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# The Strain Energy, Geometrical Structure, and Spin-Spin Coupling Constants of Cyclic Hydrocarbons

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The thermochemical data and spin-spin coupling constants (SSCC) are compared with the geometrical parameters of molecules investigated in the gas phase by electron diffraction and microwave spectroscopy. Cycloalkanes $C_nH_{2n}$, cycloalkenes $C_nH_{2n-2}$, cyclo-1,3-dienes, bicyclo[$n$.1.0]alkanes, and bicyclo[$n.m$.1]alkanes have been chosen as objects of investigation. Using the method of least squares, 13 empirical equations, relating the strain energy and the SSCC, on the one hand, to the internuclear distances and the valence and dihedral angles, on the other, have been fitted. The equations can be used to estimate the characteristics of compounds which have not been investigated.
The bibliography includes 170 references.

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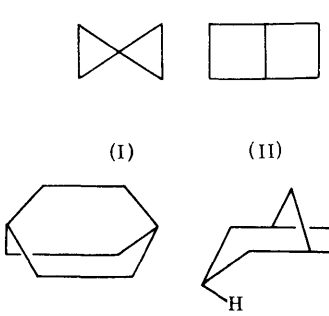
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## I. INTRODUCTION

Two features are characteristic of the concept of strain, which is widely used in organic chemistry. On the one hand, the fundamental postulates of the concept are intuitively understood and permit easy qualitative predictions; on the other hand, quantitative estimates are difficult and are of a conventional kind, because the concept of "strain" has no rigorous definition[1].

It has come to be assumed that the molecule has a certain excess energy if its geometrical parameters differ from those characteristic of the "unstrained" system, adopted by convention as the starting point for calculations, the reference system, or standard. In order to discover individual types of strain in the molecule, it is sometimes sufficient to inspect its structural formula. In other cases it is necessary to construct three-dimensional models or to carry out special calculations. We shall describe as an example several molecules whose geometry is known.

For example, angular strain can be specially readily deduced in the spiropentane (I).[2] The deformations of the internuclear distances are less evident, but it can be assumed that the common bond in bicyclo[2.2.0]hexane (II) [3] must be extended if it is supposed that the molecule is formed from cyclohexane by the insertion of a bond between the 1- and 4-positions. Bicyclo[2.2.2]octane (III) may serve as an example of a molecule with a dominant torsional strain (the presence of eclipsed conformations).[4] Finally, repulsive van der Waals interactions between non-bonded hydrogen atoms have an appreciable influence on the conformation of a molecule such as that of bicyclo[3.3.1]nonane (IV).[5]




(I) (II) (III) (IV)

Thermochemical data constitute the experimental basis for the quantitative estimation of the strain energy $E_S$. Information about the geometrical structure of the molecules has been most frequently resorted to for their interpretation, although quantitative correlations have not been analysed[6-10]. On the other hand, an appreciable parallelism between the changes in $E_S$ and molecular characteristics such as, for example, spectroscopic properties[11] and Compton profiles[12] has also been noted.

Comparison with the geometry is widely used also in the analysis of the spin–spin coupling constants (SSCC); the correspondence between the structure factors, the strain in the molecules, and the SSCC has been frequently pointed out in NMR studies.

For a number of reasons, cyclic hydrocarbons constitute the most promising objects for the search for a correlation between the above parameters:

$$E_s\text{-molecular geometry-SSCC.} \quad (1)$$

Firstly, cyclisation of a hydrocarbon is as a rule accompanied by considerable changes in its geometry, which lead sometimes to the appearance of strain amounting to several tens of kcal $mol^{-1}$. Secondly, cyclic hydrocarbons are the most important structural units in organic chemistry, forming sequences of molecules with similar structures gradually increasing in complexity, which are being actively investigated by thermochemical and NMR methods. Accurate geometrical data obtained in the gas phase are available for many compounds. This is very important because only in the gas phase is the molecular geometry closest to the equilibrium geometry as a consequence of the absence of intermolecular interactions[13].

In the present review an attempt is made to compile and survey the experimental data published up to 1979 and characterising the strain energy, the geometrical structure, and the SSCC of cyclic hydrocarbons and to analyse the relation between these parameters using a minimum number of assumptions. It was found that the relations between the parameters can be analysed only in relation to cycloalkanes, cycloalkenes, cyclo-1,3-dienes, bicyclo[$n$.1.0]alkanes, and bicyclo[$n.m$.1]alkanes, which have been most thoroughly investigated on the lines indicated. We confined ourselves to the consideration of only unsubstituted hydrocarbons, since little information is available about substituted cycloalkanes and it is non-systematic. An exception has been

made for hydrocarbons of the cyclopropane series in order to survey the numerous thermochemical data which have been published in the last decade.

## 1. Calculation of the Strain Energies

The strain energy $E_S$ of a cyclic compound is understood as the energy of the molecule in excess of that of the corresponding acyclic chain. The quantitative estimation of $E_S$ presents considerable difficulties and is of a conventional kind[1,10,14]. The energies $E_S$ can be estimated from the experimental enthalpies of combustion ($\Delta H_c^\circ$) or formation ($\Delta H_f^\circ$) and the enthalpies of hydrogenation ($\Delta H_h^\circ$) with the aid of additive computational schemes and by methods of calculation based on a mechanical model of the molecule and approximate quantum-chemical calculations.

Approximate quantum-chemical calculations of $E_S$ are performed comparatively rarely and are of interest for an approximate estimation of $\Delta H_f^\circ$.[15] In calculations on complex molecules by this method, it is necessary to introduce many approximations, which leads to a considerable freedom in the selection of parameters and discrepancies between the results obtained by different workers[16].

Within the framework of the mechanical model of the molecule[9] (the term "molecular mechanics" is used in the foreign literature[17,18]), the energies $E_S$ are calculated as sums of the individual contributions of the energies associated with the deformations of the bond lengths and angles (compared with ideal molecules), the torsional strain, and the interaction of atoms not linked by valence bonds. The method of molecular mechanics has been examined critically by Engler et al.[18] (see also other communications[19-21]).

The values of $E_S$ obtained by comparing the experimental $\Delta H_f^\circ$ with quantities calculated assuming additivity for hypothetical unstrained molecules with the same number and types of bonds are used in the present study. Hence it follows that the values of $E_S$ depend both on the reliability of the experimental thermochemical data and on the selected method for their calculation for the chosen unstrained reference molecules, which are usually open-chain analogues (as in structural studies).

Not all compounds with an open chain of carbon atoms are free from strain. In branched acyclic molecules repulsive interactions inevitably arise between non-bonded atoms (mainly *gauche*-interactions). In estimating $E_S$ one must therefore employ only computational schemes (based on the additivity of the bond energies or group contributions) in which the contribution of the *gauche*-interactions is isolated and highly branched acyclic molecules (for which interactions of another type are characteristic) are not considered. Table 1 presents the values of $E_S$ for cyclo-alkanes obtained by computational schemes of this type[10,22-24].

It follows from Table 1 that there are discrepancies between the values of $E_S$ even when isotypical computational schemes are used. For a comparison of the $E_S$, it is therefore desirable to employ the same computational scheme for all the compounds considered. In the present study the $E_S$ were evaluated by an additive scheme[22] in which the group contributions were obtained not only for hydrocarbons but also for their derivatives, which extends its applicability. The strain energy is defined as the difference between the experimental and calculated enthalpies of formation $\Delta H_f^\circ$:

$$E_s = \Delta H_{f(G),e}^\circ - \Delta H_{f(G),c}^\circ \qquad (2)$$

where $\Delta H_{f(G),c}^\circ$ is equal to the sum of the group contributions.

Table 2 presents only those group contributions which we used to calculate the $\Delta H_{f(G)}^\circ$ for hypothetical unstrained molecules corresponding to the hydrocarbon considered.

Table 1. The strain energies of cycloalkanes ($E_S$, kcal mol$^{-1}$) at 298 K.

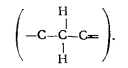
| $n$ | 1 [22] | 2 [10] | 3 [23] | 4 [24] | $n$ | 1 [22] | 2 [10] | 3 [23] | 4 [24] |
|---|---|---|---|---|---|---|---|---|---|
| 3 | 27.6 | 28.1 | 28.0 | 27.5 | 7 | 6.4 | 7.7 | 7.3 | 6.3 |
| 4 | 26.6 | 27.3 | 27.1 | 26.5 | 8 | 9.9 | 11.3 | 10.9 | 9.7 |
| 5 | 6.0 | 6.9 | 6.7 | 5.9 | 9 | 12.8 | 14.4 | 14.0 | 12.6 |
| 6 | 0.2 | 1.3 | 1.0 | 0.1 | 10 | 12.6 | 14.4 | 13.9 | 12.4 |

Notation: $n$ is the number of carbon atoms in the ring and the numerals 1, 2, 3, and 4 denote computational schemes. Note. The numbers in square brackets in this and other Tables as well as in the formulae in the text denote references (Ed.of Translation).

Table 2. The group contributions to $\Delta H_{f(G)}^\circ$ (kcal mol$^{-1}$) at 298 K*.

| Group | Contribution | Group | Contribution |
|---|---|---|---|
| C—$(C)_2(H)_2$ | —4.95 | C—$(C_d)_2(H)_2$ | —4.29 |
| C—$(C)_3(H)$ | —1.90 | $C_d$—(C)(H) | 8.59 |
| C—(C)$(C_d)(H)_2$ | —4.76 | $C_d$—$(C_d)$(H) | 6.78 |

*The designations of the groups are the same as in the review of Benson et al.[22] For example, C—(C)$(C_d)(H)_2$ means that the group contains a saturated carbon atom C linked to one similar carbon atom (C), to one carbon atom involved in a double bond ($C_d$), and to two hydrogen atoms $(H)_2$, i.e. it represents the group



The extent to which $E_S$ is arbitrary depends on the possibility of selecting an unstrained system (computational scheme), as mentioned above, and on the different influences (not taken into account when any computational scheme is employed) of (a) temperature, (b) zero-point energy (i.e. the energy of nuclear movement), and (c) the energy $p\Delta V$ on the $\Delta H_{f(G)}^\circ$ for the real cyclic molecule and the hypothetical molecule assumed to be unstrained.

It is necessary to estimate the limits within which the values of $E_S$ can vary as a result of the influences of the three factors.

(a) The heat capacities of acyclic hydrocarbons can be assumed to be additive. For example, the contribution of the group [C—$(C)_2(H_2)_2$], i.e. of —$CH_2$—, to $C_p$ is 5.5 cal mol$^{-1}$ K$^{-1}$.[11] The contribution of the —$CH_2$— group obtained from the experimental $C_p$ (25.40 cal mol$^{-1}$ K$^{-1}$) for cyclohexane[22] is 4.2 cal mol$^{-1}$ K$^{-1}$. Owing to the difference between the values of $C_p$ per —$CH_2$— group in the ring and in the hypothetical unstrained molecule, the value of $E_S$ for a six-membered ring is too low by more than 2 kcal mol$^{-1}$ at 298.15 K.

(b) The vibrational energy in n-alkanes can also be regarded as additive (on average, 17.50 kcal mol$^{-1}$ corresponds to the $-CH_2-$ group[25-27]). A specific vibrational energy different from that of a hypothetical unstrained molecule is characteristic of each cyclic compound, but the difference should not be large, because the main contribution to the zero-point energy comes from the vibration frequencies of the C–H bonds, which are comparatively insensitive to molecular structure. For the majority of hydrocarbons considered, the zero-point energy cannot be calculated because the complete set of vibration frequencies is unknown. Quantitatively this can be illustrated in only a few examples: the vibrational energy for cyclohexane, calculated as $N\sum_i \frac{1}{2}h\nu_i$ (where $N$ is the Avogadro number, $h$ the Planck constant, and $\nu_i$ the frequencies of the fundamental vibrations) is 104.5 kcal mol$^{-1}$,[26] while the value estimated from the group contributions ($6 \times 17.50$) is 105.0 kcal mol$^{-1}$; the corresponding values for cyclopentane are 86.0 and 87.5 kcal mol$^{-1}$ and those for cyclobutane are 67.3 and 70.0 kcal mol$^{-1}$. Consequently, according to these data, the value of $E_S$ may be too high owing to failure to take into account the difference between the zero-point energies, for example, by 3 kcal mol$^{-1}$ for cyclobutane. According to the results of another study[14], the energy $E_S$ for cyclobutane is too high by 4.6 kcal mol$^{-1}$ and the corresponding errors for three-, five-, and six-membered rings are 4.2, 3.7, and 3.4 kcal mol$^{-1}$.

**Table 3.** Changes in the strain energy ($\Delta E_S$, kcal mol$^{-1}$) on passing from a three-membered to a six-membered ring obtained from different thermodynamic quantities*.

| $n$ | $\Delta E$ | $\Delta E_0$ | $\Delta E_{298}$ | $\Delta E_S$ |
|---|---|---|---|---|
| 3–4 | 1.0 | 0.9 | 1.4 | 1.4 |
| 4–5 | 20.8 | 19.8 | 19.9 | 19.9 |
| 5–6 | 6.4 | 5.7 | 6.1 | 6.1 |

*Notation: $\Delta E$ are the differences between the strain energies obtained from the internal atomisation energies in the hypothetical equilibrium state at 0 K and 298 K; the $\Delta E_S$ were obtained from the enthalpies of atomisation at 298 K; $n$ is the number of carbon atoms in the ring.

The mutually compensating influences of the thermal (a) and zero-point (b) energies result in the approximate constancy of the differences in the $E_S$ on passing from one ring to another regardless of whether the thermal and zero-point energies are excluded or taken into account in the calculations. Table 3 presents the differences between the $E_S$ for several cycloalkanes according to Nelander and Sunner[14]. Consequently, in order to compare the $E_S$ for a specific series of compounds, one can also employ other available quantities, such as $\Delta H_f^\circ$ (298 K); here the error of the $E_S$ compared is 1–2 kcal mol$^{-1}$ (provided that the same additive scheme is used to calculate the $\Delta H_f^\circ$ of the unstrained molecules).

(c) The difference between the contributions of the energies $p\Delta V$ to $\Delta H_f^\circ$ for the cyclic compound and for the corresponding unstrained compound can be readily found from the relation $\Delta H_{f(G)}^\circ = \Delta U_{f(G)}^\circ + (1 - 1/2m)RT$ for compounds having the general formula $C_nH_m$. The difference between the $p\Delta V$ is incorporated in the $E_S$, where it is not constant (0.6 kcal mol$^{-1}$ for cycloalkanes and 1.2 kcal mol$^{-1}$ for bicycloalkanes) and will be eliminated in comparing the $E_S$ in a given series of compounds.

Next, a comparison will be made of the conventional values of $E_S$, obtained as differences between the experimental and calculated $\Delta H_{f(G)}^\circ$ [see Eqn.(2)] or calculated with the aid of a mechanical model[17,18] in the few instances when no experimental $\Delta H_f^\circ$ are available.

The experimental values of $\Delta H_f^\circ$ and the strain energies $E_S$ presented below are expressed in kcal mol$^{-1}$ and refer to 298.15 K. The errors in $\Delta H_f^\circ$ are expressed in terms of a 95% confidence interval and are given in round brackets. For example $\Delta H_{f(G)}^\circ$ for cyclopropane is 12.74(12) kcal mol$^{-1}$, i.e. in this case the error of the determination is 0.12 kcal mol$^{-1}$. In those cases where there are no experimental enthalpies of evaporation $\Delta H_v^\circ$, they were estimated from the Klages relation[28] in order to obtain $\Delta H_f^\circ$ for the gaseous state (the latter quantities are listed in the Table without an indication of the error).

## 2. Geometrical Parameters of the Molecules

The steric disposition of the atoms in the molecules can be described unambiguously by specifying the internuclear distances $r$ (the less rigorous term "bond length" is frequently used), the valence angles $\alpha$, and the dihedral angles $\tau$. The most accurate measurements of these molecular parameters are made in the gas phase by electron diffraction[13,29] and microwave spectroscopy[13,30]. The two methods yield geometrical parameters having a different physical significance and different indices and differing by an amount greatly exceeding the experimental error[31-33]. X-Ray diffraction analysis yields a third variety of geometrical parameters; therefore, in comparing data obtained by different methods, account must be taken of these differences.

However, even within the limits of each of the first two methods—electron diffraction and microwave spectroscopy—there exist a wide variety of parameters having a different significance. Readers wishing to make independently accurate comparisons of the internuclear distances should refer to the literature indicated above on the stereochemistry[13,30-33] and to the original studies. A rigorous comparison implies the employment of geometrical parameters of only one type within the limits of a given physical method.

In electron diffraction studies the final data are not presented in a unique manner and the authors quote distances designated by the symbol $r_g$ or $r_a$. They are related by the equation

$$r_g = r_a + u^2/r_a ,$$

where $u$ is the amplitude of the vibrations of pairs of atoms. The correction term $u^2/r_a$ can be usually readily calculated and it amounts to 0.002 and 0.006 Å for the C–C and C–H bonds respectively. Tables 4–9 (see below) present data taken directly from original communications without indication of the type of distance. The only exception has been made for cycloalkanes, in which all the distances have been recalculated on the $r_g$ basis to ensure a consistent comparison.

The distances designated by the symbols $r_0$ and $r_s$ can be obtained from microwave data. They are not simply related and there are no simple relations between them and the electron diffraction parameters $r_g$ and $r_a$.

The valence angles quoted in electron diffraction studies are believed to be the most reliable if they have been calculated taking into account the correction for the contraction effect[31]. Neglect of this correction can distort the valence angles by several degrees. The corrections are calculated on the basis of the theory of vibrations, provided that the force field of the molecule is known (for references to the last studies in this field, see Mastryukov and Dorofeeva[34]). The valence angles corrected for the contraction effect are designated by the symbol $\Phi_\alpha$ in order to show that they refer to a geometrically self-consistent $r_\alpha$ structure, in contrast to the $r_g$ and $r_a$ structures.

We shall now proceed to the description of the comparison of the geometrical parameters carried out to find correlations with $E_S$. For this purpose, it is desirable to employ a simplified equation for the calculation of the strain energy $E_S$ within the framework of the mechanical model (for more complex versions of the equation, see the relevant communications[18-21]):

$$E_s = E(r) + E(\alpha) + E(\tau) + E_{nv} = \\ = \frac{1}{2}K_r(r - r_0)^2 + \frac{1}{2}K_\alpha(\alpha - \alpha_0)^2 + \frac{1}{2}K_\tau(1 + \cos 3\tau) + E_{nv} \qquad (3)$$

Here each term refers to individual components of the strain mentioned previously: the deformation of the distances ($r$), the valence angles ($\alpha$), and the dihedral angles ($\tau$) and also the energies of non-valence interactions $E_{nv}$. The reference values are designated by the subscript 0.

It follows from Eqn.(3) that the strain energy is a complex function of many variables and by an empirical comparison one can only hope to find a parameter (or parameters) on which the $E_S$ for a series of molecules with similar structures depend preferentially. For this purpose, it is necessary to analyse three pair combinations: $E_S$–$r$, $E_S$–$\alpha$, and $E_S$–$\tau$. We shall not consider the non-valence interactions in quantitative terms and shall confine ourselves to referring to the system of van der Waals radii[35], which are usually resorted to for comparisons of this kind.

Inspection of Eqn.(3) shows that, for example, in the case of internuclear distances a linear correlation is to be expected in terms of the variables $E_S$ and $n(r - r_0)^2$, where $n$ is the number of deformed bonds. This is also true of the valence angles. However, tests have shown that the simplest relations of the type $E_S$–$(r - r_0)$ and $E_S$–$(\alpha - \alpha_0)$ are much more convenient and we shall henceforth employ these.

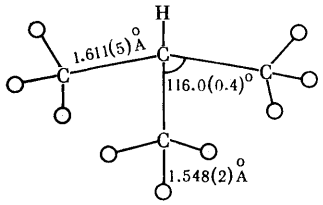
The second general observation about Eqn.(3) concerns the choice of the reference values of $r_0$ and $\alpha_0$. In the mechanical model these quantities are empirical parameters without physical significance and are selected to ensure the best agreement between the calculation and experiment. We prefer to employ geometrical data for the reference molecules investigated. Admittedly in most instances such choice is not of fundamental importance, since the relative changes in $r - r_0$ and $\alpha - \alpha_0$ are necessary only for a qualitative derivation of a correlation with $E_S$, and the final quantitative characteristics, i.e. the correlation equations, have been usually derived not for the relative but for the absolute values of the geometrical parameters. The correlation equations make it possible in their turn to estimate independently certain values of $r_0$ and $\alpha_0$ (see Section III).

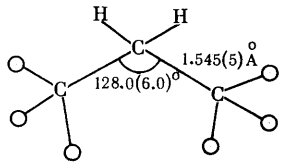
The selection of the reference values for the dihedral angle $\tau$, which should be 60° for the *gauche*-orientation and 180° for the *trans*-orientation in acyclic systems, presents a special difficulty[36]. However, cyclisation distorts these values so much that they become of little practical use for a comparison. Furthermore, in the majority of structural studies there is simply no explicit information about the dihedral angles. For these reasons, we confined ourselves to comparing certain dihedral angles in repeating fragments of similar molecules.

As already mentioned, the most suitable standard for saturated hydrocarbons is a normal chain with the *trans*-disposition of all the C–C bonds, although at the usual temperatures there is also a considerable amount of other conformers. Electron diffraction studies on alkanes ranging from ethane to n-heptane established that the average parameters of these molecules are appreciably constant and we shall use them henceforth for the comparison: the average distance $r_g$(C–C) = 1.533(1) Å† and the average valence angle ∠C–C–C = 112.6(0.1)°.[37,38] More detailed information about the structures of different hydrocarbons can be found in the book of Volkov et al.[13]

A recent investigation[39] showed that the above constancy of the C–C bond lengths breaks down on passing to higher alkanes. Thus the distance for $n$-$C_{16}H_{34}$ is 1.542(4) Å, which has been attributed to the influence of non-valence interactions. A reinvestigation of n-$C_4H_{10}$ [40] taking into account the contraction effect led to a more accurate C–C–C valence angle, equal to 113.8(0.4)°. We shall use the previous average value if only because in the majority of studies on cyclic hydrocarbons quoted here such corrections were not introduced.

Since the entire subsequent data refer to cyclic hydrocarbons, in conclusion of this section we shall present examples of strained acyclic molecules as an illustration. In such systems the strain increases with increasing branching of the chain, which is particularly notable for the t-butyl group. When two such groups are linked together, the distance between them is significantly increased and reaches 1.582(10) Å.[41] The greatest C–C distance (1.611 Å) has been recorded in the $(t\text{-}C_4H_9)_3CH$ molecule[42] and in the similar molecule of $(t\text{-}C_4H_9)_2CH_2$ [43] the C–C–C angle is appreciably increased. The structural data for these two unusual molecules are presented below (the methyl group is illustrated by a circle).




†As in the representation of the thermochemical data, here and henceforth the experimental errors referring to the last decimal places are given in round brackets, i.e. in this instance $r_g$ = 1.533 ± 0.001. A more detailed form of notation is usually employed for angles, i.e. 112.6(0.1)°, although a formulation of the type 112.6(1)° can also be encountered in the literature.

The strain has also distorted the conformational characteristics of the butyl and methyl groups for which the deviations of the dihedral angles $\Delta\tau$ from the staggered orientation, which serves as the starting point of the calculation ($\tau = 0°$), are presented:

| Molecule | $(t\text{-}C_4H_9)_3CH$ | $(t\text{-}C_4H_9)_2CH_2$ |
|---|---|---|
| $\Delta\tau$ ($C_4H_9$) | 10.8 (0.5)° | 15.1 (6.0)° |
| $\Delta\tau$ ($CH_3$) | 18.0 (6.0)° | 13.2 (7.0)° |

### 3. The Spin–Spin Coupling Constants

In the literature on the NMR spectroscopy of organic compounds a considerable number of publications (including review publications) are devoted to the discussion of the question of the correspondence between the spin–spin coupling constant (SSCC) and the structural, conformational parameters of the molecule[44–74]. The influence of molecular structure on the SSCC between the nuclei of like and unlike atoms, both linked directly and separated from one another, has been investigated. In connection with the development of $^{13}C$ NMR spectroscopy, there has been a growth of interest in recent years in the study of the SSCC between the carbon nuclei constituting the skeleton of an organic molecule. These constants are significantly smaller than the corresponding SSCC for protons, but this deficiency is compensated by the simplicity of the observation of the $J_{C-C}$.[71,75–77].

At the same time one should note that few systematic data, enabling one to trace the "geometry–SSCC" relation for a series of structurally similar compounds, are available. Among cyclic hydrocarbons, the SSCC for vicinal protons $^3J_{H-H}$ (the coupling constants of the $^1H$ nuclei via three bonds) and the coupling constants for the $^{13}C$ and $^1H$ nuclei via one bond $^1J_{^{13}C-H}$ (obtained either from high-resolution $^{13}C$ NMR spectra or by analysing the $^{13}C$ satellites in proton spectra), for which definite correlations with the structure have been established (see below), constitute an exception in this respect.

In this review we shall not be concerned with the theoretical aspects associated, in particular, with the mechanism of the spin–spin coupling, to which due attention has been devoted in the series of reviews quoted here. We shall only note that the true cause of the changes in the SSCC is still not altogether clear. They can be caused by an alteration of the *s* character of the corresponding orbital and hence can serve as a measure of the *s* character of the bond. (Minimum values of the $^1J_{^{13}C-H}$ constant are characteristic of carbon atoms with $sp^3$, $sp^2$, and *sp*-hybridisations, amounting to ~125, 156, and 250 Hz respectively.) Formulae linearly relating the degree of *s* character of the hybrid orbital of the carbon atom in the C–H bond to the $^1J_{^{13}C-H}$ constant have been proposed and have been frequently revised[44,78–86]. At the same time there exists the view that it would be premature to establish a quantitative correlation between the constant $^1J_{^{13}C-H}$ and the degree of *s* character and that it would be more correct to regard $^1J_{^{13}C-H} \cong 125$ Hz as a characteristic of tetracoordinate carbon with a tetrahedral environment[86,87].

The change in the SSCC may be a consequence of the change in the length of the corresponding bond caused by the deformation of the angles and the diminution of repulsive interactions[86]; in particular, an increase of the constant $^1J_{^{13}C-H}$ should then be expected. However, certain experimental and calculated data have shown that there is no direct relation between these quantities[48,58,67,68,79]. Despite the difficulty of interpretation, the correlation between the SSCC and the deformation of the structure is believed to have been reliably established[70]. However, one must not forget the definite (known) inaccuracy of the relations established is due to the fact that one of the parameters compared (SSCC) characterises the substance in the liquid state and the other (structural parameter) characterises the substance in the gaseous (or crystalline) state. One must also take into account the influence of the steric interactions of the neighbouring groups on the SSCC and hence the possibility of employing the observed correlations only within the limits of a series of isotypical compounds.

In this study we have analysed the "geometry–SSCC" relation on the basis of new experimental results or results which have been revised in recent years. We used mainly the constants $^1J_{^{13}C-H}$ and $^3J_{H-H}$, whose values for cyclic hydrocarbons are most systematic, as mentioned above. Certain bridged bicyclic hydrocarbons are an exception; successive changes in the SSCC between vicinal protons ($^2J_{H-H}$) and between protons via four bonds ($^4J_{H-H}$) have been described for these compounds.

## II. CORRELATION BETWEEN THE STRAIN ENERGY, THE GEOMETRICAL PARAMETERS, AND THE SPIN–SPIN COUPLING CONSTANTS

### 1. Cycloalkanes

#### (a) Correlation between the Strain Energy and the Structural Parameters

The structural data for cycloalkanes and the strain energies $E_S$ are listed in Table 4. The following dimensions are used in Tables 4–9 and in the text: kcal mol$^{-1}$ for $E_S$, Å for the internuclear distance, degrees (°) for the valence and dihedral angles, and Hz for the SSCC.

The conformational characteristics of these hydrocarbons are distinguished by their wide variety and are not susceptible to analysis on a single basis. Indeed, cyclopropane is a rigid system, cyclobutane is bent by an angle of 26°#, there is pseudorotation in cyclopentane, and cyclohexane exists in the chair conformation with a torsional angle of 54.5°. The conformations of cycloheptane, cyclooctane, and cyclodecane are also comparatively unrelated to the conformations of the preceding homologue. Since it is difficult to put forward a single scheme for the comparison of the dihedral angles in the above molecules, we shall confine ourselves to the consideration of the internuclear distances $r_g$(C–C) and the C–C–C valence angles. These geometrical parameters will be considered in much more detail for cycloalkanes than for other cyclic compounds, firstly in order to illustrate the approach employed, which is to a large extent repeated in the subsequent sections of the review and, secondly, because of the unusual nature of the results obtained for the cycloalkanes themselves.

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#The view has been established in the literature that the four-membered ring of cyclobutane is bent by an angle of ~35°.[104,105] In the latest electron-diffraction study it has been shown that allowance for the pendulum shifts of the methylene groups (for a more detailed description of this effect, see Mastryukov et al.[106]) leads to a significant decrease of the non-planarity of the cyclobutane ring, which confirms the results of non-empirical quantum-chemical calculations[107].

**Table 4.** The enthalpies of formation, strain energies, structural parameters, and SSCC of cycloalkanes*.

| Molecule | $\Delta H_f^\circ$(L) (expt) | $\Delta H_f^\circ$(G) (expt) | $\Delta H_f^\circ$(G) (calc.) | $E_s$ | $r_g$ (C–C) | $r_g$ (C–H) | ∠C–C–C, | ∠H–C–H | Ring shape | $^1J_{^{13}C-H}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_6$ | — | 12.74 (12) | —14.85 | 27.6 | 1.512 (2) [89]** | 1.095 (3) | 60.0 | 114.1 (1.0) | planar | 161 [44]; 162 [97, 98]; 160.45 [99] |
| $C_4H_8$ | 0.88 (12) | 6.79 (12) | —19.80 | 26.6 | 1.551 (3) [90] | 1.109 (6) | 88.5 | 107 (3) | bent by 26(3)° | 134 [44]; 136 (1) [97] |
| $C_5H_{10}$ | —25.60 (17) | —18.74 (19) | —24.75 | 6.0 | 1.546 (1) [91] | 1.113 (1) | 104.1 | 106.0 | non-planar; pseudorotation | 128 [44]; 131 (2) [97]; 128.221 (0.005) [100] |
| $C_6H_{12}$ | —37.36 (07) | —29.47 (07) | —29.70 | 0.2 | 1.536 (2) [92, 93] | 1.121 (4) | 111.4 (0.2) | 107.5 (1.5) | chair with a torsional angle of 54.9(0.4)° | 123 (124) [44]; 127 (2) [97]; 125.00 [101]; 124.56 [102] |
| $C_7H_{14}$ | —37.45 (12) | —28.25 (14) | —34.65 | 6.4 | 1.540 (1) [94] | 1.118 (3) | 115.3 (0.3) | | twisted chair*** | 122 [44]; 127 (2) [97] |
| $C_8H_{16}$ | —40.08 (22) | —29.73 (22) | —39.60 | 9.9 | 1.542 (5) [95] | 1.113 (15) | 116.6 | 108.0 | mixture of conformers | 123 [44]; 126 (2) [97] |
| $C_9H_{18}$ | —43.31 (22) | —31.74 (38) | —44.55 | 12.8 | | | | | | 125 (2) [97]; 124 (3) [103] |
| $C_{10}H_{20}$ | —49.40 (22) | —36.88 (36) | —49.50 | 12.6 | 1.545 (3) [96] | 1.115 (3) | 116.1 (1.1) | 105.4 | boat-chair-boat**** | 118 [44]; 121 (3) [103]; 126 (2) [97] |

*The experimental values of $\Delta H_f^\circ$ were taken from Pedley and Rylance[88].

**In this and subsequent Tables the references indicated for one of the geometrical parameters refer to all the structural data presented.

***The content of the main conformer was 76 ± 6%.

****The content of the main conformer was 49 ± 3%.

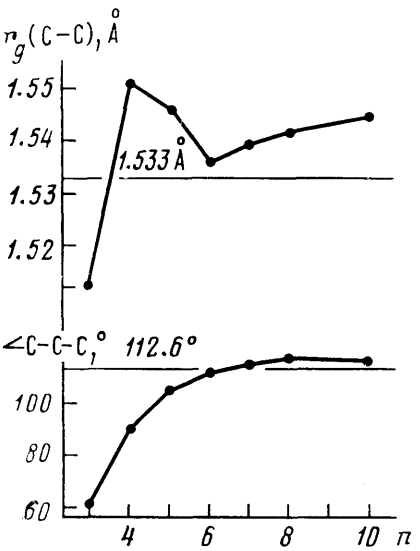



**Figure 1.** Variation of the C–C internuclear distances $r_g$ and the C–C–C valence angles in the cycloalkanes $C_nH_{2n}$ with ring size $n$. The horizontal lines correspond to reference values.

The distances $r_g$(C–C) and the valence angles in the cycloalkanes investigated are illustrated in Fig. 1. The range of variation of the distances (1.512–1.551 Å, i.e. ±2.5% relative to the average value) is significantly smaller than the range of variation of the valence angles (60–116.6°, i.e. ±64% relative to the average value). However, the variation of the internuclear distances is more complex, while the variation of the valence angles has the simpler form of curves with saturation§. The variation of the geometrical parameters of cycloalkanes expressed in this direct form has no analogy whatever with the variation of the $E_S$ for these compounds illustrated in Fig. 2.

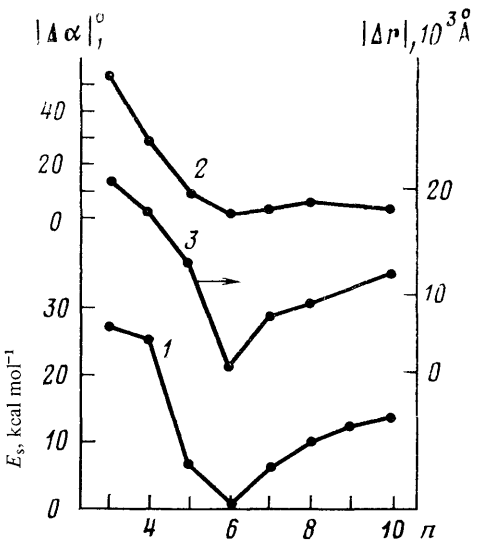



**Figure 2.** Variation of the strain energy $E_S$ (curve 1) and of the differences $\Delta\alpha = |112.6° - \alpha|$ (curve 2) and $\Delta r = |1.533 - r| \times 10^3$ (Å) (curve 3) in the cycloalkanes $C_nH_{2n}$ with ring size $n$.

§It is of interest to note that the introduction of a heteroatom into the cyclic system does not alter significantly the features found for hydrocarbons[108].

As mentioned above, the strain energies $E_S$ must be compared with the deviations of the geometrical parameters of the molecule under consideration from the reference values. Since the symmetrical deviations from the reference values must make the same contributions to the $E_S$ (in the mechanical model this phenomenon is described by Hooke's law), the absolute differences are employed for the comparison with the $E_S$: $\Delta r = |1.533 - r| \times 10^3$ Å for the C–C distances and $\Delta\alpha = |112.6° - \alpha|$ for the C–C–C angles. These differences are in fact illustrated in Fig. 2. It is quite evident that even such relative geometrical parameters reproduce correctly in qualitative terms the decrease of $E_S$ on passing from $C_3H_6$ to $C_6H_{12}$ with a subsequent increase on further ring expansion.

Fig. 2 shows that the curve illustrating the variation of the internuclear distances closely imitates the form of the $E_S$ curve. A direct confirmation of this observation follows from the correlation equations

$$E_s = -5.74 + 1.56\ \Delta r\ , \qquad (4)$$

$$E_s = 6.19 + 0.48\ \Delta\alpha\ , \qquad (5)$$

obtained by the least squares method and presented in a graphical form in Figs. 3 and 4. These relations clearly show that the values of $E_S$ for cycloalkanes are very closely related to the changes in the internuclear distances in these molecules.

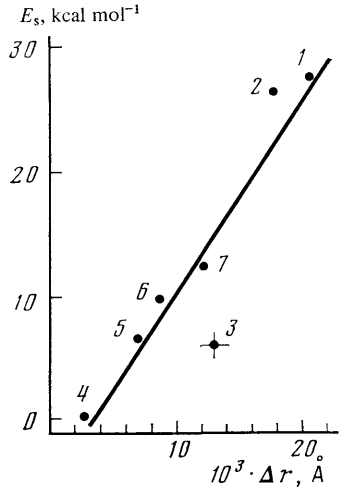



**Figure 3.** Variation of the strain energy $E_S$ with $\Delta r$ for different hydrocarbons: *1*) $C_3H_6$; *2*) $C_4H_8$; *3*) $C_5H_{10}$; *4*) $C_6H_{12}$; *5*) $C_7H_{14}$; *6*) $C_8H_{16}$; *7*) $C_{10}H_{20}$. The error in the measurement of the internuclear distances (±0.001 Å) and the approximate error in the estimation of $E_S$ (±1.5 kcal mol$^{-1}$) for cyclopentane as an example are indicated by horizontal and vertical lines; straight line—calculation by Eqn. (4).

As a consequence of the satisfactory linear relation between $E_S$ and $\Delta r$, Eqn. (4) can be used for quantitative estimates of the C–C distances in the hydrocarbons for which only thermochemical data are available. For example, the $rg$(C–C) = 1.545 Å distance has been estimated from $E_S$ in $C_9H_{18}$¶.

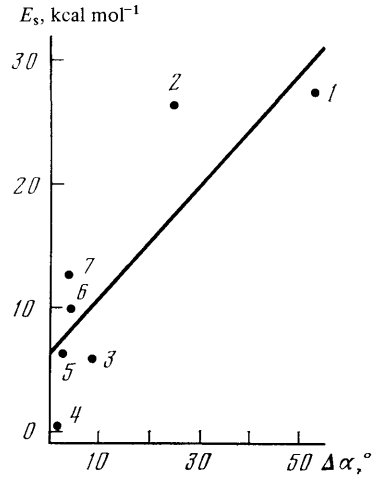



**Figure 4.** Variation of the strain energy with $\Delta\alpha$: *1*)–*7*) see Fig. 3; straight line—calculation by Eqn. (5).

The preferential correlation of $E_S$ with the deformations of the internuclear distances rather than the valence angles conflicts with the generally accepted hypothesis that the values of $E_S$ for cycloalkanes are mainly determined by the angular Baeyer strain. The same conflict obtains also in the mechanical model: a change in distances is believed to be so unfavourable energetically that in some calculations this effect is simply neglected[9].

In more accurate calculations[17–21] it is assumed that a 10% deformation of the C–C distances (for example, a change from 1.54 to 1.70 Å) is accompanied by a change in the strain energy by only 3.1 kcal mol$^{-1}$.[18] The result obtained in the above study shows that the changes in the C–C distances in the range 1.512–1.551 Å are satisfactorily correlated with the changes in $E_S$ in the range 0.2–27.6 kcal mol$^{-1}$. It is noteworthy that the cyclopropane molecule does not deviate from this relation, although it has the shortest bond. The minimum C–C distance in this compound has been interpreted by some workers within the framework of the special concept of "bent bonds".[13,109]

We do not believe that the above contradictions indicate deficiencies of the computational procedure based on the mechanical model, because our treatment is extremely limited and empirical, as already mentioned. Attention need only be drawn to the fact that the analysis of the direct dependence of $E_S$ on the geometrical parameters of cycloalkanes

¶The structural data for $C_7H_{14}$ have been published only recently[94] and the initial version of Eqn. (4) was therefore derived without taking them into account and had the form $E_S = -6.37 + 1.59\ \Delta r$. On substituting the value of $E_S$ for cycloheptane in this expression, it is possible to calculate $r_g$(C–C) = 1.541 Å, which is larger than the experimental value only by 0.001 Å.

can yield an interesting and unusual result, which was not discussed previously and which can be used to estimate internuclear distances from thermochemical data (or conversely). Cycloalkanes occupy a special position, because the strain energies of cycloalkanes and bicyclic hydrocarbons are better correlated with the deformation of the valence angles (as will be seen from the exposition below).

We shall not deal with the H–C–H angles whose deformation also contributes to the strain energy, because the angles ∠C–C–C ($\alpha$) and ∠H–C–H ($\beta$) vary in a concerted manner[110] in accordance with the linear equation

$$\beta = 126.1 + 0.17\,\alpha \ .$$

As a result of this relation, the behaviour of the difference $\Delta\alpha$ illustrated in Fig. 4 should reflect correctly the overall deformation component of the strain energy in cycloalkanes.

As already mentioned in the introduction, substituted cyclic hydrocarbons will not be considered systematically. The only exception was made for hydrocarbons of the cyclopropane series. In recent years extensive experimental data have accumulated for the $\Delta H_f^\circ$ of cyclopropanes which have not been surveyed. Using these data, we considered the influence of the introduction of substituents of different types on the $E_S$ for the three-membered ring. The data in Table 5, which lists the values of $\Delta H_f^\circ$ and $E_S$ for substituted cyclopropanes and cyclopropenes, show that $E_S$ is constant (27–28 kcal mol$^{-1}$), within the limits of the error of the determination, for all saturated hydrocarbons with the exception of the seventh and eighth compounds†. The strain energy $E_S$ of alkenyl derivatives of cyclopropane with the double bond separated from the ring by a $\sigma$-bond is close to $E_S$ for cyclopropane itself, which indicates either the absence of an effect of $p-\pi$ conjugation or its very small magnitude. The introduction of an exocyclic or endocyclic double bond greatly increases $E_S$ for the three-membered ring.

The estimated strain energy per trigonal atom in cyclopropene, evaluated as half the difference between the values of $E_S$ for cyclopropene and cyclopropane, is 13.1 kcal mol$^{-1}$. Subsequent calculation of $E_S$ for methylenecyclopropane, defined as the sum of $E_S$ for cyclopropane and 13.1 kcal mol$^{-1}$, leads to 40.7 kcal mol$^{-1}$, which fully agrees with the value calculated from the experimental $\Delta H_{f(G)}^\circ$ for methylenecyclopropane (Table 5). This agreement suggests that the contributions of the trigonal carbon atom (*endo*- or *exo*-) to the strain energy in the systems considered are approximately the same.

Thus the data presented show that the introduction of the substituents into the molecule hardly alters the overall strain energy. At the same time in approximate quantum-chemical calculations[116] a relatively strong steric interaction between the $CH_3$ groups is postulated.

### (b) Correlation between the Structural Parameters and the SSCC

On the basis of the changes in the constants $^1J_{^{13}C-H}$ in the series of cyclic saturated hydrocarbons (ranging from cyclopropane to cyclododecane), a linear correlation was observed as early as 1963 between the SSCC and the angle ∠C–C–C, described by the equation[44]

$$^1J_{^{13}C-H} = 203 - 0.720\,\alpha \ . \qquad (6)$$

Using Foote's data[44], Mislow[57] derived a correlation equation expressing the dependence of the constants $^1J_{^{13}C-H}$ not on the angle $\alpha$ but on the interorbital angle $\alpha_{orb}$ (which reflects the state of hybridisation and is determined from the relation $\alpha_{orb} = 0.1340\alpha + 94.83$).[57] However, calculation of the above constant by Eqn. (6) using modern values of the geometrical parameters (Table 4) yields values of $^1J_{^{13}C-H}$ which differ appreciably in many instances from the experimental values.

**Table 5.** The enthalpies of formation and strain energies of substituted cyclopropanes and cyclopropenes.

| Molecule* | $\Delta H_{f(L)}^\circ$ ** | $\Delta H_{f(G)}^\circ$ | $E_S$ | References |
|---|---|---|---|---|
|  | — | 12.74 (12) | 27.6 | [88] |
|  | 0.41 (16) | 5.8 | 27.7 | [88] |
|  | −5.92 (19) | 0.8 | 27.6 | [88] |
|  | −7.97 (19) | −1.97 (30) | 27.6 | [88] |
|  | −6.29 (16) | 0.4 | 29.3 | [88] |
|  | −7.34 (19) | −0.9 | 28.0 | [88] |
|  | −22.99 (20) | −15.7 | 20.9 | [88] |
|  | −28.63 (22) | −20.6 | 23.7 | [88] |
|  | −21.57 (24) | −13.6 | 27.9 | [88] |
|  | −27.74 (40) | −18.5 | 28.0 | [88] |
|  | −46.14 (54) | −33.8 | 27.5 | [88] |
|  | 22.9 (90) | 30.9 (90) | 27.3 | [88] |
|  | 29.3<br>23.6<br>24.5 (20) | —<br>—<br>31.3 (30) | —<br>—<br>27.8 | [111]<br>[112]<br>[113] |
|  | 14.51 (30) | 22.4 | 27.4 | *** |
|  | 46.80 (50) | 55.8 | 28.6 | *** |
|  | 62.40 (20) | 69.8 (40) | 26.7 | [113] |
|  | — | 47.9 (40) | 40.8 | [88] |
|  | — | 94.6 (280) | — | [114] |
|  | — | 66.2 (60) | 53.8 | [88] |
|  | — | 58.2 (20) | 53.7 | [88] |
|  | 32.8 (50) | 39.6 (110) | — | *** |

*R = $CH_3$, $R^1 = C_2H_5$, $R^2 = C_3H_7$, and $R^3 = C_6H_{13}$.

**Turner et al.[115] determined the enthalpies of hydrogenation of methylmethylenecyclopropane, ethylidenecyclopropane, and 1,2-dimethylcyclopropene in solution in acetic acid at 25 °C. We did not calculate the values of $\Delta H_{f(G)}^\circ$ from these data, because the differences between the enthalpies of evaporation and solution are unknown.

***S.M.Pimenov's data (Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1982).

†The $\Delta H_f^\circ$ for 1,1,2-trimethyl- and 1,1,2,2-tetramethylcyclopropanes and vinyl-cyclopropane should be redetermined.

Fig.5 presents the changes in the constant $^1J^{13}C-H$, the C–C–C valence angles, the C–C internuclear distances, and the $E_S$ (the data from Table 4) for the series of compounds considered on passing from cyclopropane to cyclododecane (the geometrical parameters of cyclononane have still not been determined). It shows that the SSCC vary almost in parallel with the variation of the C–C–C angle only.

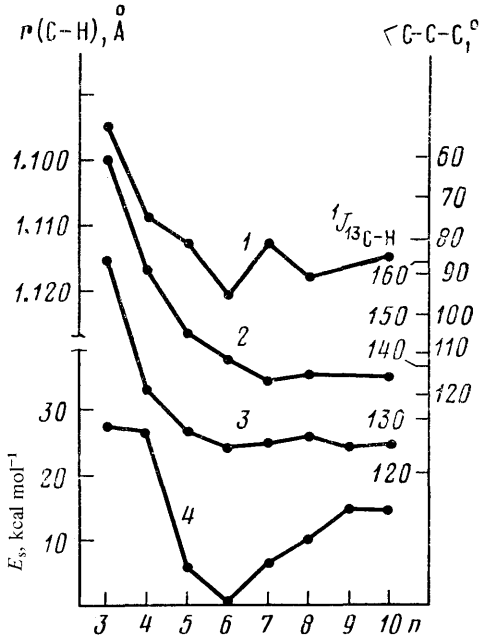



**Figure 5.** Variation of the C–H internuclear distances (curve *1*), the C–C–C valence angles (curve *2*), $^1J^{13}C-H$ (curve *3*), and $E_S$ (curve *4*) in cycloalkanes with ring size *n*.

On the basis of the data presented, a linear relation was obtained between $^1J^{13}C-H$ and the C–C–C angle ($\alpha$) for cycloalkanes ($^1J^{13}C-H = 195.7 - 0.632\alpha$), which, however, is characterised by a relatively small but appreciable scatter of the points. If the data corresponding to cyclopropane are disregarded in the calculation, then the above relations for the series of saturated cyclic hydrocarbons ranging from cyclobutane to cyclohexane fit satisfactorily on a straight line. The relation between $^1J^{13}C-H$ and ∠C–C–C for the series of cycloalkanes is best described by the parabolic equation (Fig.6)

$$^1J_{^{13}C-H} = 0.0073\,\alpha^2 - 1.963\,\alpha + 251.715 \quad . \qquad (7)$$

On the basis of the observed relation between $E_S$ and the C–C distance [Eqn.(4)], the unknown average internuclear distances in cyclononane were estimated previously. Using Eqn.(7), it is also possible to find the average C–C–C angle in this hydrocarbon; it amounts to 111° (in agreement with the data in Table 4). Eqn.(7) satisfies the corresponding parameters of propane[117] and, which is particularly interesting, strained compounds such as bicyclo[2,2,1]-heptene and bicyclo[2,2,1]hepta-2,5-diene (for the $^1J^{13}C(7) - H$ and the corresponding angles, see Table 9 below).

## 2. Cycloalkenes

### (a) Correlation between the Strain Energy and Structural Parameters

The structural data and the strain energies $E_S$ for cycloalkenes are presented in Table 6. *cis*-But-2-ene serves as a suitable standard for comparisons in this series of compounds[131]. The required parameters of this molecule are the C–C distance [1.506(2) Å], the C = C distance [1.346(3) Å], and the C–C = C angle [125.4(0.4)°]. We shall consider initially the C–C and C = C distances. Comparison with the distances in the standard reveals the following features: cyclopropene should be just as strained as cyclohexene, but both these compounds are less strained by a factor of ~1.5 than cyclo-octene. The data presented in no way agree with the $E_S$ curve in Fig.7.

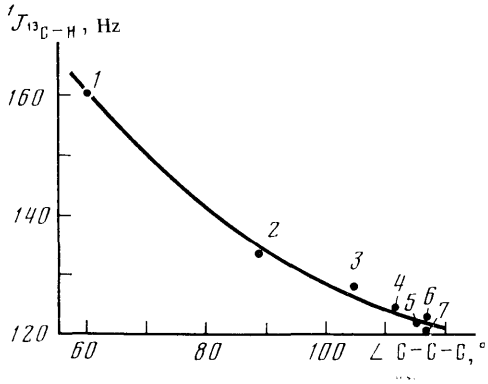



**Figure 6.** Variation of $^1J^{13}C-H$ with the C–C–C angle for cycloalkanes: *1*)–*6*) see Fig.3; *7*) $C_9H_{18}$; curve—calculation by Eqn.(7).

On the other hand, there is a satisfactory agreement between this curve and the variation of the C–C = C ($\alpha_1$) ($\Delta\alpha_1 = 125.4 - \alpha_1$) and the C–C–C ($\alpha_2$) ($\Delta\alpha_2 = 112.6 - \alpha_2$) angles, illustrated in Fig.7. Since the differences $\Delta\alpha_1$ and $\Delta\alpha_2$ have non-alternating signs, the conclusions are independent of the type of standard within the limits of a single sequence of molecules. In this case it is more useful to find correlation equations using the geometrical parameters themselves rather than the above differences#. For the above angles, the equations assume the following form:

$$E_S = 111.2 - 0.895\,\alpha_1 \quad . \qquad (8)$$

$$E_S = 100.6 - 0.894\,\alpha_2 \quad . \qquad (9)$$

Their graphical representation is illustrated in Fig.8. The parallel arrangement of the straight lines obtained on the basis of Eqns.(8) and (9) is striking. Thus, in contrast to cycloalkanes, a correlation of the strain energy only with the deformations of valence angles is characteristic of their unsaturated analogues.

#We shall adhere to a similar approach henceforth; for a qualitative determination of correlations involving $E_S$, the relative changes in the geometrical parameters are usually employed, but in the final equations the structural parameters are used directly.

**Table 6.** The enthalpies of formation, strain energies, structural parameters, and SSCC of cycloalkenes.

| Molecule | $\Delta H^\circ_{f(L)}$ | $\Delta H^\circ_{f(G)}$ | $E_s$ | CC and CH bonds | Valence angles | Dihedral angles | $^1J_{^{13}C-H}$ | $^3J_{H-H}$ |
|---|---|---|---|---|---|---|---|---|
|  | — | 66.23 (60) | 53.3 | 1—2 1.304 (3) [119, 120]<br>1—3 1.519 (2)<br>1—H 1.077 (12)<br>3—H 1.112 (15) | 2—1—H 132.9 (2.5) | — | 226 [127];<br>220 [128];<br>228.2 [129] | 1.3 [127, 129] |
|  | — | 37.45 (36) | 29.8 | 1—2 1.342 (5) [121]<br>1—4 1.517 (5)<br>3—4 1.566 (5)<br>1—H 1.083 (5)<br>3—H 1.094 (5) | 1—2—3 94.2 (0.5)<br>2—3—4 85.8 (0.5)<br>2—1—H 133.5 (0.5)<br>H—3—H 109.2 (0.5)<br>4—3—H 114.5 (0.5) | — | 170 [45, 130] | 2.7 [46];<br>2.85 [130] |
|  | 1.10 (41) | 7.81 (41) | 5.1 | 1—2 1.546 (35) [122]<br>2—3 1.519 (30)<br>3—4 1.342 (10)<br>C—H$_{av}$ 1.098 (6) | 2—3—4 111.0 (1.2)<br>H—1—H 104.8<br>H—2—H 101.8<br>3—4—H 143.5 | 2—1—5 / 2—3—4—5 28.8 (2.5) | 160 (1) [47];<br>161.6 [48] | 5.1 [46];<br>5.4 (0.1) [47];<br>5.57 [48, 49] |
|  | —9.11 (10) | —1.10 (12) | 1.1 | 1—2 1.335 (3) [123—125]<br>2—3 1.504 (6)<br>3—4 1.515 (20)<br>C—H 1.093 (15) | 1—2—3 123.5<br>2—3—4 112.1<br>3—4—5 111.0 | 1—2—3—4 —15.2<br>2—3—4—5 44.9<br>3—4—5—6 —60.2 | 157 [47];<br>158.4 [48] | 8.8 [46]; 9.6 [47];<br>10.11 (0.05) [48, 49] |
|  | — | —2.25 (22) | 4.9 | — | — | — | 156.2 [48] | 10.8 [46];<br>11.02 [48] |
|  | — | —6.45 (26) | 5.7 | 1—2 1.332 (3) [126]<br>2—3 1.499 (8)<br>3—4, 4—5, 5—6 1.549 (2)<br>3—H 1.110 (2)<br>1—H 1.103 | 1—2—3 121.9 (0.8)<br>2—3—4 104.6 (0.4)<br>3—4—5 113.8 (0.4)<br>4—5—6 118.8 (0.6)<br>2—1—H 118.4 (2.0)<br>H—C—H 106.8 (1.7) | 8—1—2—3 136.0 (0.4)<br>1—2—3—4 —91.1 (0.8)<br>2—3—4—5 54.2 (1.0)<br>3—4—5—6 —82.8 (0.6)<br>4—5—6—7 111.8 (1.0)<br>H—1—2—H 177.6 (11.2) | 156.0 [48] | 10.3 [46];<br>10.41 [48] |

Note. Here and henceforth the atoms are numbered in accordance with data obtained in structural studies. The experimental values of $\Delta H^\circ_f$ were taken from Pedley and Rylance[88]. The dihedral angles in this and subsequent tables are presented in a dual form. The first has the usual significance, for example, $\tau(1-2-3-4)$ denotes the angles between the planes drawn through the 1—2—3 and 2—3—4 carbon atoms. The second designation is in the form of a fraction in which the planes between which the angle is measured are indicated in the numerator and denominator.

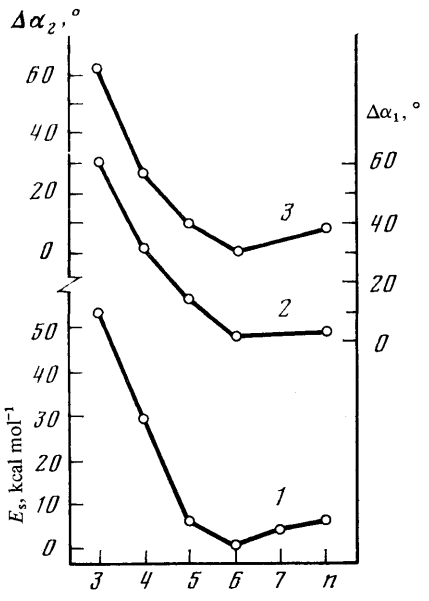



**Figure 7.** Variation of the strain energy $E_S$ (curve *1*) and the differences $\Delta\alpha_1 = 125.4° - \alpha_1$ (curve *2*) and $\Delta\alpha_2 = 112.6° - \alpha_2$ (curve *3*) in the cycloalkenes $C_nH_{2n-2}$ with ring size *n*.

### (b) Correlation between the Structural Parameters and the SSCC

It is known that in the series of *cis*-cyclo-olefins there exists a definite relation between the SSCC of the vinyl protons and the ring size[45—48,50,56,68]. The change in the constant $^3J_{H-H}$ is more likely to be due to the local geometry about the double bond[45,46] (the C = C interatomic distances and the C = C—C and C = C—H angles) rather than the overall strain energy of the molecule. The empirical correlations derived by different investigators between the above constants and the C = C interatomic distances are similar and correspond to an increase of the constant $^3J_{H-H}$ by ~0.6—0.7 Hz as the C = C bond length diminishes by 0.02 Å.[68] The comparisons of the above relations with experimental data have shown, however, that there is no direct relation between the constants $^3J_{H-H}$ and the C=C bond length[48,49,68]. Thus the change in the C = C internuclear distance from 1.342 Å in cyclobutane to 1.332 Å in cyclo-octene should have corresponded to an increase of the constant $^3J_{H-H}$ by ~0.3 Hz, while in reality the difference between the constants is ~7.5 Hz.

The relation between the constants $^3J_{H-H}$ and the C = C—H angles has been shown by the analysis of the study of Cooper and Manatt[48] to be close to the predicted theoretical relation[55], the sensitivity of the SSCC to the change in ∠C = C—H being particularly notable for angles close to 120°. The C = C—H angle is found from the C = C—C angles, which

are more readily determined experimentally, using the relation $\angle C = C-H \cong (360 - \angle C = C-C)/2$. Calculation of the dependence of the constants $^3J_{H-H}$ on the C = C–C and C = C–H angles for *cis*-buta-1,3-diene (for changes in the angles from 108° to 123° and from 114° to 124° respectively) showed that the size of the angles has an appreciable influence on the constant; the dependence of $^3J_{H-H}$ on the C = C–C angle is more explicit than that of the C = C–H angle[68].

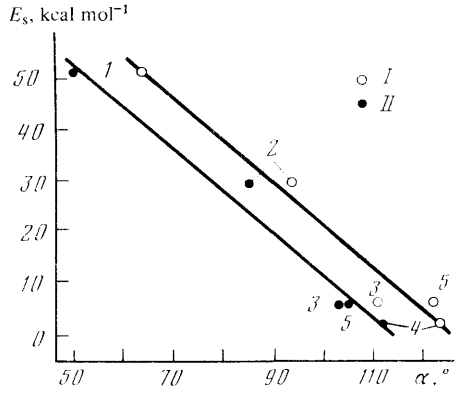



**Figure 8.** Variation of the strain energy with the C–C = C (*I*) and C–C–C (*II*) valence angles for different hydrocarbons: *1*) $C_3H_4$; *2*) $C_4H_6$; *3*) $C_5H_8$; *4*) $C_6H_{10}$; *5*) $C_8H_{14}$; *I*) calculated by Eqn.(8); *II*) calculated by Eqn.(9).

Comparisons have also been made between the structural parameters of cyclo-olefins and the constants $^1J_{^{13}C-H}$.[52,54,72] A linear relation has been established between the constant $^1J_{^{13}C-H}$ and the C = C–C angle for a series of unsaturated compounds of different types[54]. (However, the points corresponding to cyclobutene and cyclopentene do not fit on the resulting straight line.)

Fig.9 presents the variation of $^1J_{^{13}C-H}$, $^3J_{H-H}$, the C = C–C angles, the C = C distances, and the strain energies $E_S$ (according to the data in Table 6) in the series of compounds investigated ranging from cyclopropene to cyclo-octene. It is seen that the SSCC and the C = C–C angle vary in parallel, the parallelism breaking down on passing from cyclopropene to cyclobutene. There is no correspondence whatever between the variations of both SSCC and the C=C bond length; nor is there a full correlation (particularly of the constant $^1J_{^{13}C-H}$) with the strain energies $E_S$.

The linear equations describing the relations between the SSCC and $\angle C = C-C$ ($\alpha$) ($^1J_{^{13}C-H} = 277.5 - 1.014\alpha$; $^3J_{H-H} = -9.88 + 0.1556\alpha$) do not reflect the observed relation in a sufficiently clear-cut manner. (As for cycloalkanes, the linear correlation holds when data corresponding to the three-membered unsaturated ring are rejected in the calculation.) The dependence of the SSCC on $\angle C = C-C$ ($\alpha$) has been studied most completely and in this instance is described by the parabolic equations (Figs.9 and 10)

$$^1J_{^{13}C-H} = 0.0195\,\alpha^2 - 4.720\,\alpha + 443.327\ , \qquad (10)$$

$$^3J_{H-H} = 0.0039\,\alpha^2 - 0.579\,\alpha + 22.465\ . \qquad (11)$$

The question of the reason for the deviations from the linear relation of the corresponding parameters of both saturated and unsaturated three-membered rings (if the accuracy of the determinations of the quantities compared is assumed to be adequate) still remains open. Owing to the lack of systematic, uniform data for a large number of the hydrocarbons considered (in the series of cycloalkenes the entire calculation is in fact based on the parameters for 4–5 compounds), it is difficult to reach a definite conclusion. Possibly the deviations are caused by the extremum values of the geometrical parameters or a significantly different hybridisation of the carbon atom in three-membered cyclic compounds, which occupy an intermediate position between saturated, unsaturated, and acetylenic hydrocarbons.

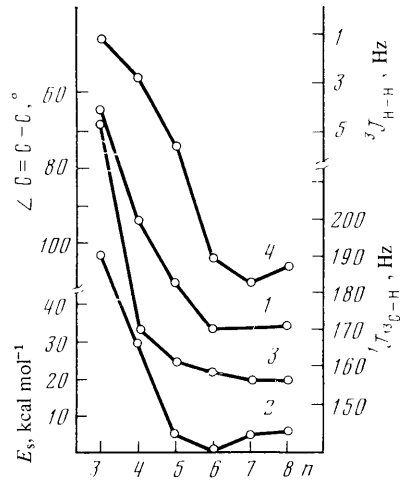



**Figure 9.** Variation of the C = C–C valence angles (curve *1*), $E_S$ (curve *2*), $^1J_{^{13}C-H}$ (curve *3*), and $^3J_{H-H}$ (curve *4*) in cycloalkenes with ring size *n*.

It is noteworthy that Eqn.(10) is also characteristic of certain other unsaturated compounds, particularly of ethylene[117], cyclohexa-1,4-diene[67], cyclo-octatetracene[52], bicyclo[2,2,1]hept-2-ene[118], and bicyclo[2,2,2]octa-2-ene[48], while correlation (11) holds satisfactorily both for the above hydrocarbons and in addition for cyclopenta- and cyclohexa-1,3-dienes[67] and cycloheptatriene[68].

### 3. Cyclo-1,3-Dienes

Few data are available for cyclopolyenes and they are not susceptible to analysis on a common basis (Table 7). In agreement with previous observations, the strain energy $E_S$ is a minimum for the six-membered ring, although the transition from the five- to the six-membered system is accompanied by only a slight decrease of $E_S$, amounting to 0.6 kcal mol$^{-1}$ (the analogous decrements in the series of cycloalkanes and cyclo-olefins are 5.8 and 4.0 kcal mol$^{-1}$ respectively).

It follows from Table 7 that the main internuclear distances (C = C, =C–C=, and =C–C–) in the dienes considered are equal within the limits of experimental error. The only

notable change occurs in the valence angles on ring expansion. For example, the C = C–C(=) valence angle§ increases in the series of compounds considered (109.21°, 120.13°, 129.1°, and 129.0°), which does not agree with the variation of $E_S$. Thus, for the given class of compounds, it is so far impossible to discover the geometrical parameter which is most closely related to the changes in $E_S$ or the SSCC $^3J_{H-H}$ of vinyl protons).

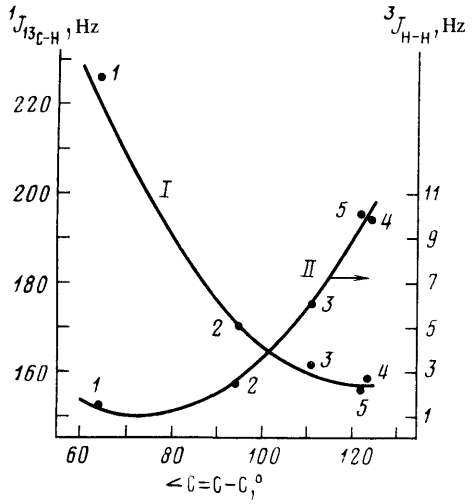



**Figure 10.** Variation of $^1J_{^{13}C-H}$ (curve *I*) and $^3J_{H-H}$ (curve *II*) with the C = C–C angles for $C_nH_{2n-2}$ cycloalkenes; *1*)–*5*) see Fig.8; *I*) calculation by Eqn.(10); *II*) calculation by Eqn.(11).

## 4. Bicyclo[*n*,1,0]alkanes

### (a) Correlation between the Strain Energy and the Structural Parameters

Thermochemical and geometrical data for bicyclo[*n*,1,0]-alkanes are compiled in Table 8. In their molecules there are several types of C–C distances which differ slightly from one another. The small differences between the C–C distances can be found accurately only by microwave measurements or by means of a combination of electron diffraction and spectroscopic data. The most interesting geometrical parameter in the above series of compounds is undoubtedly the length of the common C–C bond. The results of its measurement are available only for the first three representatives of the series, but they do not exhibit an appreciable correlation with the changes in the $E_S$ of these compounds (Fig.11). This also applies to other individual C–C distances in these molecules.

The C–C–C valence angles in bicycloalkanes differ from those in the compounds considered previously by the presence of a tertiary carbon atom. The value of this angle for isobutane (110.8°) [154] was adopted as the reference value. The sum of the differences $\Delta\alpha = (110.8° - \alpha_1) + (110.8° - \alpha_2) + (110.8° - \alpha_3)$ was adopted as the measure of the strain in the three C–C–C angles around the tertiary carbon atom. The choice of the angles $\alpha_1$, $\alpha_2$, and $\alpha_3$ is explained below in relation to bicyclo[1,1,0]butane:

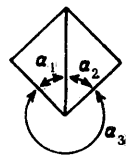



Fig.11 shows that the deformation of the angles about the tertiary carbon atom and the strain energy vary similarly in the series of condensed hydrocarbons and Fig.12 presents the variation of $E_S$ as a function of the average angle $\angle C-C-C_{av} = \alpha_{av} = (\alpha_1 + \alpha_2 + \alpha_3)/3$. The corresponding equation is

$$E_s = 168.2 - 1.374\,\alpha_{av}\,. \qquad (12)$$

An analogous relation is obtained when account is taken of the C(1)–C(2)–C(3) valence angles ($\alpha$) in a large ring, which are 60°, 89.5°, and 100.9° respectively according to calculations for the first three compounds in Table 8. The corresponding correlation equation is

$$E_s = 110.5 - 0.706\,\alpha\,. \qquad (13)$$

The dihedral angles $\theta$ at which the plane of the three-membered ring is inclined relative to the plane of the ring condensed with it have also been measured for the hydrocarbon investigated. The variation of these angles is not consistent with the variation of the $E_S$, as can be seen from Fig.13. Nor has a correlation been observed between $E_S$ and the average C–C distances, which amount to 1.498, 1.529, 1.524, and 1.535 Å respectively for the saturated hydrocarbons of the bicyclo[n,1,0] series investigated (Table 8).

### (b) Correlation between the Structural Parameters and the SSCC

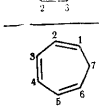
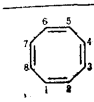
Few data are available for the SSCC for condensed bicyclic systems containing a three-membered ring. The geometrical and thermodynamic parameters of bicyclo[*n*,1,0]alkanes have been determined only for the first four members of the series. Fig.13 presents the dependence of the constant $^1J_{^{13}C-H}$ (C is the common atom of the two rings) on $E_S$ and the angle $\theta$. All the quantities in the range indicated vary in parallel but $E_S$ increases more appreciably (than $^1J_{^{13}C-H}$ and $\theta$) on passing from bicyclo[3,1,0]hexane to bicyclo-[2,1,0]pentane, but changes little on passing from the latter to bicyclo[1,1,0]butane. Nor is there a full correspondence between the changes in $E_S$ and the changes in the $(C-C-C)_{av}$ angle. At the same time the constant $^1J_{^{13}C-H}$ varies linearly with the angle $\theta$, a geometrical parameter of the bicyclic condensed molecule, which can be expressed by the equation

$$^1J_{^{13}C-H} = -176.0 + 3.123\,\theta\,. \qquad (14)$$

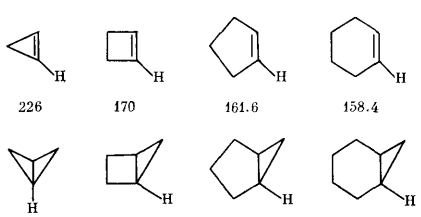
It is of interest to discover how $^1J_{^{13}C-H}$ changes when the double bond in the cycloalkene is replaced by a three-membered ring.

§The reference value of this angle, obtained[140] for butadiene, is 123.3(0.5)°.

**Table 7.** The enthalpies of formation, strain energies, structural parameters, and SSCC of cyclopolyenes.

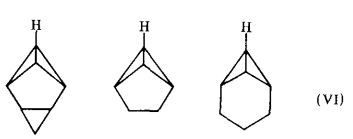
| Molecule | $\Delta H^{\circ}_{f(L)}$ | $\Delta H^{\circ}_{f(G)}$ | $E_s$ | Bonds | Valence angles | Dihedral angles | $^1J_{^{13}C-H}$ | $^3J_{H-H}$ |
|---|---|---|---|---|---|---|---|---|
|  | 25.16 (30) | 31.26 (91) | 4.8 | 1—2 1.509 (2) [133]<br>2—3 1.342 (3) | 1—2—3 109.16 (10.0)<br>2—3—4 109.21 (10.0) | planar ring | 170 [67] | 5.06 [50, 51] |
|  | 17.52 (24) | 25.41 (12) | 4.2 | 1—2 1.350 (4) [134,135]<br>2—3 1.468 (14)<br>4—5 1.523 (16)<br>5—6 1.534 (20) | 3—2—1 120.13 (0.6)<br>2—1—6 120.14 (0.5)<br>1—6—5 110.7 | non-planar ring<br>1—2—3—4 16.3 | 163 [67] | 9.42 [60];<br>9.64 [49, 51] |
|  | — | 22.51 (22) | 6.2 | 1—2 1.347 (6) [136]<br>2—3 1.450 (15)<br>4—5 1.509 (20)<br>5—6 1.522 (20)<br>1—H 1.092 (7) | 1—2—3 129.1 (0.3)<br>2—1—7 129.1 (0.3) | non-planar ring<br>deflective angle<br>5—6—7 / 4—5—7—6 63.9 (4.0) | — | 8.9 [51] |
|  | — | 19.23 | 7.9 | 1—2 1.347 (5) [137]<br>2—3 1.475 (10)<br>4—5 1.509 (5)<br>5—6 1.542 (5) | 1—2—3 129.0 (0.5)<br>4—5—6 117.2 (0.5)<br>5—6—7 105.9 | non-planar ring<br>37.8 (1.0) | — | 11.30 [51] |
|  | 34.44 (29) | 43.69 (29) | 3.7 | 1—2 1.356 (5) [138]<br>2—3 1.446 (7)<br>6—7 1.507 (7)<br>1—H 1.095 (10)<br>7—H 1.106 (10) | 1—2—3 127.2<br>2—3—4 119.8<br>5—6—7 121.8<br>H—1—2 120 (2.0) | 2—3—4—5 / 5—6—1—2 40.5 (20)<br>1—7—6 / 1—2—5—6 36.5 (20) | — | — |
|  | 60.83 (31) | 71.13 (31) | 16.9 | 1—2 1.340 (1) [139]<br>2—3 1.475 (1)<br>C—H 1.100 (4) | 1—2—3 126.1 (0.5) | 1—6—5—2 / 2—3—4—5 43.1 (0.5) | 155 [52] | — |

Note. All the experimental values of $\Delta H^{\circ}_f$ were taken from Pedley and Rylance[88] except $\Delta H^{\circ}_{f(G)}$ for cyclo-octa-1,3-diene which we calculated from the enthalpy of hydrogenation obtained in acetic acid solution at 25 °C.[7] We assume that the calculated value is reliable because the corrections disregarded in the calculation (the differences between the $\Delta H$ of solution and evaporation of cyclo-octa-1,3-diene and cyclo-octane) are in this case small. This follows from a comparison of the enthalpy of hydrogenation of its isomer cyclo-octa-1,5-diene obtained in acetic acid solution[7] with the value calculated from the enthalpies of combustion of cyclo-octa-1,5-diene ($\Delta H^{\circ}_c$ = −1186.46 ± 0.31 kcal mol$^{-1}$ [132]) and cyclo-octane[88].



| | | | | |
|---|---|---|---|---|
| $^1J_{^{13}C-H}$ | 226 | 170 | 161.6 | 158.4 |
| | (VI) | (VII) | (VIII) | (IX) |
| $^1J_{^{13}C-H}$ | 205 | 178 | 166 | 160 |

It is found that the bicyclic hydrocarbons (VI)–(IX) have higher constants than the corresponding cycloalkenes, the difference decreasing on passing from compound (VII) to (IX). The bicyclobutane (VI), for which $^1J_{^{13}C-H}$ is smaller than for cyclopropene, is an exception. The constants $^1J_{^{13}C-H}$ of the more complex polycyclic strained compounds (X)–(XII), whose composition includes the bicyclobutane fragment, are known.

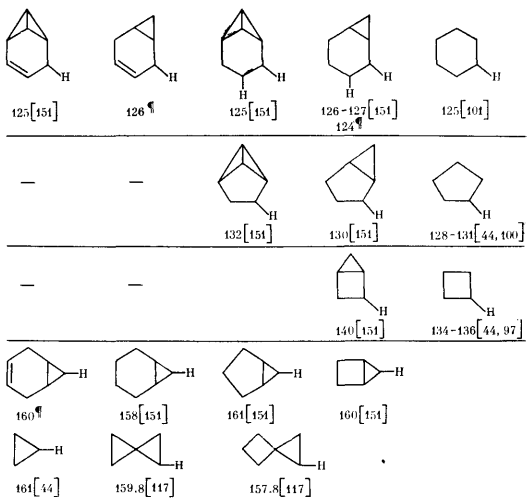


| | | | | |
|---|---|---|---|---|
| | (X) | (XI) | (XII) | (VI) |
| $^1J_{^{13}C-H}$ [151] | 215 | 212 | 205 | 205 |

Their geometrical and chemical parameters are unknown, but one can postulate that in the above series of compounds the strain energy $E_S$ and the dihedral angles $\theta$ in the bicyclobutane fragment will diminish on passing from compound (X) to (VI), i.e. in conformity with the variation of the constant $^1J_{^{13}C-H}$.[151]

It is of interest to compare the values of $^1J_{^{13}C-H}$ for certain mono-, bi- and tri-cyclic hydrocarbons. Whereas the corresponding SSCC for the carbon atom common to both rings varies significantly with increase of the size of the larger ring and varies linearly with the dihedral angle $\theta$ (Fig.14), the constant $^1J_{^{13}C-H}$ for the nuclei of the "non-bridging" carbon atoms retains the specific value characteristic of the given ring and changes only slightly from compound to compound (the values of $^1J_{^{13}C-H}$ are given

under the formulae of the compounds below):



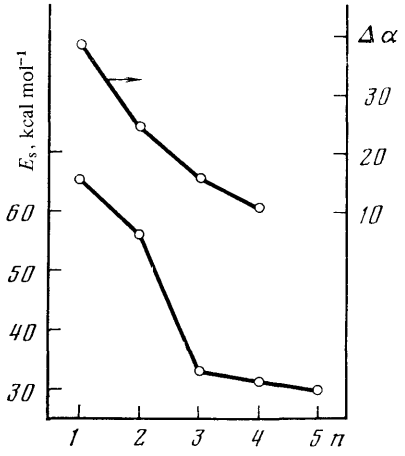
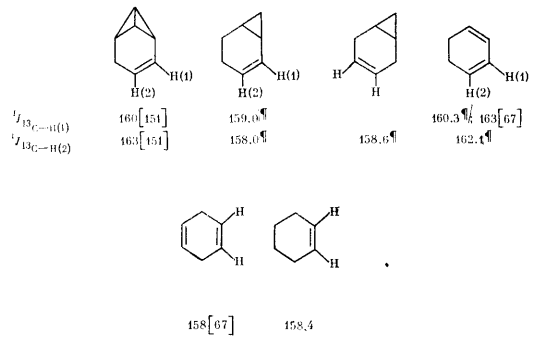




**Figure 11.** Variation of the strain energy $E_S$ and $\Delta\alpha$ involving the tertiary carbon atom in bicyclo[$n$,1,0]alkanes: *1*) bicyclo[1,1,0]butane; *2*) bicyclo[2,1,0]pentane; *3*) bicyclo[3,1,0]hexane; *4*) bicyclo[4,1,0]heptane; *5*) bicyclo[5,1,0]octane.

It is also noteworthy that virtually identical values of $^1J^{13}C - H$ (involving the double bond) are characteristic of the unsaturated hydrocarbons presented below. The constants $^1J^{13}C - H(2)$ of tricycloheptene and the conjugated cyclohexadiene are somewhat larger:




## 5. Bicyclo[$n$,$m$,1]alkanes

### (a) Correlation between the Strain Energy and Structural Parameters

The geometrical features of hydrocarbons of this class have been more thoroughly investigated than their thermochemistry†. We shall therefore carry out only a qualitative comparison of the geometrical parameters, using partly the calculated strain energies taken from Allinger et al.[17] and Engler et al.[18] (Table 9 and Fig.15).

Several hydrocarbons in this series have been reinvestigated but only in the case of norbornane were the errors of previous studies revealed by an electron diffraction investigation[163]. The situation is much less clear for bicyclo[1,1,1]pentane[158,159] and bicyclo[2,1,1]hexane[160,161]: for each of these compounds, Table 9 presents two sets of geometrical parameters. It is difficult to make a choice between them. The results for the bicyclo[2,1,1]hexane are striking: the author of a later study[161] claimed that his data were more accurate than the results of previous measurements[160]. Nevertheless his results[161] seem to be anomalous on the corresponding plots, deviating from the general relations. We therefore decided not to include them in the derivation of the correlation equations (16) and (17); they are shown in Fig.16 for comparison (see the filled circles).

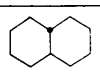
We shall consider how individual geometrical parameters vary, namely (a) the internuclear distances, (b) the valence angles, and (c) the dihedral angles.

(a) The most common geometrical element in the given series of hydrocarbons is the $-HC-CH_2-CH-$ bridge. The exact measurement of the C–C distances in the bridge involves a number of difficulties because the contributions of these distances to the overall diffraction patterns diminish significantly with increasing complexity of the molecule. We preferred to employ in this case the average distance $(C-C)_{av}$, which has been determined more accurately and which characterises the strain in the molecule as a whole. The variation of this parameter is illustrated graphically in Fig.15.

¶These data have been obtained by Yu.N.Luzikov in the Laboratory of NMR Spectroscopy of the Faculty of Chemistry of Moscow State University.

†Most thermochemical studies have been made on compounds of the norbornane series. Some compounds have been reinvestigated in different laboratories[155]. The results do not agree fully with one another and require further experimental confirmation.

**Table 8.** The enthalpies of formation, strain energies, structural parameters, and SSCC of the bridgehead C–H bond in bicyclo[*n*,1,0]alkanes.

| Molecule | $\Delta H_f^\circ$(L) | $\Delta H_f^\circ$(G) | $E_S$ | Bonds | Valence angles | Dihedral angles | $^1J_{13C-H}$ |
|---|---|---|---|---|---|---|---|
|  | 46.30 (29) | 51.91 (19) | 65.6 | 1—3 1.497 (3) [143]<br>3—4 1.498 (4) | 1—3—H 128°22′ (14′)<br>H—C—H 115°34′<br>1—2—3 59°58′ | 1—2—3 / 3—4—1 122°40′ (30′) | 205 (2) [150—152]<br>202 [153] |
|  | 31.0 (34) | 37.8 (40) | 56.4 | 1—4 1.536 (1) [144]<br>2—3 1.565 (1)<br>1—2 1.528 (2)<br>1—5 1.507 (2) | 5—1—H 121.2 (0.1)<br>4—1—H 128.6 (0.1) | 1—5—4 / 1—2—3—4 67.3 (0.2) | 178.1 (0.5) [78]<br>176 [151] |
|  | 1.22 (65) | 9.15 (20) | 32.7 | 1—6 1.515 (8) [145]<br>1—5 1.454 (9)<br>1—2 / 2—3 1.543 (4)<br>C—H 1.100 (6) | 5—1—2 109.8 (0.4)<br>1—2—H 110.2 (1.1)<br>1—6—H 128.2 (3.7)<br>5—1—H 125.8 (6.4) | 4—5—1—H 147.1 (10.1)<br>4—3—2 / 4—2—1—5 25.2 (2.8)<br>1—6—5 / 1—5—4—2 70.6 (1.1) | 166 [151] |
|  | 28.8 (70) | — | — | 1—5 1.521 (1) [146]<br>1—2 1.494 (10)<br>5—6 1.482 (6)<br>1—6 1.522 (7)<br>4—5 1.529 (15)<br>3—4 1.530 (15)<br>2—3 1.338 (10) | 1—2—3 112.0 (1.0)<br>2—3—4 111.5 (1.0) | 1—5—4 / 1—2—3—4 173.8 (1.5)<br>1—5—4 / 1—5—6 113.5 (1.0) | — |
|  | −6.49 (30) | 2.63 (31) | 31.2 | C—C 1.535 (8) [147]<br>C—H 1.10 (1) | 6—1—2 120 (1.0)<br>2—3—4 112 (1.5)<br>4—5—H 109<br>3—4—H 108<br>H—7—H 117 | 1—7—6 / 1—2—5—6 109 (2) | 160 [151] |
|  | −14.39 (26) | −3.97 (29) | 29.5 | — | — | — | — |
|  | −17.48 (60) | −5.45 (60) | 33.0 | — | — | — | — |
| *cis*-  | −16.28 (42) | −6.31 (45) | 27.2 | *cis*-C–C$_{av}$ 1.536 (6) [148] | C—C—C (6-membered ring) 112.9 (4-membered ring) 88.9 | torsional angle in 6-membered ring 48<br>torsional angle in 4-membered ring 157 | — |
| | | | | *trans*-C–C$_{av}$ 1.532 (5) | C—C—C (6-membered ring) 110.4 (4-membered ring) 87.3 | torsional angle in 6-membered ring 57<br>torsional angle in 4-membered ring 145 | |
| *trans*-  | −55.11 (21) | −43.52 (55) | −0.1 | (C–C)$_{av}$ 1.530 (3) [149]<br>C—H 1.112 (5) | C–C–C$_{av}$ 111.4 (0.4) | torsional angle 55.0 (0.5) | — |

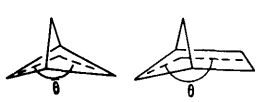
Note. The experimental values of $\Delta H_f^\circ$ for the second, fourth, and fifth compounds were taken from Kozina[141] and those for the remaining compounds are from Pedley and Rylance[88].

(b) The valence angle ∠C–C–C (α) involving the bridging carbon atom in the symmetrical bicyclo[*m*,*n*,1]alkanes increases linearly on expansion of the rings on either side of the bridge, which is described by the following equation[5]:

$$\alpha = 0.836 + 18.282p^\circ , \qquad (15)$$

where $p = m + 3$. When this relation is recalculated in terms of the deviation from the standard angle 112.6°, another plot is obtained, which is also shown in Fig. 15.

(c) The geometrical parameters considered above vary almost linearly on expansion of the rings, while $E_S$ varies non-linearly. The parameter which exhibits the best correlation with $E_S$ proved to be the dihedral angle θ; it is shown below for bicyclo[1,1,1]pentane and bicyclo[2,1,1]-hexane.



The dependence of the angle on $E_S$ is illustrated in Fig. 16 and is described by the equation

$$E_S = -1173.2 + 10.55\,\theta . \qquad (16)$$

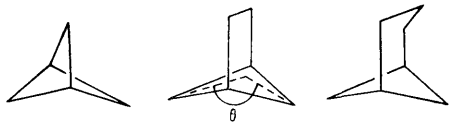
Bicyclo[*n*,1,1]alkanes, containing a four-membered fragment occupy a special place. The individual characteristics of these molecules are presented in Fig. 17; the data for cyclobutane have been included for comparison. Evidently, in contrast to the preceding case, the best correlation is observed between $E_S$ and the ∠C–C–C (α) involving the secondary carbon atom in the four-membered ring (Fig. 18), which is described by the following empirical equation:

$$E_S = 430.5 - 4.550\,\alpha . \qquad (17)$$

### (b) Correlation between Structural Parameters and SSCC

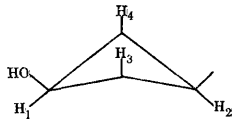
There are virtually no systematic data on the geometry and the SSCC for bridged hydrocarbons. The successive changes in the above parameters can be illustrated only in

relation to the three bicyclic hydrocarbons (XIII)–(XV):



(XIII) (XIV) (XV)

Each of these contains the cyclobutane fragment[53]. One of the characteristic parameters in the NMR spectra of compounds of this kind is the SSCC of the *exo*, *cis* protons via four σ-bonds, for which one can postulate a dependence on the dihedral angle θ in the four-membered ring (Table 9). The series of compounds considered can be logically completed by cyclobutane itself. The exact value of the constant $^4J_{H-H}$ of this compound is unknown but it is close to zero according to Meiboom and Snyder[167]. [$^4J_{H(1)-H(2)} = -0.01$ and $^4J_{H(3)-H(4)} = +0.01$ for cyclobutanol[168].]



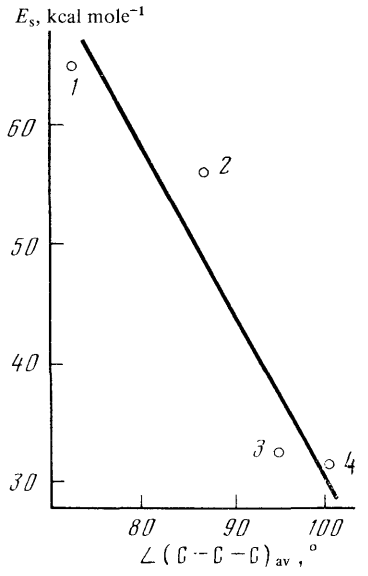



**Figure 12.** Variation of $E_S$ with the average $(C-C-C)_{av}$ valence angle involving the tertiary carbon atom in bicyclo[*n*,1,0]alkanes: *1*)–*4*) see Fig.11; straight line—calculated by Eqn.(12).

Figs.19 and 20 (based on the data in Table 9) illustrate the changes in the constant $^4J_{H-H}$ and the angle θ for the hydrocarbons (XIII)–(XV) and cyclobutane as well as the linear relation between them, described by the equation

$$^4J_{H-H} = -0.285\,\theta + 44.026 \quad (18)$$

In determining the above correlation, bicyclo[1,1,0]butane should have been included, but two experimental values of the constant $^4J_{H-H}$, differing significantly from one another, are indicated in the literature: 10 Hz [86] and 5.9 Hz [150] (the latter agrees with theoretical values[152]). According to the relation established [Eqn.(18)], $^4J_{H-H}$ = 10 Hz should correspond to a dihedral angle of 122.4° for bicyclo[1,1,0]butane; however, when account is taken of the specific features of the structure of a system with two condensed three-membered rings, then the agreement with the data of Wiberg et al.[36] cannot apparently serve as a criterion of their validity.

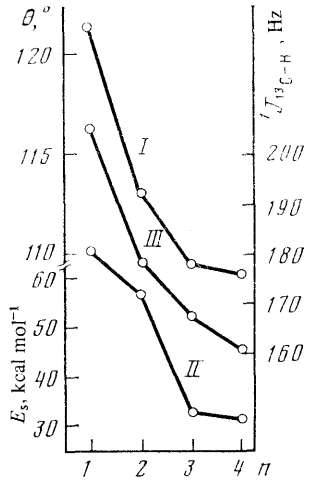



**Figure 13.** Variation of the dihedral angles θ (curve *I*), $E_S$ (curve *II*), and $^1J_{^{13}C-H}$ (curve *III*) in bicyclo[*n*,1,0]-alkanes with the size of the larger ring: *1*)–*5*) see Fig.11.

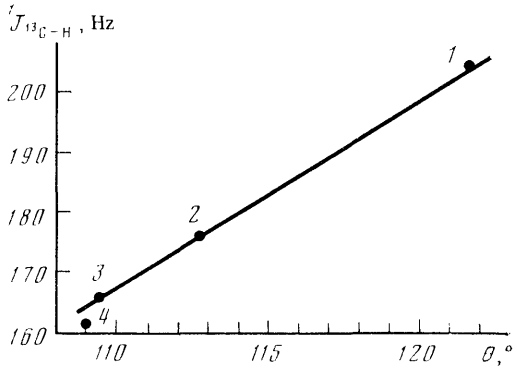
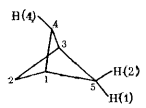
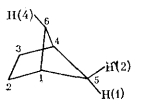
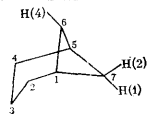
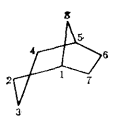
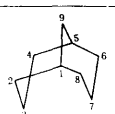
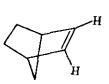
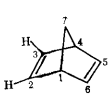
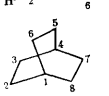
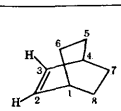



**Figure 14.** Variation of $^1J_{^{13}C-H}$ with θ for bicyclo[*n*,1,0]-alkanes: *1*)–*4*) see Fig.11; straight line—calculated by Eqn.(14).

It is possible to quote examples of successive changes in $^3J_{H-H}$ in a series of bridged hydrocarbons where five- or six-membered unsaturated rings are the repeating

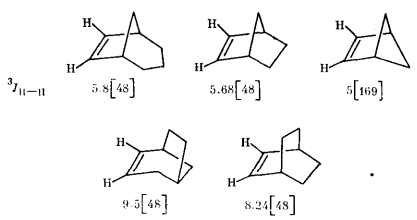
**Table 9.** The enthalpies of formation, strain energies, structural parameters, and SSCC of bicyclo[$m,n,k$]alkanes.

| Molecule | $\Delta H^{\circ}_{f(L)}$ | $\Delta H^{\circ}_{f(G)}$ | $E_s$ | Bonds | Valence angles | Dihedral angles | $^1J_{^{13}C-H}$ | $^3J_{H-H}$ | $^4J_{H-H}$ | $^5J_{H-H}$ |
|---|---|---|---|---|---|---|---|---|---|---|
|  | — | — | (92.23) [17]* | C—C 1.557(2) [158]<br>C—H 1.109(4)<br>C—C 1.545(6) [159]<br>C—H 1.100(10) | **1—2—3** 74.2(0.2)<br>**H—C—H** 111.7(1.8)<br>1—2—3 73.3(1.0)<br>H—C—H 103.9(5.0) | 120<br>120 | — | —3.0[53] | 10[53] | — |
|  | — | — | (41.21) [18]* | 1—2 1.665(24) [160]<br>1—5 1.544(15)<br>2—3 1.513(15)<br>C—H 1.112(5)<br>1—2 1.537(1) [161]<br>1—5 1.547(1)<br>2—3 1.537(1)<br>C—H 1.098(4) | 1—2—3 102.1<br>5—1—6 78.2<br>1—5—4 89.4<br>H—2—H 109.2(4.0)<br>H—6—H 100.8(6.0)<br>1—2—3 100.4(0.4)<br>1—5—4 85.4(1.1)<br>5—1—6 83.3(1.2)<br>2—1—5 100.6(0.5)<br>H—2—H 117.3(4.0)<br>H—6—H 98.8(5.9) | 1—5—4 / 1—6—4 125<br>1—5—4 / 1—6—4 129.5 | — | —6.5—7.5 [53] | 7—8 [53] | — |
|  | — | — | (35.85) [18]* | 1—2 1.511(15) [162]<br>2—3 1.534(30)<br>1—6 1.553(9)<br>C—H 1.091(5) | **1—6—5** 87.1(1.0)<br>2—3—4 113.0(1.8)<br>1—2—3 108.7(1.1)<br>6—1—**2** 110.9(0.6)<br>6—1—**7** 84.9(1.4) | 1—6—5 / 1—7—5 137.5<br>2—3—4 / 4—5—1—2 143.0 | — | —8.5—9.5 [53] | 5.5—6 [53] | |
|  | —22.01(52) [88] | —12.43(55) [88] | 16.1 | 1—2 1.536(3) [163]<br>2—3 1.553(9)<br>1—7 1.558(9)<br>C—H 1.112(2) | 1—7—4 93.1(0.6)<br>H—C—H 109.9(1.5) | 1—6—5—4 / 1—2—3—4 113.1(0.6) | C(1)—H 141 [118]<br>C(2)—H 130<br>C(7)—H 132 | — | — | — |
|  | — | — | (12.1)* | 1—2 1.553(57) [170]<br>2—3 1.532(71)<br>1—8 1.501(54)<br>1—7 1.591(25)<br>6—7 1.544(60)<br>C—H 1.109(6) | 1—8—5 102.8(1.6)<br>2—3—4 109.6(2.5)<br>H—C—H 101.2(6.0) | 1—8—5 / 1—2—4—5 117.4(1.3)<br>2—3—4 / 1—2—4—5 41.1(2.8)<br>1—8—5 / 1—7—6—5 132.6(4.4) | —<br>— | —<br>— | —<br>— | —<br>— |
|  | —42.6(20) [142] | —30.5(60) [142] | 7.9 | 1—2 1.567(4) [5]<br>2—3 1.537(4)<br>1—9 1.476(5)<br>C—H 1.116(4) | 1—9—5 111.2(1.7)<br>2—3—4 111.5(1.4)<br>H—C—H 106.3(2.4) | 1—9—5 / 1—2—4—5 124.1(0.5)<br>1—2—4—5 / 2—3—4 141.6(1.6) | — | — | — | — |
|  | 9.89(33) [156] | 19.14(35) [156] | 19.8 | — | — | — | 165[82]<br>166.5[118] | — | — | 5.6—5.9 [48,165, 166] |
|  | — | 58.0(60) [157] | 27.2** | 1—2 1.535(7) [162]<br>2—3 1.343(3)<br>1—7 1.573(14)<br>C—H 1.123(14) | 1—7—4 94.1(3.0)<br>C—C—H 124(3)<br>H—C—H 113(8) | 1—2—3—4 / 1—6—5—4 115.6(2.2) | C(1)—H 172.5+ 172.8 [48,118, 165]<br>C(7)—H 135 [118] | | | 5.05 [165]<br>5.28 [48] |
|  | —35.13(19) [88] | —23.66(22) [88] | 9.8 | 1—2 1.538(15) [4]<br>2—3 1.552(29)<br>C—H 1.107(9) | 1—2—3 109.7(0.7)<br>H—C—H 110.1(5.6) | — | — | — | — | — |
|  | —5.57(17) [88] | 4.90(19) [88] | 10.5 | 1—2 1.509(15) [164]<br>2—3 1.341(8)<br>1—8 1.549(8)<br>7—8 | 1—2—3 114.2(0.6)<br>2—3—H 122.4(6.0)<br>H—C—H 109.2(4.0) | 1—2—3—4 / 1—6—5—4 121.2(2.1) | 162.8[48] | — | — | 8.24 [48] |

*Calculated data.

**Estimated using the difference between the heats of hydrogenation of norbornene and norborna-2,5-diene.

elements[48]:




The values of $E_S$ for both series increase from left to right, i.e. in conformity with the decrease of the SSCC of the vicinal protons. Probably ∠C = C–C varies in the same sequence (analogously to the variation of the corresponding parameters for cycloalkenes).

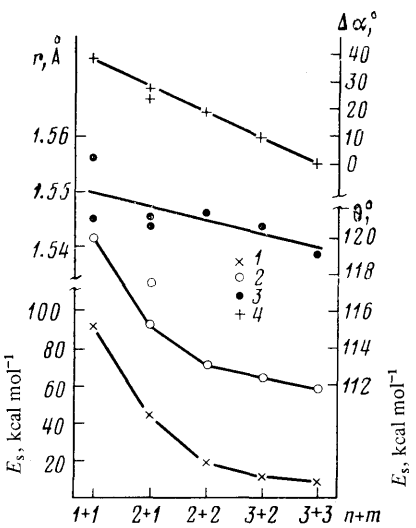



**Figure 15.** Variation of the strain energy $E_S$ (*1*), the average $(C-C)_{av}$ internuclear distance ($r$) (*3*), the difference $\Delta\alpha = 112.6° - \alpha$ ($\alpha$ is the C–C–C angle in the bridge) (*4*), and the dihedral angle $\theta$ (*2*) in bicyclo[$n$,$m$,1]alkanes with the size of the ring; bicyclo[1,1,1]pentane and bicyclo-[2,1,0]hexane were investigated twice.

## III. CONCLUSION

The most general comment which can be made on the basis of the data considered concerns Eqn.(1). The experimental data presented in Section II show that in fact two separate relations exist:

$$E_s\text{-molecular geometry and SSCC-molecular geometry.} \qquad (1')$$

They cannot be combined in terms of geometrical data because in most cases different geometrical parameters are involved in the quantitative relations.

The only deviation from this rule arises in the case of cycloalkenes [see Eqns.(8), (10), and (11)]. However, one should note that, despite the absence of quantitative relations, the SSCC vary in parallel with $E_S$. In those cases where deviations are observed from such parallel variation [for example in the cyclo-octane–cyclononane (Fig.5) and cyclohexene–cycloheptene (Fig.9) transitions], an experimental test of the corresponding parameters would be desirable.

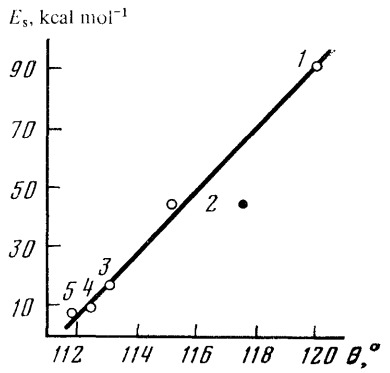



**Figure 16.** Variation of the strain energy with $\theta$ for different bicyclic hydrocarbons: *1*) bicyclo[1,1,1]pentane: *2*) bicyclo[2,2,1]hexane; *3*) bicyclo[2,2,1]heptane; *4*) bicyclo[3,2,1]octane; *5*) bicyclo[3,3,1]nonane; straight line—calculated by Eqn.(16); filled circle—Chiang's data[161].

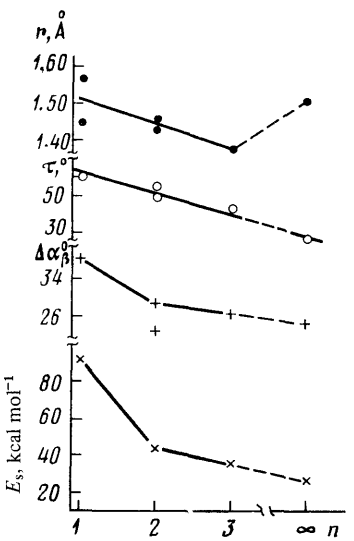



**Figure 17.** Variation of the strain energy $E_S$, the average $(C-C)_{av}$ internuclear distance ($r$), the dihedral angle in the four-membered fragment $\gamma$, and the difference $\Delta\alpha = 112.6° - \alpha$ ($\alpha$ is the C–C–C valence angle at the secondary carbon atom in the four-membered fragment) in bicyclo[$n$,1,1]-alkanes and cyclobutane (the convention is adopted that for this compound $n = \infty$).

For each series of the cyclic hydrocarbons considered, there is a definite correlation between the SSCC and the angular parameters of the molecule; no dependence on the

internuclear distances has been observed. One can postulate on the basis of the available (limited) data, that such correlations between the SSCC and the angular parameters of the molecule can be found also in other series of hydrocarbons when the amount of the relevant experimental data is sufficient.

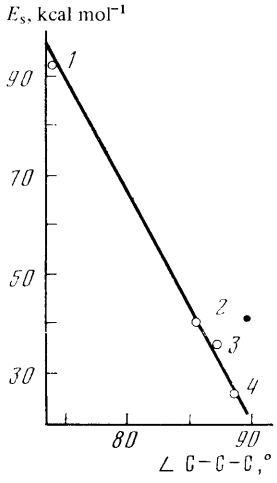



**Figure 18.** Variation of the strain energy with the C–C–C valence angle in the four-membered fragment in different bicyclic hydrocarbons: *1*) bicyclo[1,1,1]pentane; *2*) bicyclo[2,1,1]hexane; *3*) bicyclo[3,1,1]heptane; *4*) cyclobutane; straight line—calculated by Eqn.(17); filled circle—Chiang's data[161].

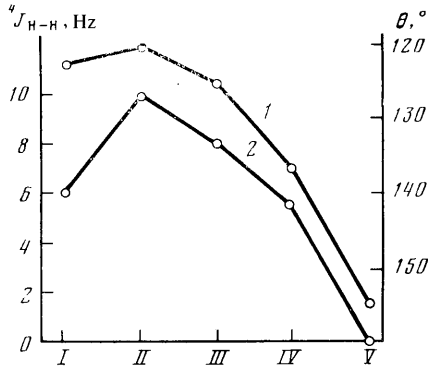



**Figure 19.** Variation of the dihedral angle θ in the four-membered fragment (curve *1*) and $^4J_{H-H}$ (curve *2*) in bicyclo[*n*.1.1]alkanes (*II–IV*), bicyclo[1,1,0]butane (*I*), and cyclobutane (*V*).

If the variation of $E_S$ in the series of compounds considered as a function of the number of carbon atoms *n* is followed {for bicyclo[*n*,1,0]alkanes, *n* is the number of carbon atoms in the larger ring and for symmetrical bridged hydrocarbons it is the number of carbon atoms in each ring} (Fig.21), it is found that the nature of the variation of $E_S$ in the series of bicyclo[*n*,1,0]alkanes and cycloalka-1,3-dienes is approximately the same, the values of $E_S$ for rings with *n* between 5 and 8 being similar. In each series of compounds hydrocarbons containing six-membered rings have the smallest values of $E_S$ regardless of which structural parameters (bond length, valence or dihedral angles) are mainly used to determine $E_S$. Bicyclo[*n*,1,0]alkanes, where the minimum is displaced to the hydrocarbon with the larger seven-membered ring, are an exception, but in this case there are grounds for recommending the redetermined values of $\Delta H_f^\circ$ for bicyclo[5,1,0]octane#.

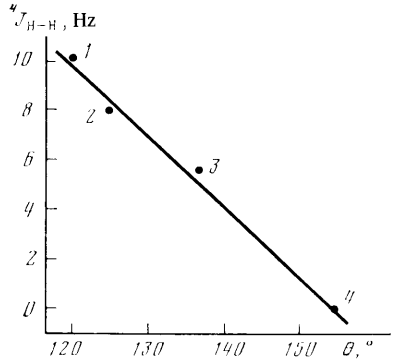



**Figure 20.** Variation of $^4J_{H-H}$ with θ: *1*)–*4*) see Fig.18.

The introduction of a correction for the contribution of the energy $p\Delta V$ to $E_S$ does not alter the nature of the curves, which are merely displaced by 0.6 or 1.2 kcal mol$^{-1}$.

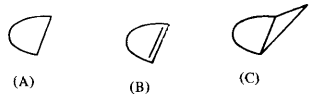
The strain energies $E_S$ of cyclohexane, cyclohexene, cyclohexa-1,3-diene, and bicyclo[2,2,2]octane per six-membered ring are −0.2, 1.1, 4.2, and 4.9 kcal mol$^{-1}$ respectively. The conformation of the six-membered ring in these hydrocarbons varies as follows: chair → half-chair → flattened half-chair → boat. However, one should note that the above values of $E_S$ cannot be used to estimate the energy of the chair → half-chair → boat conformational transition for a six-membered ring, since the values of $E_S$ reflect the overall strain energy and not the conformational energy.

We examined above how $E_S$ is related explicitly to the geometrical parameters and the SSCC and how it varies in a specific series of compounds with the number of carbon atoms. It is also of interest to trace the variation of the

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#The value of $\Delta H_f^\circ$ for bicyclo[4,1,0]heptane quoted by Dashevskii[16], whose results we have employed, differ from the other literature values by 2.3 kcal mol$^{-1}$. In this connection, the enthalpy of combustion of bicyclo[5,1,0]-octane has been redetermined. The following values (in kcal mol$^{-1}$) have been obtained at 298 K: $\Delta H_{c(L)}^\circ$ = −1218.80 ± 0.45; $\Delta H_{f(L)}^\circ$ = −11.82 ± 0.47; $\Delta H_{f(G)}^\circ$ = −1.42 ± 0.51; $E_S$ = 32.1. This value of $E_S$ is presented in Fig.21 (the experimental work has been carried out by L.P.Timofeeva).

relative values of $E_S$ characterising the transition from cycloalkanes (A) to the corresponding cycloalkenes (B) and the bicyclo[$n$,1,0]alkanes (C):



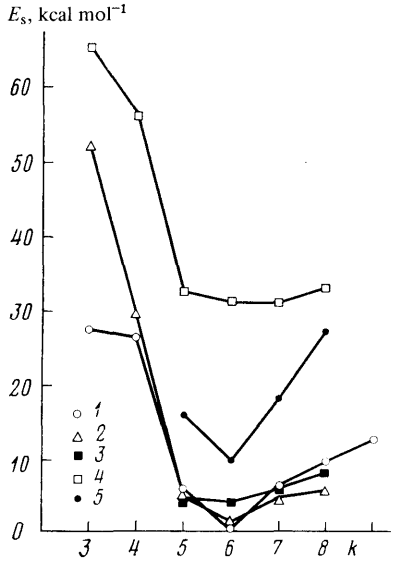
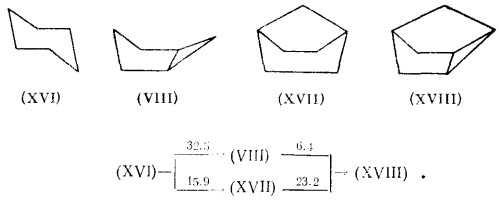




**Figure 21.** Variation of $E_S$ in the series of cycloalkanes (*1*), cycloalkenes (*2*), cycloalkadienes (*3*), bicyclo[$n$,1,0]alkanes (*4*), and symmetrical bridged bicycloalkanes (*5*) with the number of carbon atoms in the ring for (*1*), (*2*), and (*3*), with the number of carbon atoms in the larger ring for (*4*), and with the number of carbon atoms in one of the rings for (*5*).

Fig. 21 presents the variation of $E_S$ for each of these series and Fig. 22 presents the differences $\Delta E_S^{(1)} = E_S(B) - E_S(A)$ and $\Delta E_S^{(2)} = E_S(C) - E_S(A)$. Each of the quantities $\Delta E_S^{(1)}$ or $\Delta E_S^{(2)}$ considered separately corresponds to the additional strain in the cycloalkane molecule which appears as a consequence of the introduction of a double bond or a three-membered ring respectively. Comparison of the two sequences of the values of $\Delta E_S^{(1)}$ and $\Delta E_S^{(2)}$ demonstrates the approximately identical nature of their variations in series (B) and (C). It is known[145] that there are analogies between the conformations of the carbon ring in these hydrocarbons determined by the absence of internal rotation relative to the double bonds in series (B) or the common bond in the bicyclic systems (C).

It is of interest to trace the changes in $E_S$ on passing from monocyclic to bicyclic and tricyclic hydrocarbons in the series below:



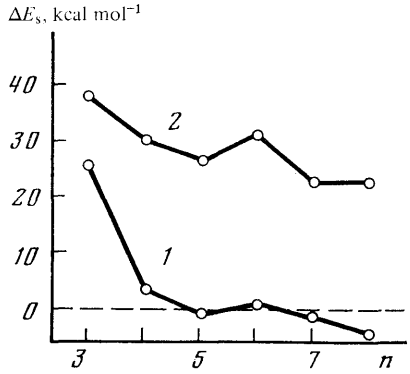




**Figure 22.** Variation of the differences $\Delta E_S^{(1)} = E_S(B) - E_S(A)$ (curve *1*) and $\Delta E_S^{(2)} = E_S(C) - E_S(A)$ (curve *2*).

(Unfortunately such examples are limited owing to the insufficient amount of experimental data.) The greatest change in $E_S$ corresponds to the introduction of a three-membered ring into the system. The methylene bridge linking the first and fourth carbon atoms causes smaller changes in $E_S$, particularly when the trimethylene ring is already in the molecule. The overall change in $E_S$ on passing from cyclohexane to the nortricyclene (XVIII) via compound (VIII) or (XIV) is virtually the same, which confirms the validity of the quantities used in the calculations.

On the basis of the empirical equations relating $E_S$ to different geometrical parameters which have been derived, a slightly different meaning can be given to the reference values of $r_0$ and $\alpha_0$. We recall that we adopted these values from data for the molecules with the minimum $E_S$, associated with the given geometrical parameter. For example, saturated hydrocarbons ranging from methane to n-heptane, *cis*-butene, and isobutane have been used as standards. With the aid of the above correlation equations, we can now carry out a kind of test of these values by determining them from the condition for the equality of $E_S$ to zero. The values obtained from the empirical equations (we shall designate them by $r_0'$ and $\alpha_0'$ respectively) can be regarded as generalised constants satisfying sets of molecules and related directly to $E_S$.

The values of $r_0$ and $\alpha_0$ used previously are compared below with their analogues $r_0'$ and $\alpha_0'$ calculated from empirical equations (4), (8), and (9):

| | | | |
|---|---|---|---|
| C–C bond | $r_0 = 1.533$ (1) Å | $r_0 = 1.537$ Å | calc. by Eqn.(4), |
| C=C–C angle | $\alpha_0 = 125.4$ (0.4)° | $\alpha_0' = 124.5°$ | calc. by Eqn.(8), |
| C–C–C angle | $\alpha_0 = 112.6$ (0.1)° | $\alpha_0' = 112.5°$ | calc. by Eqn.(9). |

It is noteworthy that the reference values of the angular parameters which we used above and the values calculated by Eqns.(8) and (9) are very similar. Evidently this shows that the selected acyclic systems are indeed free from angular strain, which arises in cyclo-olefins and is described by Eqns.(8) and (9). The discrepancy of 0.004 Å between $r_0$ and $r_0'$ may not be fortuitous and may have a perfectly definite significance, because $r_0' = 1.537$ Å is virtually identical with the C–C distance in cyclohexane (1.536 Å), for which $E_S$ is close to zero. The increase in the length of the C–C bond in cyclohexane may arise as a consequence of inevitable *gauche*-interactions[13]. Similar *gauche*-interactions in acyclic systems with a short-carbon chain are much less appreciable[39].

Analogous calculations using other empirical equations do not yield interesting results, which may be due to the specific features of the geometrical parameters considered or the inadequate number of experimental data [for example, the average angle $(C-C-C)_{av}$ in Eqn.(12)].

## REFERENCES


1. J.F.Liebman and A.Greenberg, Chem.Rev., 1976, **76**, 311.
2. G.Dallinga, R.K.Van Der Draai, and L.H.Toneman, Rec.Trav.chim., 1968, **87**, 897.
3. B.Andersen and R.Srinivasan, Acta Chem.Scand., 1972, **26**, 3468.
4. A.Yokozeki, K.Kuchitsu, and Y.Morino, Bull.Chem. Soc.Japan, 1970, **43**, 2017.
5. V.S.Mastryukov, E.L.Osina, O.V.Dorofeeva, M.V.Popik, L.V.Vilkov, and N.A.Belikova, J.Mol. Struct., 1979, **52**, 211.
6. C.T.Mortimer, "Reaction Heats and Bond Strength" (Translated from English into Russian by V.V.Mikhailov), Izd.Mir, Moscow, 1964.
7. R.B.Turner, in "Theoretical Organic Chemistry" (Russian translation from English edited by R.Kh.Freidlina), Inostr.Lit., Moscow, 1963, p.89.
8. R.M.Joshi, J.Macromol.Sci.Chem., 1972, **A6**, 595.
9. V.G.Dashevskii, "Konformatsii Organicheskikh Molekul" (Conformations of Organic Molecules), Izd.Khimiya, Moscow, 1974.
10. P.v.R.Schleyer, I.E.Williams, and K.R.Blanchard, J.Amer.Chem.Soc., 1970, **92**, 2377.
11. J.O.Halford, J.Chem.Phys., 1956, **24**, 830.
12. L.C.Snyder and T.A.Weber, J.Amer.Chem.Soc., 1979, **101**, 32.
13. L.V.Volkov, V.S.Mastryukov, and N.I.Sadova, "Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul" (Determination of the Geometrical Structure of Free Molecules), Izd. Khimiya, Leningrad, 1978.
14. B.Nelander and S.Sunner, J.Chem.Phys., 1966, **44**, 2476.
15. R.C.Bingham, M.J.S.Dewar, and D.H.Lo, J.Amer. Chem.Soc., 1975, **97**, 1294.
16. V.G.Dashevskii, Uspekhi Khim., 1973, **42**, 2097 [Russ.Chem.Rev., 1973(12)].
17. N.L.Allinger, M.T.Tribble, M.A.Miller, and D.H.Wertz, J.Amer.Chem.Soc., 1971, **93**, 1637.
18. E.M.Engler, J.D.Andose, and P.v.R.Schleyer, J.Amer.Chem.Soc., 1973, **95**, 8005.
19. S.Fitzwater and L.S.Bartell, J.Amer.Chem.Soc., 1976, **98**, 5107.
20. E.Osawa, J.B.Collins, and P.v.R.Schleyer, Tetrahedron, 1977, **33**, 2667.
21. N.L.Allinger, J.Amer.Chem.Soc., 1977, **99**, 8127.
22. S.W.Benson, F.R.Cruickshank, D.H.Golden, G.R.Hangen, H.E.O'Neal, A.S.Rodgers, and R.Walsh, Chem.Rev., 1969, **69**, 279.
23. S.-J.Chang, D.McNally, S.Shary-Tehrany, M.J.Hickey, and R.N.Boyd, J.Amer.Chem.Soc., 1970, **92**, 3109.
24. T.L.Allen, J.Chem.Phys., 1959, **31**, 1039.
25. K.S.Pitzer and E.Catalano, J.Amer.Chem.Soc., 1956, **78**, 4844.
26. J.D.Cox and G.Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Acad. Press, London–New York, 1970.
27. G.R.Somayajulu and B.J.Zwolinski, J.Chem.Soc. Faraday Trans.II, 1976, **72**, 2213.
28. J.F.Klages, Chem.Ber., 1949, **82**, 358.
29. L.V.Vilkov, M.G.Anashkin, E.Z.Zasorin, V.S.Mastryukov, V.P.Spiridonov, and N.I.Sadova, "Teoreticheskie Osnovy Gazovoi Elektronografii" (Theoretical Principles of Gas Electron Diffraction), Izd.Moskov.Gos.Univ., Moscow, 1974.
30. C.H.Townes and A.L.Schawlow, "Microwave Spectroscopy" (Translated into Russian), Inostr.Lit, Moscow, 1959.
31. K.Kuchitsu and S.J.Cyvin, in "Molecular Structures and Vibrations" (Edited by S.J.Cyvin), Elsevier, Amsterdam, 1972, p.183.
32. K.Kuchitsu, in "Gas Electron Diffraction", MTP International Review of Science, Physical Chemistry, Vol.2, (Edited by G.Allen), Butterworth, London, 1972, p.203.
33. A.G.Robiette, in "Molecular Structure by Diffraction Methods", Vol.1, (Edited by G.A.Sim and L.E.Sutton), Chemical Society, London, 1973, p.160.
34. V.S.Mastryukov and O.V.Dorofeeva, Zhur.Strukt. Khim., 1979, **20**, 592.
35. Yu.V.Zefirov and P.M.Zorkii, Zhur.Strukt.Khim., 1975, **15**, 118.
36. "Internal Rotation in Molecules" (Russian translation from English edited by Yu.A.Pentin), Izd.Mir, Moscow, 1977.
37. L.S.Bartell, J.Amer.Chem.Soc., 1959, **81**, 3497.
38. L.S.Bartell and D.A.Kohl, J.Chem.Phys., 1963, **39**, 3097.
39. S.Fitzwater and L.S.Bartell, J.Amer.Chem.Soc., 1976, **98**, 8338.
40. W.F.Bradford, S.Fitzwater, and L.S.Bartell, J.Mol.Struct., 1977, **38**, 185.
41. L.S.Bartell and T.L.Boates, J.Mol.Struct., 1976, **32**, 379.
42. H.B.Burgi and L.S.Bartell, J.Amer.Chem.Soc., 1972, **94**, 5336.
43. L.S.Bartell and W.F.Bradford, J.Mol.Struct., 1977, **37**, 113.
44. C.S.Foote, Tetrahedron Letters, 1963, 579.
45. S.Borčič and J.D.Roberts, J.Amer.Chem.Soc., 1965, **87**, 1056.
46. G.V.Smith and H.Kriloff, J.Amer.Chem.Soc., 1963, **85**, 2016.

47. P.Laszlo and P.v.R.Schleyer, J.Amer.Chem.Soc., 1963, **85**, 2017.
48. M.A.Cooper and S.L.Manatt, Org.Magnet.Reson., 1970, 2, 511.
49. M.A.Cooper and S.L.Manatt, J.Amer.Chem.Soc., 1969, **91**, 6325.
50. J.B.Lambert, L.T.Durham, P.Lepontere, and J.D.Roberts, J.Amer.Chem.Soc., 1965, **87**, 3896.
51. M.A.Cooper, D.D.Ellemann, C.D.Pearce, and S.L.Manatt, J.Chem.Phys., 1970, **53**, 2343.
52. P.Laszlo, Bull.Soc.chim.France, 1966, 558.
53. R.J.Abraham, M.A.Cooper, J.R.Salmon, and D.Whittaker, Org.Magnet.Reson., 1972, **4**, 489.
54. P.Laszlo and P.v.R.Schleyer, J.Amer.Chem.Soc., 1964, **86**, 1171.
55. M.Karplus, J.Amer.Chem.Soc., 1963, **85**, 2870.
56. O.L.Chapman, J.Amer.Chem.Soc., 1963, **85**, 2014.
57. K.Mislow, Tetrahedron Letters, 1964, 1415.
58. D.S.Bartow and J.W.Richardson, J.Chem.Phys., 1965, **42**, 4018.
59. M.Barfield and D.M.Grant, "Advances in Magnetic Resonance", Acad.Press, New York–London, 1965, Vol.1, p.149.
60. A.A.Bothner-By, "Advances in Magnetic Resonance", Acad.Press, New York–London, 1965, Vol.1, p.195.
61. W.A.Thomas, Ann.Rep.NMR Spectroscopy, 1968, 1, 44.
62. H.Booth, Progr.NMR Spectroscopy, 1969, 5, 149.
63. M.Barfield and B.Chakrabarti, Chem.Rev., 1969, **69**, 757.
64. S.Sternhell, Quart.Rev., 1969, **23**, 236.
65. G.E.Maciel, J.W.McIver, N.S.Ostlund, and J.A.Pople, J.Amer.Chem.Soc., 1970, **92**, 4497.
66. W.A.Thomas, Ann.Rep.NMR Spectroscopy, 1970, **3**, 1.
67. J.B.Stothers, "Carbon-13 NMR Spectroscopy", Acad.Press, New York–London, 1972.
68. V.N.Solkan and N.M.Sergeev, Org.Magnet.Reson., 1974, **6**, 200.
69. L.G.Voronzova and A.F.Bokov, Org.Magnet. Reson., 1974, **6**, 654.
70. G.C.Levy and P.Nelson, "Manual of Carbon-13 Nuclear Magnetic Resonance for Organic Chemists" (Translated into Russian), Izd.Mir, Moscow, 1975.
71. M.Barfield, Sh.A.Coun, J.L.Marshall, and D.E.Miller, J.Amer.Chem.Soc., 1976, **98**, 6253.
72. H.Günther and G.Jikeli, Chem.Rev., 1977, **77**, 599.
73. K.Jankowski and A.Rabezenko, Org.Magnet.Reson., 1977, **9**, 480.
74. N.M.Sergeev and O.A.Subbotin, Uspekhi Khim., 1978, **47**, 477 [Russ.Chem.Rev., 1978(3)].
75. R.Niedermeyer and R.Freeman, J.Magnet.Reson., 1978, **30**, 617.
76. P.E.Hausen, Org.Magnet.Reson., 1978, **11**, 215.
77. H.Günter and W.Herrig, Chem.Ber., 1973, **106**, 3938.
78. R.D.Bertrand, D.M.Grant, E.L.Allred, J.C.Hinshaw, and A.B.Strong, J.Amer.Chem.Soc., 1972, **94**, 977.
79. M.Randić and Z.B.Maksić, Chem.Rev., 1972, **72**, 43.
80. Z.B.Maksić and M.Randić, J.Amer.Chem.Soc., 1973, **95**, 6522.
81. G.E.Maciel, in "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other than Protons", (Edited by T.Axenrod and G.Webb), Wiley Intersci., New York, 1974.
82. M.D.Newton, J.M.Schulman, and M.M.Manus, J.Amer.Chem.Soc., 1974, **96**, 17.
83. J.N.Shoolery, J.Chem.Phys., 1959, **31**, 1427.
84. N.Muller and D.E.Pritchard, J.Chem.Phys., 1959, **31**, 768.
85. H.P.Figeis, P.Geerlings, P.Raeymaekers, G.Van Lommen, and N.Defai, Tetrahedron, 1975, **31**, 1731.
86. K.B.Wiberg, G.M.Lampman, R.P.Ciula, D.S.Connor, P.Schertler, and J.Lavanish, Tetrahedron, 1965, **21**, 2749.
87. M.S.Gil and C.F.G.C.Geraldes, in "Nuclear Magnetic Resonance Spectroscopy of Nuclei other than Protons" (Edited by T.Axenrod and G.Webb), Wiley Intersci., New York, 1974.
88. J.B.Pedley and J.Rylance, "Computer Analysed Thermochemical Data: Organic and Organometallic Compounds", Univ.of Sussex, 1977.
89. O.Bastiansen, F.N.Fritsch, and K.Hedberg, Acta Cryst., 1964, **17**, 538.
90. F.Takabayashi, H.Kambara, and K.Kuchitsu, "VII Austin Symp.on Gas Phase Molecular Structure. Austin (Texas)", 1978, p.63.
91. W.J.Adams, H.J.Geise, and L.S.Bartell, J.Amer. Chem.Soc., 1970, **92**, 5013.
92. O.Bastiansen, L.Fernholt, H.M.Seip, H.Kambara, and K.Kuchitsu, J.Mol.Struct., 1973, **18**, 163.
93. J.D.Ewbank, G.Kirsch, and L.Schäfer, J.Mol. Struct., 1976, **31**, 39.
94. J.Dillen and H.J.Geise, J.Chem.Phys., 1979, **70**, 425.
95. A.Almenningen, O.Bastiansen, and H.Jensen, Acta Chem.Scand., 1966, **20**, 2689.
96. R.L.Hilderbrandt, J.D.Wieser, and L.K.Montgomery, J.Amer.Chem.Soc., 1973, **95**, 8598.
97. P.C.Lauterbur, J.Amer.Chem.Soc., 1964, **86**, 1870.
98. L.C.Snyder and S.Meiboom, J.Chem.Phys., 1967, **47**, 1480.
99. V.S.Watts and J.H.Goldstein, J.Chem.Phys., 1967, **46**, 4165.
100. R.L.Lipnick, J.Mol.Struct., 1974, **21**, 411.
101. E.W.Garbisch and M.G.Griffith, J.Amer.Chem.Soc., 1968, **90**, 6543.
102. V.A.Chertkov and N.M.Sergeyev, J.Amer.Chem. Soc., 1978, **99**, 6750.
103. A.Streitwieser and W.R.Young, J.Amer.Chem.Soc., 1969, **91**, 529.
104. A.Almenningen, O.Bastiansen, and P.N.Skancke, Acta Chem.Scand., 1961, **15**, 711.
105. F.A.Cotton and B.A.Fenz, Tetrahedron, 1974, **30**, 1587.
106. V.S.Mastryukov, L.V.Vilkov, and O.V.Dorofeeva, Zhur.Strukt.Khim., 1975, **16**, 922.
107. D.Cremer, J.Amer.Chem.Soc., 1977, **99**, 1307.
108. V.S.Mastryukov, E.L.Osina, and L.V.Vilkov, Zhur.Strukt.Khim., 1975, **16**, 850.
109. A.D.Walsh, Trans Faraday Soc., 1949, **45**, 179.
110. V.S.Mastryukov and E.L.Osina, J.Mol.Struct., 1977, **36**, 127.
111. P.J.Fierens and J.Nasielski, Bull.Soc.chim.Belgie, 1962, **71**, 187.
112. S.W.Benson and H.E.O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", New York, 1970.
113. N.D.Lebedeva, N.M.Gutner, and L.F.Nazarova, Symposium, "Termodinamika Organicheskikh Soedinenii" (Thermodynamics of Organic Compounds), Gorky, 1977, No.6, p.26.
114. T.Bally, H.Baumgäertel, U.Büchler, E.Haselbach, W.Lohr, J.P.Maier, and J.Vogt, Helv.Chim.Acta, 1978, **61**, 741.

115. R.B.Turner, P.Gebel, B.J.Mallon, W.Doering, I.F.Coburn, and M.Pomerantz, J.Amer.Chem.Soc., 1968, **90**, 4315.
116. N.C.Baird, and M.J.S.Dewar, J.Amer.Chem.Soc., 1967, **89**, 3966.
117. J.H.Goldstein, V.S.Watts, and L.S.Rattet, "Progress in Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, 1971, Vol.8, p.104.
118. K.Tori, T.Isushima, and H.Tanida, Org.Magnet. Reson., 1974, **6**, 324.
119. P.H.Kassai, R.J.Myers, D.F.Eggers, Jr., and K.B.Wiberg, J.Chem.Phys., 1959, **30**, 512.
120. J.F.Chiang, J.Clin.Chem.(Taipei), 1970, **17**, 65.
121. B.Bak, J.J.Led, L.Nygaard, J.Rastrup-Andersen, and G.O.Sørensen, J.Mol.Struct., 1969, **3**, 369.
122. M.I.Davis and T.W.Muecke, J.Phys.Chem., 1970, **74**, 1104.
123. J.F.Chiang and S.H.Bauer, J.Amer.Chem.Soc., 1969, **91**, 1898.
124. V.A.Naumov, V.G.Dashevskii, and N.M.Zaripov, Zhur.Strukt.Khim., 1970, **11**, 793.
125. H.J.Geise and H.R.Buys, Rec.Trav.chim., 1970, **89**, 1147.
126. M.Traetteberg, Acta Chem.Scand., 1975, **B29**, 29.
127. J.B.Lambert, A.P.Iovanovich, and W.L.Oliver, J.Phys.Chem., 1970, **74**, 2221.
128. C.L.Closs, Proc.Chem.Soc., 1962, 152.
129. H.Günther and H.Seel, Org.Magnet.Reson., 1976, **8**, 299.
130. E.A.Hill and J.D.Roberts, J.Amer.Chem.Soc., 1967, **89**, 2047.
131. A.Almenningen, I.M.Anfinsen, and A.Haaland, Acta Chem.Scand., 1970, **24**, 43.
132. M.P.Kozina, L.P.Timofeeva, G.L.Gal'chenko, E.A.Gvozdeva, and V.M.Cherednichenko, Symposium, "Termodinamika Organicheskikh Soedinenii" (Thermodynamics of Organic Compounds), Gorky, 1976, No.5, p.9.
133. L.H.Scharpen and V.W.Laurie, J.Chem.Phys., 1965, **43**, 2765.
134. G.Dallinga and L.H.Toneman, J.Mol.Struct., 1967–68, **1**, 11.
135. H.Oberhammer and S.H.Bauer, J.Amer.Chem.Soc., 1969, **91**, 10.
136. K.Hagen and M.Traetterberg, Acta Chem.Scand., 1972, **26**, 3643.
137. M.Traetteberg, Acta Chem.Scand., 1970, **24**, 2285.
138. M.Traetteberg, J.Amer.Chem.Soc., 1964, **86**, 4265.
139. M.Traetteberg, Acta Chem.Scand., 1966, **20**, 1724.
140. K.Kuchitsu, T.Fukuyama, and Y.Morino, J.Mol. Struct., 1968, **1**, 463.
141. M.P.Kozina, in "Sovremennye Problemy Fizicheskoi Khimii" (Modern Problems of Physical Chemistry), Izd.Moskov.Gos.Univ., 1976, Vol.9, p.198.
142. W.Parker, W.V.Steele, and J.Watt, J.Chem. Thermodyn., 1977, **9**, 307.
143. K.W.Cox, M.D.Harmony, G.Nelson, and K.B.Wiberg, J.Chem.Phys., 1969, **50**, 1976.
144. S.N.Mathur, M.D.Harmony, and R.D.Suenram, J.Chem.Phys., 1976, **64**, 4340.
145. V.S.Mastryukov, E.L.Osina, L.V.Vilkov, and R.L.Hilderbrandt, J.Amer.Chem.Soc., 1977, **99**, 6855.
146. S.N.Mathur and M.D.Harmony, J.Mol.Spectr., 1978, **69**, 37.
147. V.A.Naumov and V.N.Bezzubov, Dokl.Akad.Nauk SSSR, 1970, **193**, 113.
148. A.Spelbos, F.C.Mijlhoff, W.H.Bakker, R.Baden, and L.Van Den Enden, J.Mol.Struct., 1977, **38**, 155.
149. L.Van Den Enden, H.J.Geise, and A.Spelbos, J.Mol.Struct., 1978, **44**, 177.
150. K.Wüthrich, S.Meiboom, and L.C.Snyder, J.Chem. Phys., 1970, **52**, 230.
151. M.Christl, Chem.Ber., 1975, **108**, 2781.
152. J.M.Schulman and Th.J.Venanzi, Tetrahedron Letters, 1976, 1461.
153. P.D.Ellis and G.E.Maciel, J.Amer.Chem.Soc., 1970, **92**, 5829.
154. R.L.Hilderbrandt and J.D.Wieser, J.Mol.Struct., 1973, **15**, 27.
155. W.V.Steele, J.Chem.Thermodyn., 1978, **10**, 919.
156. M.P.Kozina, L.V.Bychikhina, G.L.Gal'chenko, E.M.Mil'vitskaya, M.Ordubadi, and A.F.Plate, Dokl.Akad.Nauk SSSR, 1976, **226**, 1105.
157. R.Walsh and J.M.Wells, J.Chem.Thermodyn., 1975, **7**, 149.
158. J.F.Chiang and S.H.Bauer, J.Amer.Chem.Soc., 1970, **92**, 1614.
159. A.Almenningen, B.Andersen, and B.A.Nyhus, Acta Chem.Scand., 1971, **25**, 1217.
160. G.Dallinga and L.H.Toneman, Rec.Trav.chim., 1967, **86**, 171.
161. J.F.Chiang, J.Amer.Chem.Soc., 1971, **93**, 5044.
162. G.Dallinga and L.H.Toneman, Rec.Trav.chim., 1969, **88**, 185.
163. A.Yokozeki and K.Kuchitsu, Bull.Chem.Soc.Japan, 1971, **44**, 2356.
164. A.Yokozeki and K.Kuchitsu, Bull.Chem.Soc.Japan, 1971, **44**, 1783.
165. K.Tori, R.Muneyuki, and H.Tanida, Canad.J.Chem., 1963, **41**, 3142.
166. B.Franzus, W.C.Baird, N.F.Chamberlain, T.Hines, and E.I.Snyder, J.Amer.Chem.Soc., 1968, **90**, 3721.
167. S.Meiboom and L.C.Snyder, J.Amer.Chem.Soc., 1967, **89**, 1038.
168. K.B.Wiberg and D.E.Barth, J.Amer.Chem.Soc., 1969, **91**, 5124.
169. F.T.Bond, Tetrahedron Letters, 1968, 2789.
170. V.S.Mastryukov, E.L.Osina, L.V.Vilkov, and R.L.Khil'derbrandt, Zhur.Strukt.Khim., 1981, 22, 57.


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