for the unsubstituted tetrahedrane molecule. This value is greater than the dissociation energy of a single C−C bond (72–117 kcal mol^{-1})[88] and exceeds (in relation to one carbon atom) the molecular strain in other hydrocarbons studied to date. It is not surprising that numerous early attempts to synthesise tetrahedrane and its derivatives have failed.[14, 89, 90] Only in 1978, did Maier *et al.*[91] synthesise the first tetrahedrane derivative, tetra-*tert*-butyltetrahedrane **4**, by photochemical transformations of tetra-*tert*-butylcyclopentadienone.



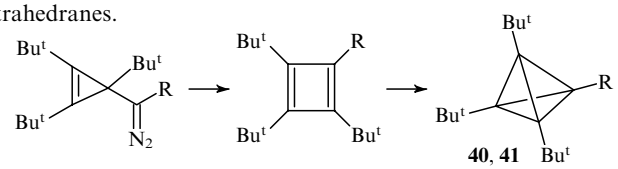
The seeming simplicity of the reaction scheme conceals great efforts of researchers aimed at selecting the optimal conditions for the preparation of a compound the possibility of isolation of which seemed unlikely at that time. The compound **4** is a stable crystalline substance isomerising into tetra-*tert*-butylcyclobutadiene only at 130 °C. Stability is attained owing to the presence of bulky *tert*-butyl substituents, which ensure the steric shielding (so-called 'corset effect') of the central strained fragment of the molecule by shielding it from the attack by reagents and preventing intramolecular rearrangements. The *tert*-butyl groups in the molecule **4** are remote from each other as far as possible but in the transformations of compound **4**, they approach each other, which results inevitably in an increase in the strain energy.

Tri-*tert*-butylisopropyltetrahedrane (**38**) proved to be much less stable than the compound **4**: its thermal isomerisation to cyclobutadiene **39** proceeds over several minutes at 80 °C.[92]



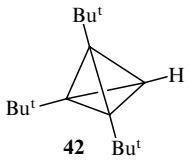
For a long period, researchers did not succeed in preparing other tetrahedrane derivatives.

It was another 10 years after the synthesis of **4** before a new derivative was prepared; this was tri-*tert*-butyl(trimethylsilyl)tetrahedrane (**40**).[93, 94] The approach to substituted cyclopropenyldiazomethane proposed by Masamune *et al.*[95] permitted Maier and co-workers to prepare other silyl- [96] and alkyl-substituted [92] tetrahedranes.



R = $SiMe_3$ (**40**), $SiMe_2OPr^i$ (**41**).

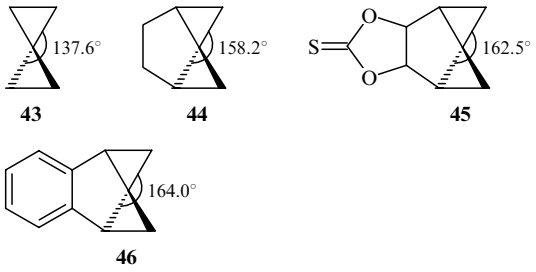
The reaction of compound **41** with the fluoride ion affords highly reactive trisubstituted tetrahedrane **42**.[96]



X-Ray diffraction data for the compound **4** showed that the C−C bond length in it (1.485 Å)[97] is shorter than the typical value (1.53 Å) and is even shorter than the C−C bond length in cyclopropane (1.499 Å).[77] This is due to rehybridisation of the cage atoms and bond bending. Early molecular mechanics calculations (MM2) showed that, due to the steric repulsion of the *tert*-butyl groups, the chiral structure (group of symmetry T) is energetically more favourable (by 2–6 kcal mol^{-1}) than the achiral structure (T_d).[98] This conclusion was confirmed by *ab initio* quantum-chemical calculations [B3LYP/6-311+G(d)//B3LYP/6-31G(d)].[99] The difference between the energies of these forms was 0.5–2.0 kcal mol^{-1}. The chemical properties of the compound **4** have also been studied. Besides the above-mentioned thermal rearrangement of the substituted tetrahedrane **4** into tetra-*tert*-butylcyclobutadiene, protonation with gaseous HCl and oxidation into the corresponding radical cation are known.[100]

2. Scissors type distortion: an increase in the C−C−C bond angle

Increased bond angles in the molecules with tetrahedral carbon atoms are observed, naturally, in the same cases where substantially reduced bond angles are found. For example, in the tetra-*tert*-butyltetrahedrane molecule discussed in the preceding Section, the angles between the exocyclic bonds and the bonds in the tetrahedral cage are 144.7 °, according to X-ray diffraction data.[97] A search through the CSDB provided examples of structures with even larger C−C−C angles. The vast majority of these compounds are spiropentane (**43**) or bicyclobutane (**26**) derivatives. According to X-ray diffraction analysis, the bond angles at the spiro carbon atom in the spiropentane molecule amount to 137.6 ° and 136.7 °.[101] The largest C−C−C bond angles were found in bridged derivatives of **43** — molecules **44**–**46** (the greater of the two increased bond angles is given for each molecule).[102]

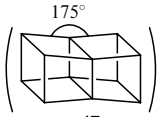


43 **44** **45**

46

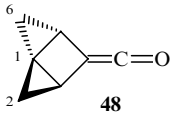
Analysis of DED maps for spiropentane and its derivatives has been carried out.[101] In all cases, substantial exocyclic dispacement of DED maxima in the planes of the three-membered rings was found.

An increase in one bond angle at the tetracoordinated carbon atom to 180° would result in a configuration intermediate between the tetrahedral and pyramidal ones (see Fig. 1 *d*). The carbon atoms in dicubane **47** may have a similar configuration. The possibility of synthesis of dicubane has been discussed.[103] The C−C−C bond angle in this molecule was calculated to be ~175°.



47

According to calculations (MP2/6-31-G*, HF/6-31G*),[104] a carbon configuration with a C(2)−C(1)−C(6) angle of ~180° is also possible in the molecule of compound **48**.



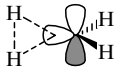
48

This highly reactive tricyclo[3.1.0.0^{1,3}]hexane derivative was detected by IR spectroscopy in an inert matrix at 15 K.[105]

3. Planar configuration of a tetracoordinated carbon atom

In recent years, researchers have devoted particular attention to types of distortion such as tetrahedral compression and digonal twist, resulting in a flattened CX_4 fragment.[106–110]

The search for compounds with such an unusual structure was stimulated by a publication by Hoffmann *et al.*,[111] in which the molecular orbitals in a hypothetical planar methane molecule were analysed and suggestions were made about possible ways of stabilisation of the planar configuration of carbon. According to qualitative analysis of the electronic structure of the planar methane molecule, the carbon atom in this molecule should be sp^2-hybridised. This atom should have two electrons in a non-hybridised *p* orbital and should form two two-electron two-centre C−H bonds and one two-electron three-centre H···C···H bond.



The strain energy of this molecule substantially exceeds the C−H bond dissociation energy; the energy difference (MP2/6-31-G*//6-31G*) between the tetrahedral (T_d) and planar (D_{4h}) methane configurations amounts to 159.7 kcal mol^{-1}. The possibility of existence of the planar structure, even as the transition state in the methane inversion, has been called in question.[112] Calculations[113] [MCSCF/6-31G(d,p), 6-31+G(d,p), TZV++G(d,p)] showed that the planar structure with D_{4h} symmetry does not match any minimum on the PES, whereas the planar structure with C_s symmetry corresponds to a saddle point on the PES. A molecule with this symmetry could represent a transition state formed in the methane inversion: its energy is almost 40 kcal mol^{-1} lower than the energy of the molecule with D_{4h} symmetry (nevertheless, its strain energy is still greater than the energy of C−H bond rupture by 7 kcal mol^{-1}). The same conclusion has also been drawn by other researchers,[114] who used extended basis sets [6-311+G(3df,2p), 6-311G*] to analyse the problem of methane inversion.

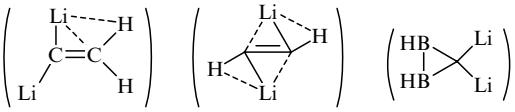
Hoffmann *et al.*[111] were the first to consider stabilisation factors of a planar configuration of the formally tetracoordinated carbon atom. One of these factors is electronic stabilisation caused by substituents exhibiting σ-donor and/or π-acceptor properties; the former provide the deficient σ-electron density, while the latter delocalise the increased π-electron density. Delocalisation of the lone electron density of the carbon atom with a planar configuration in the $(4n+2\pi)$-system should also facilitate stabilisation.

The idea of electronic stabilisation has been further extended by Schleyer and coworkers,[115] who found by RHF/STO-3G calculations that the energy of 1,1-dilithiocyclopropane molecule with a planar carbon (**49a**) is lower by 7 kcal mol^{-1} than the energy of the corresponding molecule with the tetrahedral carbon configuration (**49b**).



49a **49b**

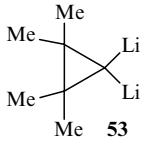
Later, Sorger and Schleyer[110] made calculations for a number of molecules that may have a planar configuration of a tetracaroordinated carbon atom stabilised by σ-donor and/or π-acceptor substituents. These include, for example, 1,1- and 1,2-dilithioethylenes (**50** and **51**, respectively) and 3,3-dilithio-1,2-diboracyclopropane (**52**).



50 **51** **52**

According to calculations (B3LYP/6-31G*), for the last-mentioned compound, the energy of the molecule with a planar carbon configuration is 18.7 kcal mol^{-1} lower than that in the case of tetrahedral configuration.

1,1-Dilithio-2,2,3,3-tetramethylcyclopropane (**53**) has been synthesised;[116] however, its structure has not been determined. The structural studies for this type of compound are complicated by the high degree of aggregation.



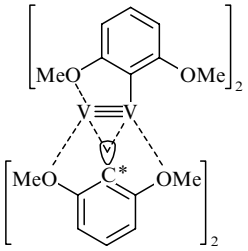
53

Spectroscopic detection of the $[CAl_4]^{2-}$ dianion has been reported.[117] It was suggested that the planar (according to B3LYP/6-311+G* calculations) $[CAl_4]^{2-}$ dianion can be stabilised in the solid phase by an appropriate counter-ion, for example, Na^+.

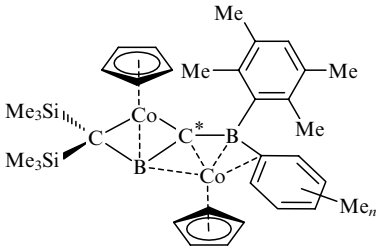
Organometallic compounds of transition metals the molecules of which contain a tetracoordinated carbon atom with a planar configuration are also known. Complex **54** was the first crystallographically characterised compound of this type.

It is of interest that only two years after the publication of the paper by Cotton and Millar[118] reporting the structural data for complex **54**, Keese *et al.*[119] noticed the unusual planar environment of the carbon atom (marked by an asterisk) in this compound. Quite a few other complexes of this type are also known;[107] however, the mechanisms of stabilisation of the planar configuration of the carbon atom in them are different.[108] In most of the molecules, the carbon atom under interest is a part of an unsaturated (often, aromatic) system, which is an additional stabilising factor. Molecules in which a tetracoordinated carbon

atom with a sum of bond angles equal to ~360° is stabilised only by σ-donor and π-acceptor substituents (as has initially been suggested for planar methane analogues) are found rather rarely; among them, compounds **55**, **56** were the first to be characterised and studied [108] (the carbon atom having a planar configuration is marked by an asterisk).



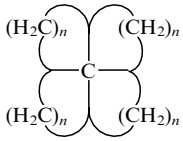
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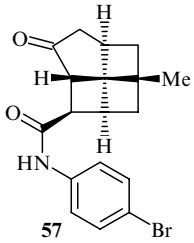
n = 4 (**55**), 3 (**56**)

Stabilisation of a planar methane molecule can be attained by oxidation to give a mono- or di-cation. As shown by calculations [ST4CCD/6-311 + G(2df,2p)],[120] the carbon atom in CH_4^{2+} has a planar environment (the symmetry group is C_{2v} rather than D_{4h}). This cation has been detected experimentally in mass spectra.[121]

The attempts to synthesise compounds in which the carbon atom with a planar configuration would be embedded into a rigid carbon cage have not yet been crowned with success. Hoffmann *et al.*[111] suggested that this type of carbon atom could exist in [*n.n.n.n*]fenestranes



Numerous studies have been devoted to the synthesis of fenestranes; elegant strategies for their synthesis have been developed.[106] However, fenestranes with *trans*-fused five- and four-membered rings (the case in which the greatest distortions of the bond angles at the central carbon atom are expected) have not yet been obtained. Of the fenestranes studied by X-ray diffraction analysis, the greatest distortion has been found in the molecule of [4.4.4.5]fenestrane derivative **57**,[122] in which the opposing bond angles at the central carbon atom are 128° and 129°.

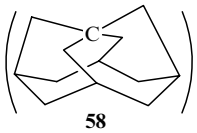


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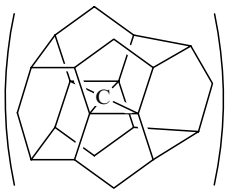
A highly distorted tetrahedral, although still not perfectly planar, configuration of the central carbon atom is also expected in the hypothetical structure **58**, which was called bowlane; initially, a pyramidal configuration of the central carbon atom was suggested for this compound.[123]

Ab initio calculations (HF/6-31G*) have shown [124] that the bowlane molecule should have C_{2v} symmetry and a distorted tetrahedral configuration of the central carbon atom with maximum sizes of the opposing angles at this atom of 170.9° and 148.1°. The predicted strain energy of the molecule **58** (RMP2/6-31G*, 166 kcal mol^{-1}) is approximately the same as that found experimentally for cubane (157–181 kcal mol^{-1});[23] therefore, the synthesis of bowlane appears quite possible.[125] However, it is beyond doubt that the reactivity of the distorted CC_4 fragment accessible to attack by reagents from outside would hamper the synthesis. Even in the case of [4.4.4.5]fenestranes (in which the distortion of this fragment is less pronounced), the reactivity is still rather high. Many thermal and photochemical reactions of [4.4.4.5]fenestranes proceed with cleavage of the bonds at the central carbon atom.[126]

The first and not yet synthesised neutral saturated hydrocarbon with a predicted perfectly planar configuration of the carbon atom the structure of which corresponds to a minimum on the PES is dimethanospiro[2.2]octaplane (**59**).



58



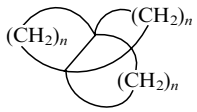
59

The MP2/6-31G(d) calculations predict for the compound **59** a structure with D_{2h} symmetry and a perfect planar configuration of the central carbon atom.[127,128] The highest occupied molecular orbital in **59** is represented by the *p* orbital of the central atom with a lone electron pair. Unusual physical properties of the octaplane **59** were predicted, in particular, a low ionisation potential (~5 eV) comparable with those of alkali metals. In this compound, the planar carbon atom is shielded by the hydrocarbon cage, which may decrease the reactivity.

4. The inverted and pyramidal configurations of the tetracoordinated carbon atom

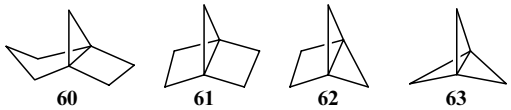
Now we shall consider examples of molecules containing a carbon atom with bonds located on one side of the plane that passes through this atom (see Fig. 1 *b*,*c*). Inverted and pyramidal configurations should be distinguished.[123,129] The inversion means that one bond of the carbon atom points to a direction opposite to its direction in the tetrahedral configuration, resulting in a fragment with C_{3v} symmetry (see Fig. 1 *b*). In the pyramidal CX_4 fragment, the carbon atom occupies a vertex of a tetragonal pyramid with C_{4v} symmetry (see Fig. 1 *c*).

The existence of inverted configurations was first discussed in relation to propellanes, *i.e.*, structures in which two bonded carbon atoms are additionally connected by three bridges.

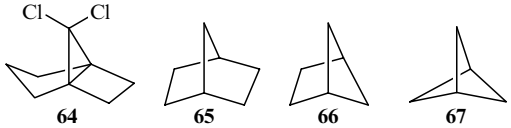


[*n*, *n*, *n*]propellanes

The first representative of small-ring propellanes, [3.2.1]propellane (**60**), was synthesised in 1969.[130] At about the same time, discussion concerning the inverted configuration of the carbon atom was initiated. It was suggested that in small-ring propellanes such as **60**–**63**, unusual configuration of the central atoms is possible. The results of X-ray diffraction analysis of 8,8-dichlorotricyclo[3.2.1.0^{1,5}]octane (**64**) provided the first evidence supporting this hypothesis.[131]



60 **61** **62** **63**



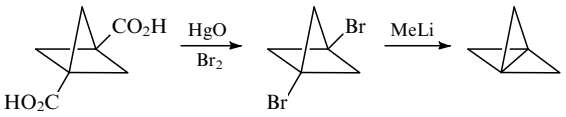
64 **65** **66** **67**

[3.2.1]Propellane **60** proved to be thermally stable but still extremely reactive (it reacts with oxygen and enters into diverse radical addition reactions).[130] An even more strained propellane (**61**) was stabilised only in an argon matrix at 29 K.[132] It appeared that the simplest [1.1.1]propellane **63** could hardly be expected to

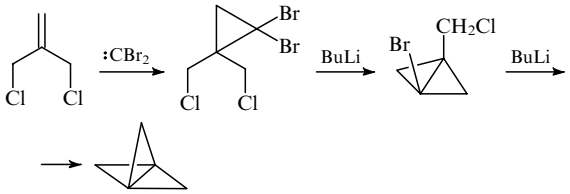
be more stable. However, in 1982, Wiberg and Walker [133] predicted theoretically the possibility of synthesis and the highest stability, among the compounds **61**–**63**, for [1.1.1]propellane and later they synthesised it. For the compound **63**, not only the possibility of synthesis and stability were predicted, but also the enthalpy of formation and photoelectron and IR spectra were calculated. The [1.1.1]propellane molecule is the first polyatomic molecule for which correct theoretical predictions preceded the synthesis.[134]

The relative stability of **63** is interpreted in the following way.[134] The molecules **61**–**63** have approximately equal strain, while the strain of the corresponding bicyclic hydrocarbons **65**–**67** with no bond between the central carbon atoms sharply increases on passing from [2.2.1]bicycloheptane (**65**) to [1.1.1]bicyclopentane (**67**).[135] Since the reactions of propellanes include rupture of the bond between the bridging carbon atoms to give species having the skeleton of the corresponding bicyclic hydrocarbons, the energy barrier to the reactions of [1.1.1]propellane is higher than the corresponding values typical of its homologues.

[1.1.1]Propellane was first synthesised from 1,3-dibromobicyclo[1.1.1]pentane, which is difficult to obtain.



Later, a procedure for the synthesis of the propellane **63** from more easily accessible precursors was developed;[136] this allows the preparation of tens of grams of this compound.

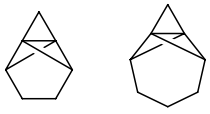


A similar approach has been used to prepare substituted [1.1.1]propellane derivatives.[137] The latest achievements in the synthesis, study of the chemical properties and application of [1.1.1]propellanes are covered in a review.[138]

The structure of [1.1.1]propellane was determined using vibrational spectroscopy,[139] gas-phase electron diffraction [140] and X-ray diffraction analysis.[141] The results of investigations by these methods confirmed the presence of the inverted configuration of the carbon atoms at the bridgehead in the structure of this compound.

The nature of the bond between the central carbon atoms in the compound **63** was the subject of numerous theoretical studies.[134] The energy of this bond was estimated (based on MP2/6-31G* calculations) to be approximately 70% of the energy of a single C–C bond (59 kcal mol^{-1}).[142]

Experimental information on the nature of the central bond in propellanes are provided by studies on the electron density distribution from X-ray diffraction data. Studies of this type have been attempted;[141, 143] however, the accuracy of experimental data proved to be inadequate to draw ultimate conclusions. The most accurate results of X-ray structure determination (at 81 K) and electron density distribution have been reported [143] for two [1.1.1]propellane derivatives, compounds **68** and **69**.

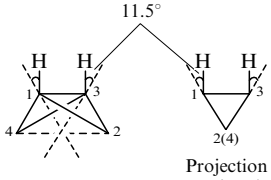


68 **69**

As expected, the DED maxima for non-bridging bonds proved to be concentrated outside the three-membered rings, which is typical of bent (banana) bonds. However, the DED values between the central carbon atoms are negative for both molecules. Nevertheless, this fact alone does not prove the absence of bonds between these atoms and does not contradict the results of the electron density calculation carried out by Wiberg.[144]

The negative DED values on the lines connecting atoms are encountered quite often; this is due to over-subtraction of the electron density of the 'pro-molecule' (combination of spherical non-interacting atoms) from the total density. This is due to the nature of the DED maps — they are differential. Therefore, in investigations of these bonds, a more promising approach includes analysis of the electron distribution topology and construction of non-differential maps, in particular, the Laplacian (the second derivative) of the experimental and theoretical electron density.[75]

The inverted configuration of the bridgehead carbon atoms was also observed in bicyclobutane derivatives (the structure was determined by microwave spectroscopy [145]).

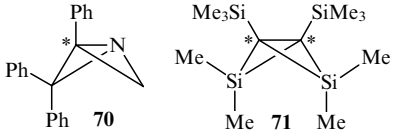


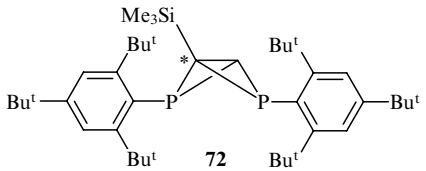
Projection along the straight line passing through C(2) and C(4)

In this molecule, the C(1)–H and C(3)–H bonds form an angle of 11.5° with the plane passing through the C(1), C(2) and C(4) atoms.

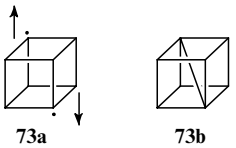
X-Ray diffraction data for other bicyclobutane derivatives with inverted configurations of bridgehead carbon atoms have also been published.[146–148]

The Cambridge Database contains also structural data on bicyclobutane heteroanalogues which also incorporate carbon atoms with inverted configurations. Examples are provided by compounds **70**–**72** (the carbon atoms with inverted configurations are marked by asterisks).[149–151]





The presence of carbon with inverted configuration in 1,4-dehydrocubane has been doubted based upon the results of theoretical (*ab initio* 6-31G*) and experimental data.[152–154] It is more likely that this highly unstable molecule exists as singlet biradical **73a** and contains no diagonal bond, as shown in **73b**.



73a **73b**

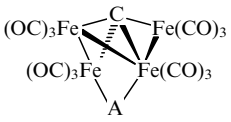
Theoretical calculations have been performed for the molecules of polycyclic hydrocarbons **74**–**76** [MP2/6-31G(d,p), 6-311++G(d,p), B3LYP/6-31G(d,p)][155] and [2.2.2]propellatriene **77** (CASSCF/6-31G*),[156] in order to find other structure types where existence of 'inverted' carbon atoms is possible.



74 **75** **76** **77**

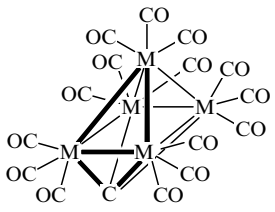
The pyramidal configuration of the carbon atom (see Fig. 1 *d*) is more exotic than the inverted one, and calculation methods still remain the most efficient tool for the investigation of compounds with this type of atom. Noteworthy are studies by Minkin *et al.*,[157, 158] who were the first to demonstrate that among the possible non-tetrahedral configurations of the carbon atom in methane, the pyramidal rather than planar configuration is energetically most favourable. The researchers cited discuss the factors that stabilise the pyramidal configuration; they are similar to those for the planar configuration, namely, the presence of σ-donor or π-acceptor substituents as well as incorporation of a pyramidal carbon atom in a rigid polycyclic cage, especially in small rings.

Known and structurally characterised systems with a pyramidal configuration of carbon (as well as compounds with the planar configuration of carbon) are represented exclusively by organometallic compounds of transition metals. Some of these structures are deposited in the CSDB; most of them are carbido clusters of iron, ruthenium, or osmium in which the carbon atom occupies an open cavity formed by metal atoms. The most frequently encountered types of structures are those present in compounds **78**, **79** (with the so-called butterfly geometry [159, 160]) and compounds **80**, **81**, in which the carbon atom lies below the base of the tetragonal pyramid formed by the metal atoms.[161, 162]



78, **79**

A = H^+ (**78**), CO (**79**)

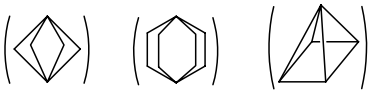


80, **81**

M = Fe (**80**), Ru (**81**)

In recent years, interest in these clusters has substantially increased because they were shown to be the key intermediates in the catalytic reduction of CO with hydrogen to give hydrocarbons, *i.e.*, the Fischer – Tropsch synthesis.[163] The first complex of this type was prepared as a side product of the reaction of $Fe_3(CO)_{12}$ with alkynes;[161] at present, preparative procedures for the synthesis of these compounds in high yields have been developed.[164] The carbon atoms in carbido clusters form σ- and π-bonds involving transition metal *d* orbitals; this stabilises the clusters. Similar complexes containing no carbido (interstitial) ligands are less stable.

Numerous theoretical studies of hypothetical organic molecules having the carbon atoms with pyramidal configuration have been carried out. About 10 years ago, the lack of computer resources and the absence of advanced software did not allow sufficiently accurate and reliable determination of the structural parameters of strained molecules. Many structures calculated at that time have later (according to the results of more advanced methods of calculation) proved unreal, *i.e.*, either not matched by minima on the PES or inaccurate. For example, [1.1.1.1]- and [2.2.2.2]paddlanes (**82**, **83**), which were initially supposed to have pyramidal configurations of carbon atoms, did not correspond to minima on the PES calculated by modern *ab initio* methods.[124]

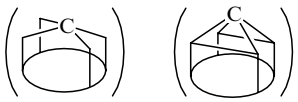


82 **83** **84**

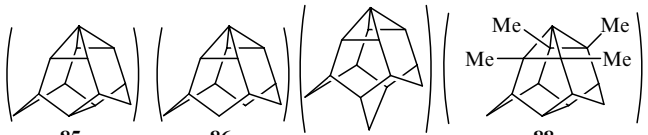
The molecular mechanics calculations for bowlane **58** had also showed the presence of a carbon atom with pyramidal configuration, but *ab initio* calculations carried out later refuted this conclusion.

The C_{4v} structure of pyramidane (**84**) with the pyramidal configuration of a carbon atom corresponds to a local minimum on the PES (MINDO/3,[165] HF/STO-3G [166] and HF/6-31G* [124]).

Rasmussen and Radom [167] have reported results of *ab initio* calculations (B3LYP/6-31G(d)//MP2/6-31G(d)) for hemialkaplane (bowlane **58** is a representative of this class of polycyclic hydrocarbons) and hemispiroalkaplane molecules; according to their data, the central carbon atom has a pyramidal configuration. The general formulae of hemialkaplanes (on the left) and hemispiroalkaplanes (on the right) are shown below:



On the basis of calculations of the molecular strain and the so-called apical strain (which characterises the strain of the separate molecular fragment containing the carbon atom with the pyramidal configuration), the researchers concluded that hemispirobioctaplane **85**, hemispirooctaplane **86** and hemispirobinonaplane **87** are the most promising synthetic targets. Analogues of the systems **85** – **87** containing methyl groups (for example, compound **88**) might prove to be easier to prepare because the presence of methyl groups contributes to the kinetic stability of the molecule. The compounds **85** – **88** were predicted to be highly basic.[167]



85 **86** **87** **88**

The existence of rigid polycyclic organic molecules, for which the presence of a carbon atom with a pyramidal configuration had been predicted, was later proved experimentally. For example, Wiberg *et al.*[168, 169] have detected one of them, namely, highly reactive tricyclo[2.1.0.$0^{1,3}$]pentane **89**.



89

VII. Distortions of bond and torsion angles at the double bond in alkenes

The research into the distortions of the bond and torsion angles in the molecules of alkenes has a long-standing history. Back in 1890, Baeyer [170] arrived at the conclusion that substantial strain should be expected in the *trans*-cyclohexene molecule and, therefore, isomerisation of *cis*-cyclohexene into the *trans*-isomer is unlikely. Later, when analysing the strain in unsaturated bicyclic molecules, Bredt,[171, 172] formulated a rule according to which the cage of camphane, pinane or other related compounds cannot have a double bond to a bridgehead position. At present, vast theoretical and experimental material on this point has been accumulated and reflected in numerous reviews (see, for example, studies [28, 173 – 176]).

The types of distortion of a planar alkene fragment are illustrated by Fig. 2.

Mathematical analysis of the distortions of the bond and torsion angles in the ethylene molecule has been described in detail in the literature (see, for example, reviews [28, 177]).

Distortions of only one type are seldom encountered in alkene molecules. However, in most cases, the prevailing type of distortion can be distinguished, which determines the total strain of

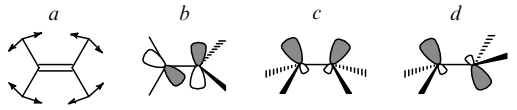
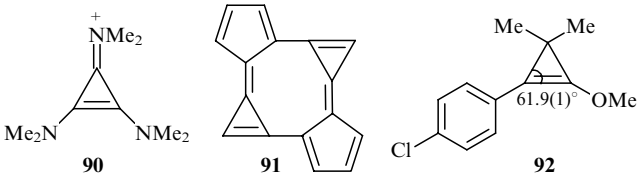


Figure 2. Types of distortion of the planar alkene fragment: (*a*) in-plane distortions; (*b*–*d*) out-of-plane distortions: (*b*) twist, (*c*) *syn*- and (*d*) *anti*-pyramidalisation.

the alkene.[28] Below we consider compounds in which the strain of the molecule is mainly due to the contribution of one type of distortion.

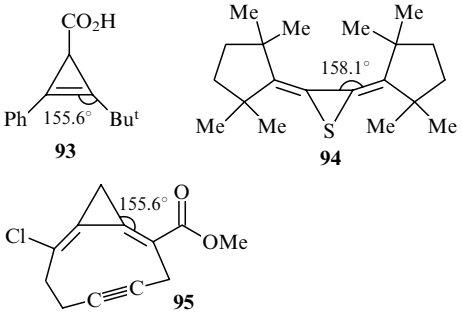
1. In-plane distortions of an sp^2-hybridised carbon atom

The bond angles at the sp^2-hybridised carbon atom can differ appreciably from the ideal value, equal to 120°. Indeed, the internal C–C=C angle in cyclopropene derivatives can be twice as small. The results of a search through the CSDB demonstrated that this angle is about 60° in the molecules of cyclopropene derivatives that also contain an exocyclic double bond (there are 10 structures of this type), for example, **90**, **91**.[178,179]

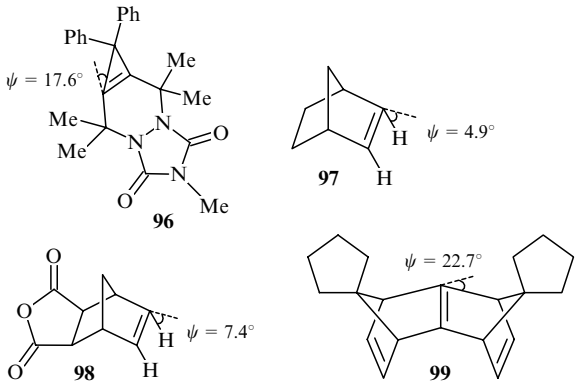


In these molecules, a major contribution to the resonance hybrid is made by canonical forms with the cyclopropenylium cation. In other cyclopropene derivatives, the internal C–C=C angle is close to 60°; for example, in molecule **92** this angle is 61.9°.[180]

The external R–C=C angles in cyclopropene derivatives can be greater than 150° in the case of bulky R substituents, for example, the angle is 155.6° in molecule **93**.[181] Bond angles exceeding 150° have also been found at exocyclic double bonds in compounds with saturated three-membered rings. The deviations of these angles from 150° are caused by steric repulsion of bulky groups (as in compound **94**)[182] or by the fact that double bonds are incorporated in rings (as, for example, in compound **95**).[183]



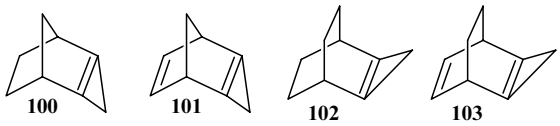
A decrease in the R–C=C angle results in pyramidalisation of the carbon atoms of the double bond. This fact was predicted theoretically:[184] model calculations (RHF/STO-3G) showed that if the H–C=C angles in the planar ethane molecule are less than 100°, pyramidalisation becomes energetically favourable. X-Ray diffraction analysis of compound **96** confirmed this fact experimentally.[185] In molecule **96**, the C–C=C angles in the cyclopropene fragment amount to 64.8° and 65.3°, and the ψ angle characterising pyramidalisation equals 17.6°.



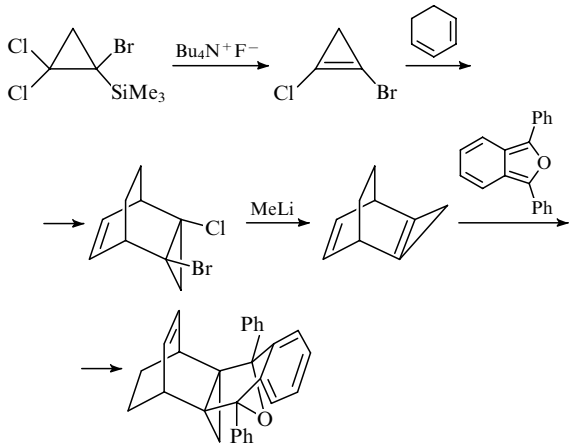
For the norbornene molecule (**97**), pyramidalisation of the carbon atoms of the double bond was predicted theoretically (for example, according to the STO-3G *ab initio* calculations,[186] the hydrogen atoms at the double bond are displaced in the *endo*-direction and the ψ amounts to 4.9°). X-Ray diffraction data for norbornene have not been obtained.

In a norbornene derivative, anhydride of *exo*,*exo*-2,3-norborn-5-enedicarboxylic acid (**98**), the structure of which has been determined by neutron diffraction, the ψ angle proved to be 7.4°.[187] In compound **99**, as shown by X-ray diffraction analysis, the fusion of two norbornyl cages (and, probably, steric repulsion between the cyclopentane rings) accounts for quite a noticeable pyramidalisation: ψ = 22.7°.[188,189]

An exceptionally high pyramidalisation of the carbon atoms at the double bond can be expected, according to calculations (HF, TCSCF, MP2, B3LYP, B3PW91/6-31G*),[190] in compounds **100**–**103**, the synthesis of which has been reported.[191–195]



It follows from calculations that each of the tricyclic structures **100**–**103** is matched by two minima on the PES, which correspond to the *endo*- and *exo*-isomers. In the case of the compounds **100** and **101**, a lower energy is found for *endo*-isomers (their energy is 2.2–7.5 kcal mol^{-1} lower than that of the corresponding *exo*-isomers), whereas for the compound **103**, the *exo*-isomer is lower in energy (by 2.2–3.3 kcal mol^{-1}). The carbon atoms of the double bonds in the compounds **100**–**103** should be strongly pyramidalised (ψ > 40°). Experimental verification of these theoretical conclusions would be a complicated task because the strained molecules **100**–**103** are highly reactive (for example, the existence of the compound **103** can only be proved by analysing the products of reactions involving this molecule).[193]



2. Twisting of the double bond

The loss of π-bonding upon distortion of the torsion angles at the double bond (twist) is partially counterbalanced by rehybridisation of carbon atoms, resulting in their pyramidalisation.[196–198] Therefore, when comparing the degree of twisting of double bonds in the molecules of different alkenes, it is not always legitimate to use the dihedral angle between the *a*C(1)*b* and *c*C(2)*d* planes (Fig. 3). Therefore, the so-called twist angle τ was introduced, which is found as the arithmetic mean of the *a*C(1)C(2)*d* and *b*C(1)C(2)*c* dihedral angles.

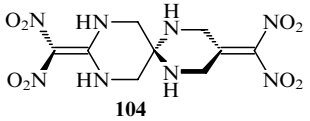
$$\tau = \frac{a\mathrm{C}(1)\mathrm{C}(2)d + b\mathrm{C}(1)\mathrm{C}(2)c}{2}.$$

This angle is equal to the angle between the *a*C(1)*b* and *c*C(2)*d* planes in the case where no pyramidalisation takes place. The degree of pyramidalisation of the C(1) and C(2) atoms is evaluated from the departure of the *a*C(1)C(2)*c* and *b*C(1)C(2)*d* dihedral angles from 180° and from the pyramidalisation angles $\chi_{C(1)}$ and $\chi_{C(2)}$:

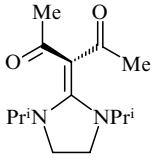
$$\chi_{C(1)} = b\mathrm{C}(1)\mathrm{C}(2)c - b\mathrm{C}(1)\mathrm{C}(2)d + \pi,$$

$$\chi_{C(2)} = a\mathrm{C}(1)\mathrm{C}(2)d - b\mathrm{C}(1)\mathrm{C}(2)d + \pi.$$

The results of theoretical investigations demonstrate that twisting of the molecule of an alkene with all electron-donating or all electron-withdrawing substituents by 90° (τ = 90° or −90°) should give rise to a singlet biradical,[199–201] and the maximum twisting in the molecules of non-symmetrical alkenes (so called push – pull alkenes) yields bipolar species.[202] Twisted systems correspond to the transition state of the *cis–trans*-isomerisation of alkenes. For simple alkenes, the activation free energy of the *cis–trans*-isomerisation found experimentally lies in the range from 51 to 67 kcal mol^{-1} (see Refs 203 – 205). For push – pull alkenes, this barrier is substantially lower.[202] This is why the 'record-holder' molecules in which the τ angle for the C=C bond is close to 90° (or −90°) are represented in the CSDB by push – pull alkenes. For example, according to X-ray diffraction data, in the molecules **104** and **105**, the τ angles are 85.1° and 84.3°, respectively.[206, 207]



104



105

When the double bond is conjugated with other π-bonds or aromatic systems, the barrier to the *cis–trans*-isomerisation also decreases. Among the structures of compounds with conjugated double bonds, numerous examples can be found in which the |τ| values are close to 90°. Thus in the octaisopropylcyclooctatetraene molecule (**106**), the τ angles for all multiple bonds exceed 64°.[208]

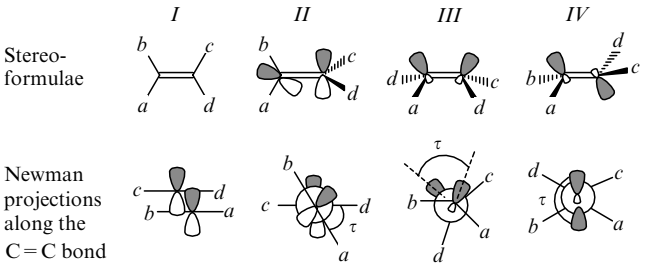
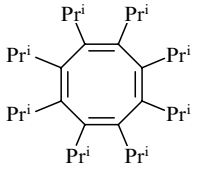


Figure 3. Twist distortion of the C=C bond and definition of the twist angle τ: (*I*) unstrained double bond; (*II*) twisting of double bond without pyramidalisation of the carbon atoms; (*III*, *IV*) twisting + pyramidalisation; *a*–*d* are substituents.

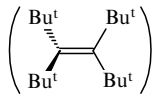


106

If push – pull alkenes and compounds with conjugated double bonds are excluded from consideration, the number of structures with τ angles lying in the range of 20° < |τ| < 90° included in the CSDB sharply decreases. Considerable twist-type distortions of the C=C bond were found both in acyclic and in cyclic or polycyclic compounds.

a. Acyclic twisted alkenes

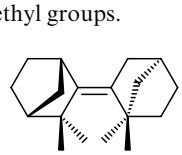
In acyclic alkenes, twist distortions take place if bulky substituents are present at the double bond. The largest twist of the double bond not incorporated in a ring or a polycyclic system and bearing only hydrocarbon substituents is expected in the tetra-*tert*-butylethylene molecule (**107**). Numerous attempts at synthesising this compound were undertaken; however, they have not yet met with success. *Ab initio* (BLYP/DZd) calculations for the molecule **107** [209] predict a singlet ground state (D_2 symmetry) with τ = 45°, slight pyramidalisation and a strain energy of 93 kcal mol^{-1}. The energy of the triplet state of **107** with τ ≈ 87° would be 12 kcal mol^{-1} higher than the energy of its singlet state.



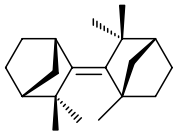
107

The alkenes **2**, **108**, and **109** have been prepared by methods used in the attempts to synthesise the compound **107**. In the molecules of these compounds, as in the molecule of **107**, the quaternary carbon atoms are linked directly to the double bonds. However, the steric repulsion in the molecules **2**, **108** and **119** is weaker than that in tetra-*tert*-butylethylene due to the presence of additional bonds between substituents.[210–213]

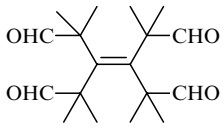
Krebs *et al.* [214, 215] approached very closely the synthesis of the compound **107**; they succeeded in synthesising tetrakis(2-formylpropan-2-yl)ethylene (**110**) (τ = 28.6°, according to X-ray diffraction data). However, the formyl groups proved to be so nonreactive that the researchers were unable to reduce them to the methyl groups.



108



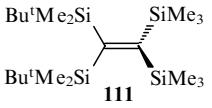
109



110

The relatively low reactivity of the double bond in the compounds **2** and **108**–**110** should also be mentioned. In all probability, this is due to the shielding of the π-system by bulky substituents. The *cis–trans*-isomerisation of strained alkenes proceeds much more readily than isomerisation of unstrained compounds (the energy barrier can be almost twice as low in the former case). This was used in a study [205] to estimate the energy barrier to the isomerisation of alkenes. Since isomerisation of strained alkenes takes place at relatively low temperatures, side reactions do not complicate the kinetic measurements. The standard enthalpies of formation (with an applied correction for steric effects found by MM2 calculations) of these alkenes were employed to calculate the activatiom barrier to the *cis–trans*-isomerisation (69.5 ± 0.9 kcal mol^{-1}), which does not depend on the nature of substituents at the double bond.

According to the results of a search through the CSDB, the greatest twist distortion of the double bond among acyclic compounds is found in compound **111**.[216]

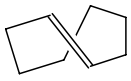


111

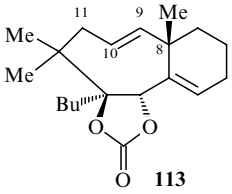
In the tetra(trialkylsilyl)ethylene **111**, the τ angle equals 49.6° (note that this value is greater than that predicted for tetra-*tert*-butylethylene **107**), no pyramidalisation of the carbon atoms of the C=C bond takes place, and the double bond length (1.370 Å) exceeds the typical value (1.32 Å).

b. *trans*-Cycloalkenes

Among monocyclic compounds, a substantial distortion of the double bond (mainly twist-type distortion) can be attained in *trans*-cycloalkenes in which the number of carbon atoms in the ring does not exceed nine. *trans*-Cyclooctene (**112**) is the unsubstituted compound with the smallest ring that can be isolated in a pure state at room temperature.[217, 218] The structure of *trans*-cyclooctene was determined by electron diffraction.[219] According to these studies, the C–C=C–C dihedral angle in the molecule **112** amounts to 136°. For a derivative of *trans*-cyclooctene, compound **113**, X-ray diffraction data have been published.[220] The C(8)–C(9)–C(10)–C(11) dihedral angle in the molecule **113** is 139.3°.



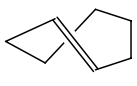
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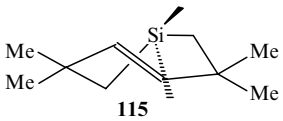
113

Further contraction of the ring containing a *trans*-double bond results in a substantial increase in the reactivity and the tendency for isomerisation to the *cis*-form. *trans*-Cycloheptene (**114**) can be synthesised at low temperatures.[221] Complexes of **114** with transition metals stable at room temperature have also been obtained.[222] Unsubstituted *trans*-cyclohexene (like *trans*-cyclopentene) has not been experimentally detected yet.

Monocyclic compound **115** with the smallest-possible ring containing a *trans*-double bond and stable at room temperature contains a silicon atom in the seven-membered ring and methyl groups in the α-positions relative to the double bond.[223] This compound proved to be sufficiently stable to be studied by X-ray diffraction analysis. The kinetic stability is ensured by the methyl group, while the presence of two C–Si bonds, which are longer than C–C bonds, makes the strain in the molecule **115** lower than that found in *trans*-cycloheptene.



114

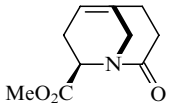


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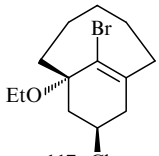
A substantial distortion of the double bond in **115** is reflected in the size of the C–C=C–C dihedral angle, which is 130.97°. It is of interest that the H–C=C–H dihedral angle is 173°, and pyramidalisation of the carbon atoms in the molecule **115** is insignificant. The C=C bond length (1.330 Å) deviates only slightly from the typical value, despite the substantial distortion of the dihedral angles. It should be noted that *trans*-cycloalkenes are chiral; the racemic **115** was partially resolved by column chromatography using a chiral adsorbent.

c. Polycyclic compounds with twisted double bonds: anti-Bredt alkenes

Among numerous anti-Bredt alkenes deposited in the CSBD, one can find structures in whose molecules a *trans*-double bond is incorporated into an eight-membered ring. As examples, one can mention compounds **116** and **117** (the molecule of **116** contains also a twisted amide bond [224]).



116



117

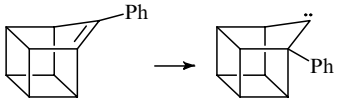
The following parameters have been found for the molecule **116**:[225] the angle τ = 10.8°, the average degree of pyramidalisation of the carbon atoms at the double bond χ = 28.45°.

The size of the τ angle attests to an even greater twist distortion of the double bond (τ = 29.3°) in the molecule **117**, although the degree of pyramidalisation in this molecule is lower, χ = 17.1°.[226]

The alkene **117** is very sensitive to moisture and atmospheric oxygen; the compound **116** is less reactive.

Anti-Bredt alkenes with a *trans*-double bond incorporated in rings containing not more than seven carbon atoms are known. The substantial strain in the molecules of these compounds accounts for their enhanced reactivity. The exceptionally reactive alkene **1** contains a *trans*-cyclohexene ring.[227, 228] This compound was stabilised in a solid argon matrix, and the IR absorption frequency for its double bond was determined. The unusually low frequency (1481 cm^{-1}) indicates that the π-bonding has been considerably reduced as a result of angle distortion in the molecule of **1**.

An even more strained molecule of 9-phenyl-1(9)homocubene (**118**) contains a *trans*-'double' bond in the five-membered ring. No spectroscopic or structural characteristics have been obtained so far for this compound because of its high reactivity.[229] The compound **118** rearranges into carbene **119** even at low temperatures.



118 **119**

This reaction is uncommon for alkenes (the reverse transformation takes place much more often); the fact that this reaction does proceed implies that the properties of the double bond change substantially upon geometric distortion.

Although the compounds **1** and **118** can be regarded as 'record-breaking twisted alkenes', the *p* orbitals of their 'double' bonds are not orthogonal: the calculated τ values are much smaller than 90° (for example, τ = 64° in the molecule of **1**).[227, 228] Due to the pyramidalisation of non-bridging carbon atoms of the C=C bonds, the orbital overlap is partly restored and the τ value decreases. Perhaps, an ideally orthogonal arrangement of the π orbitals could be realised in 'fixed betweenenes' (or orthogonenes) **120**, **121** (MM2 and semiempirical calculations; no *ab initio* calculations for these structures have been carried out).[230] Tentative results on the synthesis of orthogonenes have been published.[231]



120, **121**

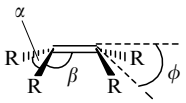
n = 0 (**120**), 1 (**121**).

3. Out-of-plane distortions of angles at the C=C bond: pyramidalisation

It is well-known that alkenes in which the double bond occurs in a non-symmetric environment are often characterised by a pyramidal configuration of the double-bond carbon atoms. This pyramidalisation is slight; the reasons for it are discussed in the

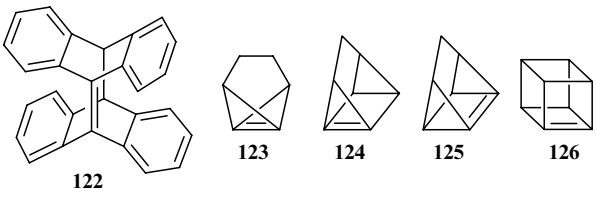
literature (see, for example, the reviews [232, 233]). Pyramidalisation accompanies also in-plane and twist distortion of a double bond (see above). Calculations [234] have shown that *anti*-pyramidalisation of the carbon atoms of the double bond is energetically more favourable than *syn*-pyramidalisation. However, this conclusion requires verification by means of more advanced methods of calculations than those used in the study cited.[234]

In this Section, we consider compounds the structural features of which impose pronounced *syn*-pyramidalisation. As a rule, these compounds contain a rigid polycyclic cage having two mutually perpendicular planes of symmetry one of which accommodates the double bond.[175] Examples of non-symmetric molecules have also been reported.[235] When discussing pyramidalisation in these molecules, in addition to χ, it is convenient to use the angle ϕ



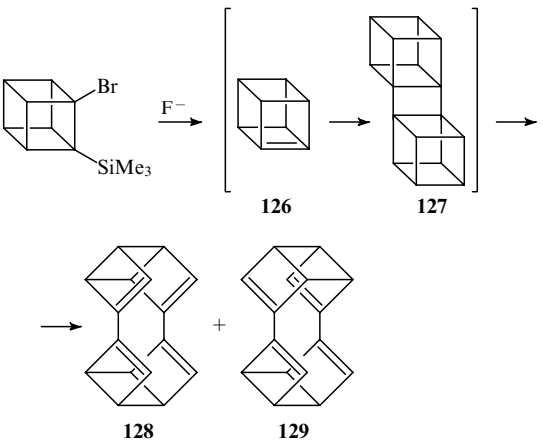
$$\cos\phi = -\frac{\cos\beta}{\cos(0.5\alpha)}$$

The first synthesised compound with a considerable pyramidalisation of the carbon atoms at the double bond (**122**) was reported more than 30 years ago;[236] at present, dozens of compounds of this type are known, for example, **123**,[237, 238] **124**,[239–241] **125**[242] and **126**.



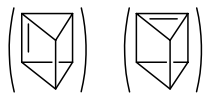
122 **123** **124** **125** **126**

In the cubene molecule (**126**), the angle ϕ, according to the SCF/3-21G calculations, is equal to 84.1°.[243] The possibility of synthesis of the compound **126** was predicted theoretically and then realised in practice.[244] Rough thermodynamic data for cubene [245] and the first results of the study of chemical properties of this highly reactive compound [246] have been published. The calculations showed that, despite the pronounced pyramidalisation of the double-bond carbon atoms, the overlap of the *p* orbitals in the molecule **126** is sufficient for regarding this compound as an alkene rather than a biradical (TCSCF/6-31G* for the singlet state, ROHF/6-31G* for the biradical).[153] This is also indicated by an observed reaction typical of alkenes with highly pyramidalised carbon atoms of the double bond,[247] namely, cubene dimerisation to give the corresponding propellane **127** with subsequent transformation into tetraenes **128** and **129**.



126 **127** **128** **129**

The attempts to synthesise derivatives with even more pyramidalised carbon atoms of the C=C bond, prismene, have so far been unsuccessful.[248] Both prismene isomers, **130** and **131**, have been studied theoretically [HF/6-31G(d), MP2/6-31G(d)].[249] According to calculations, the energy of the molecule **131** is lower than the energy of **130**.



130 **131**

VIII. Distortions of the bond and torsion angles in the molecules of aromatic compounds

Cyclic unstrained aromatic systems are normally planar. The benzene structure,[250] which serves as a sort of standard in discussion of the nature of aromaticity,[251] has been studied in the gas phase (spectroscopic methods and electron diffraction) with high accuracy: the molecule has D_{6h} symmetry, the carbon atoms form a regular hexagon, and the C–C bond length is 1.399 ± 0.001 Å.

The types of distortion investigated for benzene derivatives include changes in the bond angles in the aromatic ring plane and out-of-plane distortions; compounds with 'conformations' similar to those of cyclohexane, *i.e.*, a chair, a boat, and a twist 'conformation,' have been obtained (Fig. 4). Below we consider only benzene derivatives (strained molecules of aromatic heterocyclic compounds have received much less attention in the literature).

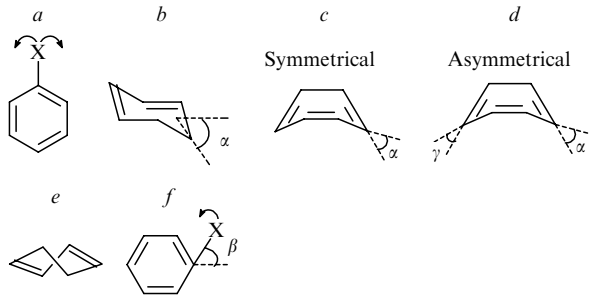
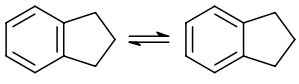


Figure 4. Bond angle distortions in benzene derivatives. (*a*) in the ring plane; (*b*–*f*) out-of-plane distortions: (*b*) chair, (*c*) symmetrical boat, (*d*) asymmetrical boat, (*e*) twist, (*f*) deviations of the C–X bond from the ring plane. The angles characterising the degree of distortion are marked.§

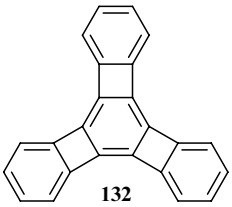
1. Changes in the bond angles in the plane of the benzene ring

The C–C–X bond angles at the carbon atoms of the benzene ring can markedly depart from the ideal value, equal to 120°. These distortions may be caused, in particular, by annelation of small rings to benzene. Mills and Nixon [252] postulated that annelation of cyclopentane to benzene shifts the equilibrium between the two Kekule structures.

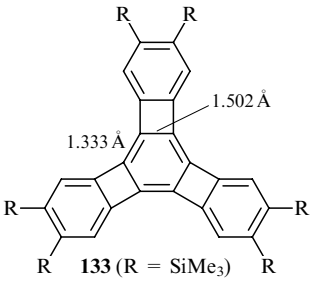


Later, the hypothesis of the existence of an equilibrium between the Kekule structures in benzene derivatives was admitted to be faulty;[50] however, localisation of the double bonds induced by annelation of strained rings was actually discovered.[253] The first experimental proof of this phenomenon was provided by the synthesis of cyclohexatrienes **132** and **133**.[254]

§ These designations of angles are used only in this Section.

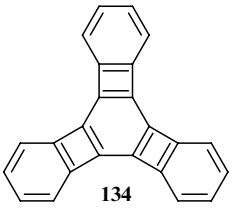


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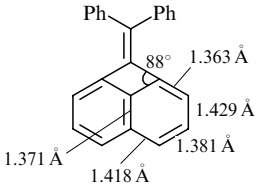


133 (R = $SiMe_3$)

The compound **133** contains, according to X-ray diffraction analysis, noticeably alternating bonds in the central ring. The unusually easy hydrogenation of the central ring in **132** also points indirectly to a substantial localisation of the double bonds.[255] Thermochemical data for this reaction have been published.[256] However, in this type of compound, localisation of the double bonds can be interpreted by assuming a smaller contribution of the structure **134**, with antiaromatic cyclobutadiene rings, to the resonance hybrid. Calculations (B3LYP/6-31G*) demonstrated that it is the bond localisation caused by annelation rather than other π-effects (aromaticity – antiaromaticty) that is responsible for the structure of these compounds.[257]



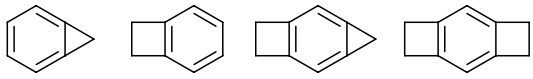
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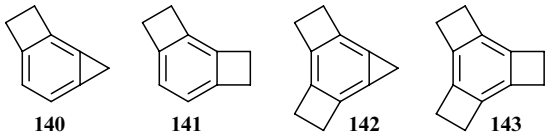
135

The clear-cut bond alternation has been found by X-ray diffraction analysis [258] in the molecules of naphthalene derivative **135**. The bond angles at the carbon atom at the *peri*-positions of the naphthalene ring differ appreciably from 120°.

Alternation of single and double bonds was to be expected in dehydrocyclobuta- and cyclopropabenzenes. It proved to be very difficult to perform the synthesis and X-ray diffraction analysis of strained compounds such as **136**–**143**. However, unexpectedly, no noticeable bond alternation was found in the molecules of these compounds.[259]

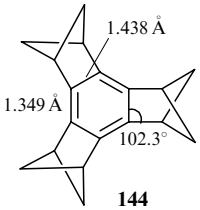


136 **137** **138** **139**

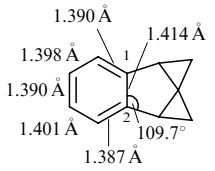


140 **141** **142** **143**

On the one hand, these results are at variance with the calculations (MP2/3-21G, HF/6-31G*) for model systems (benzene molecules with distorted C–C–H bond angles), according to which the decrease in the C–C–H angle to 90° is accompanied by pronounced localisation of the double bonds.[260] However, on the other hand, clear-cut alternation of bonds was found in the benzene ring annelated to bicyclic fragments. In the most strained molecule of this type of compound, tris(tetrahydrobicyclo[2.1.1]-hexa)benzene (**144**), noticeable bond alternation was found, first, by *ab initio* calculations [6-31G(D)(LDF)],[261] [MP2/6-31G(D)],[262] and then by X-ray diffraction analysis.[263] The C–C–C angle in the structure **144** is equal to 102.3° (which is much smaller than 120°). The reason for the observed bond alternation in the structure **144** is currently under discussion.



144



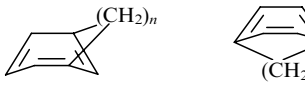
145

The alternation might be caused by the strain in the bicyclic fragments of **144**, which results in elongation of those bonds in the benzene ring at which the bicyclic fragments are annelated. A similar effect was observed for the compound **145**.[101]

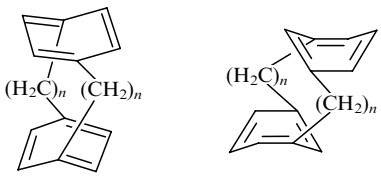
2. Out-of-plane distortions of the benzene ring

a. Compounds with benzene rings in the boat 'conformation'

Among the molecules in which the benzene rings are distorted to form a boat 'conformation' typical of the cyclohexane ring, cyclophanes should be mentioned first of all.[264] In recent years, strained molecules of meta-, para- ([*n*]- and [*n.n*]-) cyclophanes have been vigorously studied. The synthesis and properties of these compounds have been considered in detail in reviews.[265–268]



[*n*]metacyclophanes [*n*]paracyclophanes



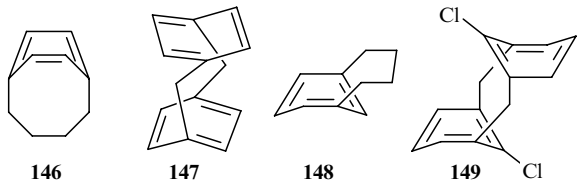
[*n,n*]paracyclophanes [*n,n*]metacyclophanes

The interest in these compounds, like that in the benzene derivatives **133**–**143** described above (cyclobuta- and cyclopropabenzenes can be treated as [*n*]orthocyclophanes), is related to some extent to the discussion of the nature of aromaticity.

In the case of [*n*]paracyclophanes, the benzene ring is not strained when $n = 9$; however, with a decrease in the bridge length, the ring becomes non-planar; in addition, the exocyclic C–C bonds are also distorted, in particular, they decline from the plane of the two adjacent bonds of the benzene ring (see Fig. 4 for the definition of the α and β angles characterising these distortions). Analogous distortions of the benzene rings in [*n*]metacyclophanes take place when $n \leqslant 7$. In [*n.n*]para- and -metacyclophanes, the benzene rings deviate substantially from the planar configuration at $n \leqslant 3$.

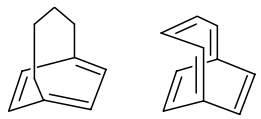
[2.2]Metacyclophane was synthesised in 1899,[269] and [2.2]paracyclophane was prepared in 1949 [270] by closure of the bridge. In the case of homologues with smaller *n* values, [*n*]paracyclophanes with $n \leqslant 7$, or [*n*]metacyclophanes with $n \leqslant 6$, this classical approach is inapplicable. The syntheses of cyclophanes with small *n* values include isomerisation of appropriately substituted valence isomers of benzene as the key stage. Six isomers of this type can be conceived (if only the CH fragments are combined, while charged species are excluded).[267] Different research groups have used four isomers,[271] most often, 3,3′-bicyclopropenyl derivatives.[265]

A decrease in the length of the bridge in cyclophane molecules results in a dramatic increase in their reactivity. The unsubstituted cyclophanes with the smallest *n* (with a saturated bridge) known to date, [4]paracyclophane (**146**) [272,273] and [1.1]paracyclophane (**147**),[274] can be stabilised only in inert matrices at low temperatures, while [4]metacyclophane (**148**) [275] and an extremely unstable [1.1]metacyclophane derivative (compound **149**) [276] were detected as short-lived intermediates.



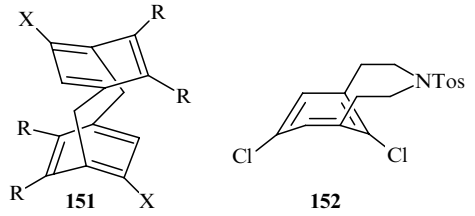
146 **147** **148** **149**

A highly unstable and, apparently, the most strained among the known [*n*]paracyclophanes, bicyclo[4.2.2]decapentaene, has been synthesised.[277] The results of experimental and theoretical studies (MP2, taking account of electron correlation)[278] suggest that the compound has the structure **150a**, which has a lower energy than the other isomer (**150b**).



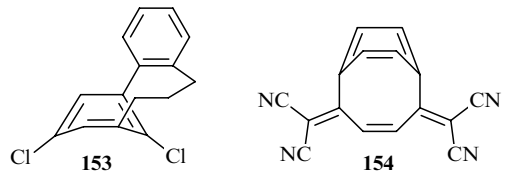
150a **150b**

To study the chemical and spectral properties and the structure of these compounds, it is necessary for them to be stable under experimental conditions. Sufficient stability was attained for strained cyclophanes having electron-withdrawing substituents or bulky groups shielding the most reactive centres, *i.e.*, bridging carbon atoms. Among the known stabilised cyclophane derivatives, the molecules of compounds **151**–**154** contain the most distorted benzene rings.[279–282]



151 **152**

R = CH_2SiMe_3, X = $CONMe_2$, Tos is *p*-toluenesulfonyl.

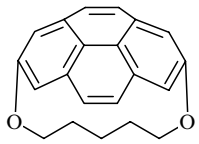


153 **154**

X-Ray diffraction data are available for the compounds **151** and **152**. Appreciable distortion of the benzene ring is indicated by the α and β angles: in the molecule **151**, $\alpha = 25.6°$ and $24.3°$, $\beta = 26.8°$ and $22.9°$, while in the molecule **152**, these parameters are even greater: $\alpha = 27.4°$, $\gamma = 12.3°$, $\beta_{max} = 48.7°$. The distance between the opposing bridging carbon atoms in the cyclophane derivative **151** is equal to 2.376(5) Å. Despite this heavy distortion of the aromatic rings, no bond alternation was detected in the compounds **151** and **152**, and the bond lengths fall in the ranges typical of unstrained benzene derivatives.

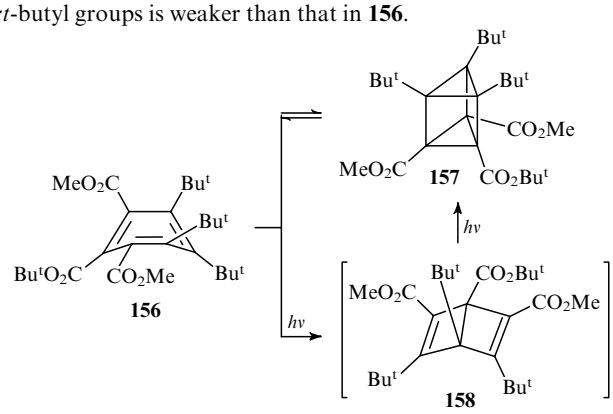
The presence of π-electron delocalisation is also indicated by NMR studies of strained cyclophanes including compounds **153** and **154**. The ^1H and ^{13}C NMR signals are exhibited in the chemical shift regions characteristic of aromatic compounds. Thus, despite the substantial distortions, the strained molecules of cyclophanes can still be regarded as aromatic. The system of π-bonds in these molecules is an 'observer' rather than a 'manager' and adapts itself to changes in the σ-core. This was confirmed by *ab initio* calculations for strained [*n*]metacyclophanes.[283] The benzene ring distortion of up to $\alpha = 30°$ is not accompanied by noticeable bond alternation. It may seem that these conclusions contradict the data on the chemical properties of strained cyclophanes, most of all, the data on the ability of these compounds to enter readily into Diels–Alder and nucleophilic substitution reactions.[266] However, one should take into account the fact that the molecules of compounds with non-planar benzene rings possess substantial strain. The reactions of the compounds result in strain relief, which is the driving force of their unusual chemical transformations.[265]

Distorted benzene rings serve as structural blocks of fullerenes; therefore, studies of strained cyclophanes are related to fullerene chemistry. Particular interest was aroused by the synthesis of compounds with fused non-planar aromatic rings, fullerene fragments,[284] for example, of 1,7-dioxa[7](2,7)pyrenophane (**155**).[285] In accordance with X-ray diffraction data, the pyrene residue in this compound is distorted to a greater extent than the similar fragment in C_{70} fullerene; the planes of non-annelated benzene rings make an angle of 109.2°.



155

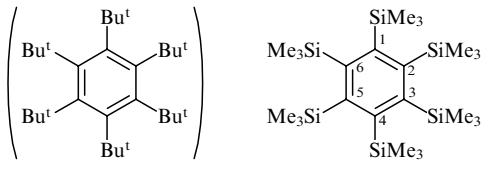
In conclusion, it should be noted that distortions of the benzene rings to a boat 'conformation' can be found not only in cyclophanes. In the molecules of 1,2,3-trisubstituted benzene derivatives, this conformation results in a decrease in the steric strain if the substituents are sufficiently bulky. According to analysis of CSDB structures, among benzene derivatives with bulky substituents in the 1,2,3-positions, the molecule **156** has the most distorted benzene ring.[286] The angle values $\alpha = 30.1°$, $\gamma = 11.6°$, and $\beta_{max} = 16.4°$ are comparable with the sizes of these angles in the cyclophane derivative **152**. Nevertheless, in compound **156**, no double bond localisation is found either. The strain in **156** accounts for the unusual reactivity of this compound, first of all, the tendency for isomerisation into prismane **157** [with the intermediate formation of the corresponding derivative of the Dewar benzene (**158**)], in which the steric repulsion between the *tert*-butyl groups is weaker than that in **156**.



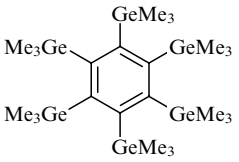
156 **157** **158**

b. Twist and chair 'conformations' of benzene rings

Due to steric repulsion of bulky substituents, the benzene ring can assume twist and chair 'conformations'. According to calculations, the chair 'conformation' can be found in the benzene ring of hexa-*tert*-butylbenzene (**159**).[287] This compound has not been synthesised so far but its less strained silyl-[288] and germyl-containing[287] analogues **160** and **161** are known.

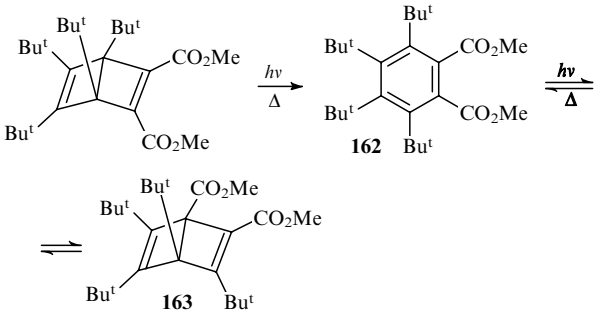


159 **160**

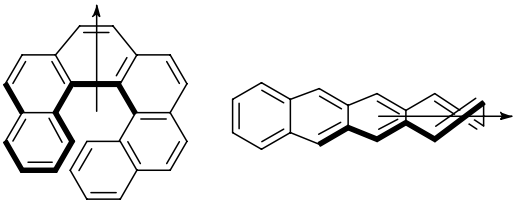


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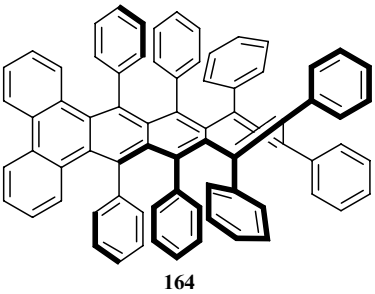
X-Ray diffraction analysis of the compound **160** showed that four carbon atoms of the benzene ring [C(1), C(3), C(4), C(6)] are located approximately in one plane, whereas the C(2) atom lies above this plane by ~0.1 Å and the C(5) atom is ~0.1 Å below this plane. The mean value of the C−C−C−C dihedral angle amounts to 9.8° and the C−Si bond deflects from the plane of the benzene-ring bonds adjacent to it by 22.2°. Despite the considerable distortions of the bond angles comparable to the distortions in the molecules **151**–**154**, the bond lengths in the benzene ring are normal for aromatic compounds. Analysis of the spectroscopic properties of the compound **160** shows that the compound can be considered to be aromatic but having an unusually high reactivity. The molecule **160**, similarly to the molecule **156**, is readily rearranged on exposure to radiation giving rise to a Dewar benzene derivative, hexakis(trimethylsilyl)bicyclo[2.2.0]hexa-2,5-diene (further [2 + 2]-cycloaddition to a substituted prismane was not observed). The rearrangement of the compound **160** occurring on heating resulted in benzene ring cleavage; in this case, 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene was isolated. Interestingly, the benzene derivative **162** containing four *tert*-butyl groups in the adjacent positions is thermodynamically less stable than the isomer **163**, which is a Dewar benzene derivative.[289]



The twist 'conformation' of the benzene ring has been observed in molecules of fused aromatic compounds. Typically, these molecules contain an aromatic polycyclic system twisted to form a helix the axis of which is either perpendicular or parallel to the benzene-ring planes.



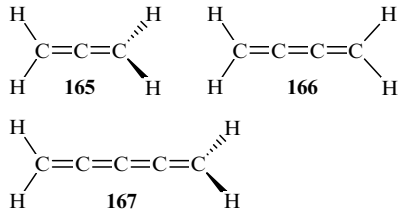
In the molecule **164**, the angle between the terminal bonds of the linear polybenzene system is 105°. Despite the steric strain, the compound **164** is exceptionally stable: it does not decompose on heating to 400 °C.[290]



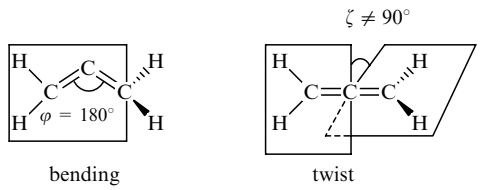
164

IX. Distortions of cumulated double bonds

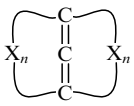
Cumulenes are hydrocarbons containing two (or more) double bonds with shared carbon atoms. Strain-free cumulene molecules, for example, allene (1,2-propadiene) (**165**), 1,2,3-butatriene (**166**) and 1,2,3,4-pentatetraene (**167**) have a linear carbon skeleton of cumulated double bonds. The four substituents are located either in mutually perpendicular planes (for an even number of cumulated double bonds) or in one plane (for an odd number of these bonds).



Distortions of cumulenes can include bending and twisting of the linear system of bonds. For allene, these distortions can be represented as follows:



Below we consider only allene and 1,2,3-butatriene derivatives in which cumulated double bonds are incorporated in a ring. In the molecules of these compounds, the cumulene fragment is not only bent; twist type distortion is also always observed. The properties of strained cyclic allenes have been analysed in several reviews (see, for example, reviews [291, 292]). Only few publications have been devoted to the study of molecules with predominating twist distortion such as [*n*.*n*]betweenallenes. In the known betweenallenes, the ζ angle between the planes formed by substituents at the terminal C(sp^2) atoms deviates insignificantly from 90°.[293, 294]



[*n*,*n*]betweenallenes

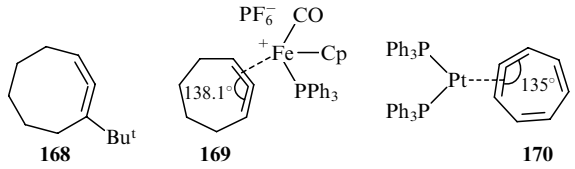
Even strain-free molecules of cumulenes are highly reactive (reactions involving them readily give stabilised intermediates).[295] Molecular distortions result in a further increase in reactivity and even in a qualitative change in the chemical properties of cumulenes.

1. Strained cyclic allenes

If the allene fragment is incorporated in a carbocycle that consists of not more than ten atoms, it inevitably becomes bent and, in addition, substituents tend to be arranged in one plane, which implies twist distortion. Model calculations showed that bending is always accompanied by twist — optimisation of an artificially bent system of two cumulated double bonds results in a twisted structure.[296] The strain energy of the molecules of cyclic allenes gradually increases up to $\varphi = 20°$ (by ~4 kcal mol^{-1}, according to the SCF/4-31 + G calulations);[297] however, subsequently it rises very steeply.

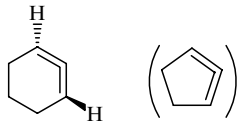
Even slight angle distortions in allene molecules entail a pronounced increase in the compound reactivity, which is anyway rather high, first of all in the tendency for polymerisation. 1,2-Cyclooctadiene the strain energy of which is calculated to be only

14 kcal mol^{-1}, has not yet been isolated in a pure state.[291] Bulky substituents at double bonds ensure the kinetic stability of allenes; the *tert*-butyl derivative of 1,2-cyclooctadiene **168** represents the smallest-ring carbocyclic allene that has been isolated at room temperature.[298] A cyclic allene with a smaller ring, 1,2-cycloheptadiene, has been stabilised in metal complexes. For compound **169**, X-ray diffraction data have been published,[299] pointing to a substantial distortion (bending and twist) of the allene fragment. Among metal complexes of this type deposited in the CSDB, the most pronounced bending of the allene fragment is found in the molecule of compound **170**, in which the φ angle is 135°.[300]



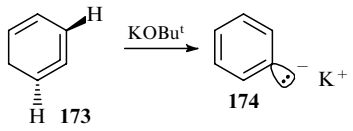
168 **169** **170**

1,2-Cyclohexadiene (**171**) has been known since 1968 when this compound was detected as a short-lived intermediate.[301] Later, it was detected by IR spectroscopy in an argon matrix at 11–170 K.[302] The compound **171** has now been thoroughly studied; according to calculations, the φ angle in this molecule is 138° (MINDO) or 134.8° (HF/6-31G**).[291] The attempts at synthesising 1,2-cyclopentadiene (**172**) have not yet met with success.[303]



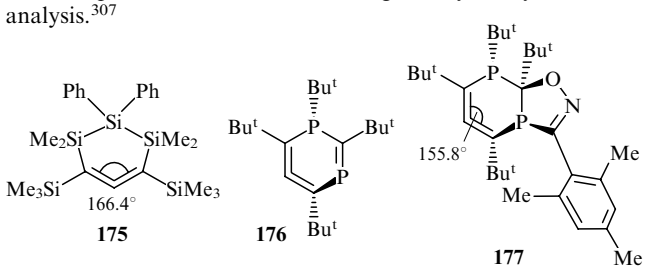
171 **172**

Cyclohexa-1,2,4-triene ('isobenzene') (**173**) has also been studied.[304] There is evidence that deprotonation of the compound **173** gives rise to the phenyl anion (**174**).[305]



173 **174**

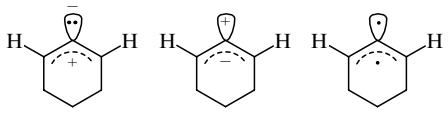
Stable six-membered heterocyclic compounds with a 1,2-diene fragment containing two or three heteroatoms, silicon and phosphorus, have been synthesised. The allene fragment in the cyclic allene **175** is less distorted than that in the six-membered carbocycle **171**; however, the former is stable, which allowed X-ray diffraction analysis of this compound.[306] According to X-ray diffraction data, the allene fragment is bent (φ = 166.4°) and the ζ angle between the Si—C(1)—C(2) and Si—C(3)—C(2) planes is 64.6°. Among stabilised cyclic compounds, the most distorted 1,2-diene group is found in diphosphaisobenzene **176**. A derivative of **176**, compound **177**, has been investigated by X-ray diffraction analysis.[307]



175 **176** **177**

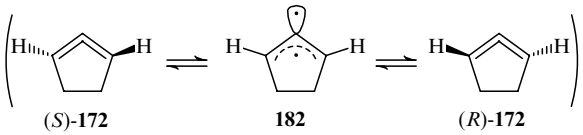
The values for the φ (155.8°) and ζ (40.7°) angles in the molecule **177** significantly depart from the ideal values (180° and 90°, respectively); steric shielding of the central fragment caused by the *tert*-butyl groups is responsible for the rather low reactivity of compound **177**.

The accumulated knowledge makes it possible to form a picture of molecular and electronic structures of highly strained allenes. Several variants of the spatial and electronic structures of these compounds can be suggested. For example, for 1,2-cyclohexadiene, apart from the chiral allene **171**, structures with the planar HC(1)C(2)H fragment and a non-bonding sp^2-hybridised orbital located in the plane of this fragment are also possible, *i.e.*, zwitter-ions **178**, **179**, and singlet (**180**) and triplet (**181**) biradical.



178 **179** S- **180**, T- **181**

The MCSCF/3-21G [308] and HF/6-31G* [309] calculations and experimental data [302, 309, 310] favour a non-planar chiral structure, at least, in 1,2-cycloheptadiene and 1,2-cyclohexadiene. The calculated τ angle at each double bond amounts to ~20°; this is sufficient for effective overlap of *p*-orbitals.[309] In the case of the 1,2-cyclopentadiene **172**, *ab initio* (STO, MP2/3-21G) calculations predict a relatively low energy barrier to racemisation (which might involve the intermediate formation of singlet biradical **182**) — 2–5 kcal mol^{-1} (see Ref. 311). This low value is within the error of the calculation techniques; therefore, experimental data are required to verify the results of theoretical methods.

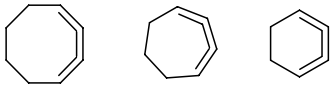


(*S*)-**172** **182** (*R*)-**172**

As regards the chemical properties of cyclic allenes, one should mention their enhanced tendency to enter into cycloaddition reactions, which were used in experiments on trapping short-lived molecules such as 1,2-cyclohexadiene. Strained allenes undergo the Diels–Alder reactions even with dienes having very low reactivity. These reactions are regioselective and *endo*-stereoselective; however, in the case of chiral allenes, no diastereoselectivity was observed. This fact was interpreted using the results of *ab initio* calculations (B3LYP/6-31G*),[312] which showed that in this case, the mechanism involving biradicals is preferred over the synchronous mechanism.

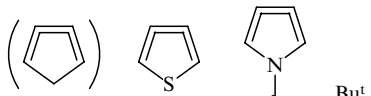
2. Cyclic butatrienes

The unstrained 1,2,3-butatriene fragment can be incorporated into a carbocycle if the number of carbon atoms in it is more than ten. Ring contraction causes bending of the linear C=C=C=C fragment, resulting in rehybridisation of carbon atoms and a substantial increase in the reactivity. Tentative experimental results showed [313] that, among unsubstituted cyclic 1,2,3-butatrienes, the minimum size of the ring which allows isolation of this compound at room temperature, is found in 1,2,3-cyclooctatriene (**183**). Homologues with smaller rings, 1,2,3-cycloheptatriene [314] (**184**) and a benzene isomer, 1,2,3-cyclohexatriene [315] (**185**), are highly reactive short-lived intermediates; only the products of cycloaddition of these species to dienes have been isolated.



183 **184** **185**

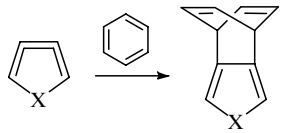
1,2,3-Cyclopentatriene (**186**) has not been prepared to date; however, its heterocyclic analogues, 3,4-didehydrothiophene (**187**) [316] and 1-*tert*-butoxycarbonyl-3,4-didehydro-1*H*-pyrrole (**188**),[317] have been synthesised, and their chemical properties have been studied using trapping reactions.



186 **187** **188**

The compound **187** was prepared and identified without substantial difficulties, although it is highly reactive. Meanwhile, the high reactivity of the heterocyclic triene **188** became a serious obstacle in the attempts to prove its existence. Among the strained butatrienes known currently, the geometry of the C=C=C=C system of bonds deviates most appreciably from linearity in the molecule **188**.[317]

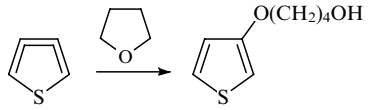
Cyclic 1,2,3-butatrienes, like highly strained allenes, readily react with dienes. The high reactivity of the compounds **187** and **188** can be illustrated by their reaction with benzene, which affords cycloadducts **189** and **190**.



189, **190**

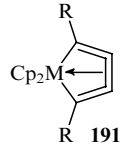
X = S (**189**), NCO_2Bu^t (**190**).

It was suggested that rehybridisation of the carbon atoms of the bent C=C=C=C system of bonds (like pyramidalisation of double bonds, see above) changes the electronic properties of the compounds **187** and **188** so dramatically that they can be regarded as biradicals. To support this, the researchers cited [316] reported the reaction of the heterocyclic triene **187** with tetrahydrofuran.



However, an ionic mechanism of this reaction is also possible. It has been shown above in relation to cubene that, even in the case of a very strong pyramidalisation of the carbon atoms of the double bond, alkenes do not exhibit properties of biradicals. Therefore, the conclusion that the compounds **187** and **188** are biradicals appears unlikely and requires further analysis.

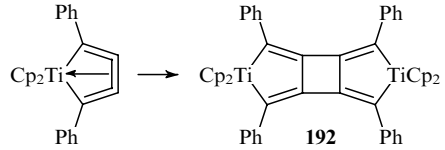
Among isolated and structurally characterised cyclic butatrienes, we shall consider metallacyclocumulenes (**191**) with a five-membered ring consisting of a 1,2,3-butatriene fragment and a metal (titanium or zirconium).[318]



191

M = Ti, R = Bu^t, Ph; M = Zr, R = Bu^t.

The stability of compounds of the type **191** is attributable to the additional stabilisation upon the coordination of the central double bond to the metal. This coordination changes the electronic structure of cumulenes; nevertheless, for some of the complexes **191**, dimerisaition to give radialene (**192**) has been observed.[319]

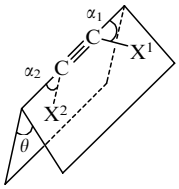


192

This reaction is also characteristic of purely organic strained cumulenes.[320] Metallacyclocumulenes have been investigated by X-ray diffraction analysis. The data obtained indicate that the central double bond is elongated and that the cumulene fragment deviates substantially from the linear geometry: the φ angle varies from 147° to 150°.

X. Bending of the $X^1-C\equiv C-X^2$ fragment

The unstrained $X^1-C\equiv C-X^2$ fragment is linear. The deviations of the bond angles at the carbon atoms from 180° are similar to the analogous deviations found in allene and butatriene molecules. The geometric distortions of the $X^1-C\equiv C-X^2$ fragment can be characterised by variation of the α_1, α_2 and θ angles.

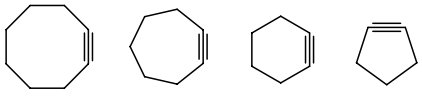


Below, we shall discuss the *cis*- ($\theta = 0°$) and *trans*- ($\theta = 180°$) bendings. Note that it is the *cis*-bending that is found in each organic molecule with a strained triple bond. The calculations showed, however, that *trans*-bending requires less energy than *cis*-bending (in a similar way as *anti*-pyramidalisation of the double bond is energetically more favourable than *syn*-pyramidalisation).[234] Probably, the lower energy of the transition state which contains a *trans*-bent fragment with a triple bond can account for the preferential *trans*-attack of alkyne molecules by nucleophilic reagents. This hypothesis has not been verified experimentally because no organic molecules with a *trans*-bent $X^1-C\equiv C-X^2$ fragment have been synthesised to date.

1. *cis*-Bending

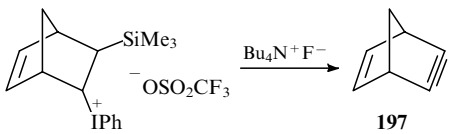
The only known way of realisation of *cis*-bending is incorporation of the $X^1-C\equiv C-X^2$ fragment into a ring or a polycyclic cage.[292, 321] This fragment is bent in carbocyclic alkynes with the number of carbon atoms not exceeding ten. The first strained cyclic alkyne, cyclooctyne (**193**), was synthesised in 1938;[322] later, it was isolated in a pure state.[323]

Cyclooctyne is smallest-ring carbocyclic alkyne stable at room temperature. Cycloheptyne (**194**) polymerises in less than 1 min even at −25 °C in dilute solutions (at −76 °C, it is stable over several hours).[324] Homologues with smaller ring sizes, cyclohexyne (**195**)[325, 326] and cyclopentyne (**196**),[327–333] are highly reactive. They have been detected as intermediates and studied in inert matrices.



193 **194** **195** **196**

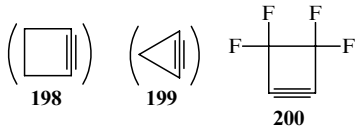
The highly strained molecules **194**–**196** can be prepared using elimination and cycloelimination reactions and by carbene rearrangements.[321] Elimination from appropriate precursors, hypervalent iodine compounds, has proved effective for this purpose.[334] Using this reaction, it was possible to prepare, perhaps, the most strained known (according to MP2/6-31G* calculations) carbocyclic molecule with a bent C−C≡C−C fragment, namely, bicyclo[2.2.1]hept-2-en-5-yne (**197**) molecule.[335]



197

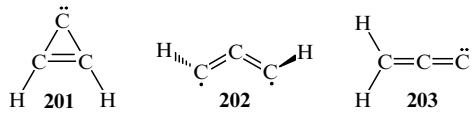
Cyclobutyne (**198**) and cyclopropyne (**199**) have not yet been synthesised. The results of calculations (MCSCF(4,4)/6-31G*, MP4/6-31G*//MP2/6-31G*) indicate that the compound **198** is

highly susceptible to a rearrangement to cyclopropylidenemethylene;[336] apparently, this makes this molecule 'elusive'. The existence of perfluorocyclobutyne (**200**) as an intermediate, possibly, more stable than **198**, has now been proven experimentally.[337] Metal complexes with cyclobutyne acting as a two-electron ligand have been prepared; however, cyclobutyne itself was not formed as an intermediate during the synthesis of these complexes.[338, 339]



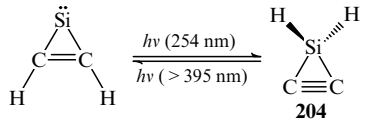
198 **199** **200**

The structure of cyclopropyne (unlike cyclobutyne) does not correspond to a minimum on the PES, even when the PES is calculated using advanced quantum-chemical techniques [such as SCF, TCSCF, CISD, TC-CISD/DZP; CCSD(T)/TZ(2df,2dp)];[340] Cyclopropyne is the only C_3H_2 isomer that has not yet been prepared. The other three isomers — cyclopropenylidene (**201**), propargylene (**202**) and propadienylidene (**203**), have been synthesised and studied in inert matrices.[341] It should be noted that investigation of the potential energy surface of C_3H_2 arouse considerable interest, among other reasons, due to the fact that the molecules **201** [342, 343] and **203** [344] were found in the interstellar space.



201 **202** **203**

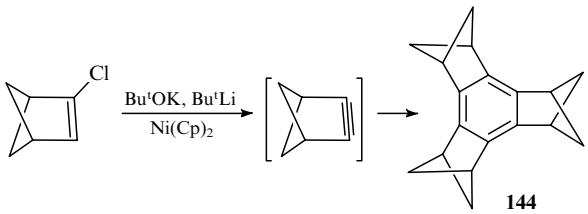
Maier *et al.*[345, 346] synthesised a heteroanalogue of cyclopropyne, silacyclopropyne (**204**).



204

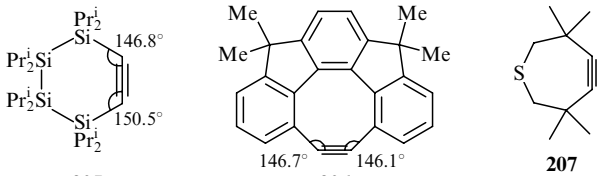
The identification of the compound **204** was at variance with the results of SCF/DZ calculations published previously, which indicated that the silacyclopropyne structure has properties of a saddle point rather than a minimum on the PES.[347] Maier *et al.*, who used higher-level calculations (MP2/6-31G**) demonstrated that the structure of **204** still corresponds to a local minimum on the PES; however, the IR frequencies they obtained differed somewhat from those observed experimentally. Only recent calculations [340] have given vibration frequencies on the basis of which the compound **204** was identified. The necessity of using advanced quantum-chemical methods for the prediction of properties of strained molecules such as **204** was demonstrated once again. The difference between the stabilities of cyclopropyne and silacyclopropyne can be explained by the difference between the energies of the carbenes and silapropadienylidenes $^{\cdot\cdot}C=C=XH_2$ (X = C, Si), which are formed presumably upon decomposition of the compound **199** and **204**. The energy of this species with X = Si is higher than the energy of the initial molecule **204**, whereas in the case where X = C, calculations predict the opposite situation.[346]

Cycloalkynes with a bent $X^1-C\equiv C-X^2$ fragment are susceptible to addition reactions with electrophiles, nucleophiles, and radicals.[321] Cycloaddition and oligomerisation also proceed with these molecules much more easily than with strain-free alkynes. Indeed, whereas cyclotrimerisation of strain-free alkynes requires catalysts (transition metal compounds), a similar reaction in the case of cyclic strained alkynes proceeds easily without catalysts. Moreover, the detection of benzene derivatives in the products of elimination reactions of cyclic alkenes can serve as evidence for the formation of highly strained alkynes as intermediates.[348] Trimerisation gave the above-discussed benzene derivative with annelated bicyclic fragments (**144**).



144

Cyclic alkynes stable due to either bulky substituents at the α-position relative to the C≡C bond (for example, as in molecule **205** [292]) or annelation of benzene rings (for example, as in molecule **206** [349]) have been studied by X-ray diffraction analysis. The search through the CSDB showed that in the molecules characterised by the most bent $X^1-C\equiv C-X^2$ fragment, the α_1 and α_2 angles approach ~30°.

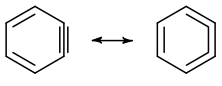


205 **206** **207**

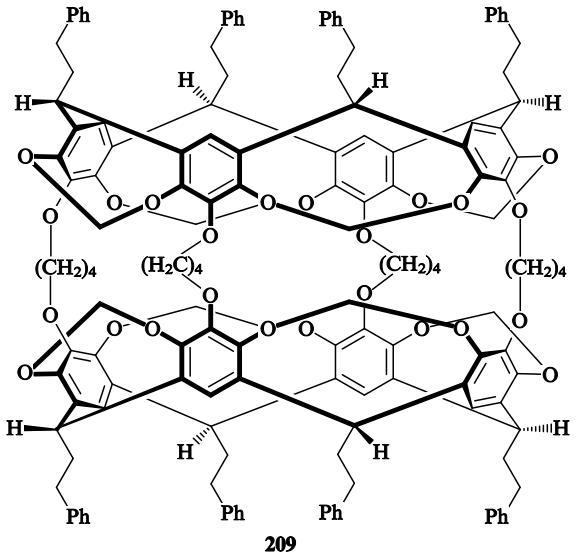
The structure of compound **207** has been studied by electron diffraction in the gas phase.[350–352]

The α_1 and α_2 angles in the molecule **207** are 34.2° and 30.7°, which is somewhat greater than those in **205** or **206**. Despite the pronounced bond angle distortions, the C≡C bond lengths in the compounds **205** and **207** remain within the limits typical of acyclic linear alkynes. Only in some cases (for example, in the molecule **206**), was the triple bond elongated (1.20–1.23 Å).

Finally, we should mention a new, original method of stabilisation of strained molecules and reactive intermediates, which allows one to gain spectroscopic data for these species in solutions at room temperature. The idea of this approach is to generate unstable molecules inside 'molecular vessels' — carcerands and hemicarcerands. Cyclobutadiene [353] and 1,2-dehydrobenzene (**208**) [354, 355] have been fixed in this way. Warmuth [354] has tackled the question whether the molecule **208** should be assigned to strained alkynes or to bent cumulenes. 1,2-Dehydrobenzene was prepared by exposure to UV light of benzocyclobutenedione inside hemicarcerand (**209**). For the compound **208** stabilised in



208a **208b**



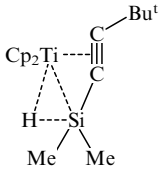
209

this way, it was possible to record the ^{1}H and ^{13}C NMR spectra before the compound has reacted with the host molecule.

Analysis of the NMR spectra led to quite an unexpected conclusion: the spectroscopic data are best described by a hybrid of two contributing structures, **208a** and **208b**, with a predominant contribution of **208b**. This interpretation, however, is inconsistent with the results of other studies (see, for example, Ref. 356).

2. *trans*-Bending

Synthesis of a molecule with a *trans*-bent $X^1-C\equiv C-X^2$ fragment is a difficult task: the shortage of substituents at a triple bond precludes creation of such a bending. However, *trans*-bending of an alkyne ligand can be attained in metal complexes. The first complex of this type **210** was prepared in 1995.[357]



210

A whole series of titanium and zirconium complexes of this type are currently known.[358] In the compound **210**, the agostic Si···H···Ti interaction ensures the *trans*-arrangement of substituents at the C≡C bond coordinated to titanium. The angles $\alpha_1 = 30.5°$ (for Si−C≡C) and $\alpha_2 = 44.8°$ (for C−C≡C) indicate a substantial distortion of bond angles at a triple bond. However, it should be noted that metal coordination also changes substantially the properties of a triple bond, for example, in the complex **210**, the bond length is increased to 1.275(9) Å.

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