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The Structure and Valence Isomerisation of Antiaromatic Compounds

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Various criteria of aromaticity and their relation with molecular structure are discussed. The characteristics of the quantum-chemical calculations of the electronic structure and geometry of antiaromatic molecules, determined by the specific structure of their potential energy surfaces corresponding to the ground and lowest excited states, are analysed.
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I. INTRODUCTION

Among the theoretical ideas of organic chemistry, it is difficult to find another concept like aromaticity which is as general and plays as important a role in systematic treatment of structural characteristics, stability, physical properties, and reactivity and is at the same time so vaguely but physically unambiguously defined. Indeed, the brief survey below of the unceasing attempts to canonise the concept of aromaticity demonstrates the possibility of enclosing it within a rigorously fixed framework whatever the theoretical and experimental approaches employed.

This factor is the cause of the unceasing controversy whether or not the term "aromaticity" is legitimate. Binsch[1] expressed an extreme point of view. In his paper "Aromaticity—an Exercise in Chemical Gibberish" he defines the main purpose of the concept of aromaticity simply as an "alibi for a certain aura of intellectual respectibility necessary to the investigator when the conclusions arising from his work are on the edge of banality".[1] In fact, it is impossible to isolate a single physically defined structural or energetic parameter which would characterise the degree of aromaticity of a molecule or ion. However, many other concepts of theoretical organic chemistry, whose fruitfulness arouses no doubts, would not withstand such a rigorous criterion. It is sufficient to recall concepts such as isomerism,[2,3] tautomerism,[3,4] conformation, and configuration.[5] The very concept of molecular structure is far from unambiguous when subjected to a rigorous analysis.[5,6]

Numerous reviews[7-11] and monographs[12-16] have been devoted to the analysis of the development of the concept of aromaticity. The energetic aspect, the relative stability of the structure, is nowadays associated primarily with aromaticity or aromatic character. Although individual attempts have been made to extend the concept of aromaticity to acyclic compounds (for example, the concept of Y-aromaticity has been introduced[17]) and saturated compounds (σ-aromaticity[18]), in general it is used to describe the enhanced stability of a particular type of cyclic structures relative to acyclic structures.[9,19,20] Finally, a tendency has become increasingly clear to relate the enhanced stability of aromatic structure to the closed nature of its electron shell.[17]

The synthesis and theoretical studes of various types of cyclic structures, for which the above conditions are realised and which therefore possess an increased relative stability, have led to the formation of a whole series of new structural concepts refining the concept of aromaticity and demonstrating its fruitfulness. The scheme illustrated in Fig.1 provides a by no means complete representation of various structural types of aromaticity.

The task of the present review is to examine the problem of antiaromaticity, mainly from the standpoint of its structural aspect. Since the concept of antiaromaticity is set against that of aromaticity, it is evident that the main feature of antiaromaticity is cyclic destabilisation, i.e. the energetically unfavourable nature of a planar cyclic structure of a conjugated molecule or ion with declocalisation of π-bonds.

As will be shown below, the main cause of the antiaromatic character of a structure is specific features of the structure of the electron shells of the corresponding cyclic conjugated compounds. A detailed understanding of these features involves a fairly profound theoretical study of the problem, requiring the application of the most refined methods of modern quantum chemistry. Because of the instability of antiaromatic compounds and the consequent difficulty of their experimental study, the quantum-chemical approach assumes a particular importance in this instance.

The data obtained with the aid of quantum-chemical calculations can be used to identify the most promising trends in preparative research and to investigate the details of the mechanisms of reactions of antiaromatic compounds. In view of this, in the present review attention is concentrated on the theoretical study of the structures of antiaromatic compounds and it is endeavoured to demonstrate to what extent the combination of the theoretical and experimental methods of organic chemistry has been fruitful in this instance.

The review deals with the principal types of antiaromatic compounds—monocyclic polymethines $(CH)_m$ with $4n\pi$-electrons, annulenoannulenes, and their heterosubstituted derivatives. Various compounds classified as antiaromatic contain fragments corresponding to these structures. In view of this, the observed characteristic features of the electronic and geometrical structures and of valence isomerisations of antiaromatic compounds are fairly general.

The instability of antiaromatic compounds is responsible for their tendency to undergo valence isomerisation reactions and rearrangements, as a result of which the energetically unfavourable planar conjugated bond system breaks down. Quantum-chemical data made it possible to interpret the instability of antiaromatic compounds from the standpoint of the properties of the corresponding potential energy surfaces (PES), which determine the wide variety of types of valence isomerisations; the PES of antiaromatic compounds are characterised by relatively low barriers to isomerisation—the proximity of the surfaces corresponding to excited states which as a rule gives rise to electronic lability of the molecule.[29-32] These features of the PES of antiaromatic compounds hinder the application of traditional computational schemes, which do not always yield equivalent results.

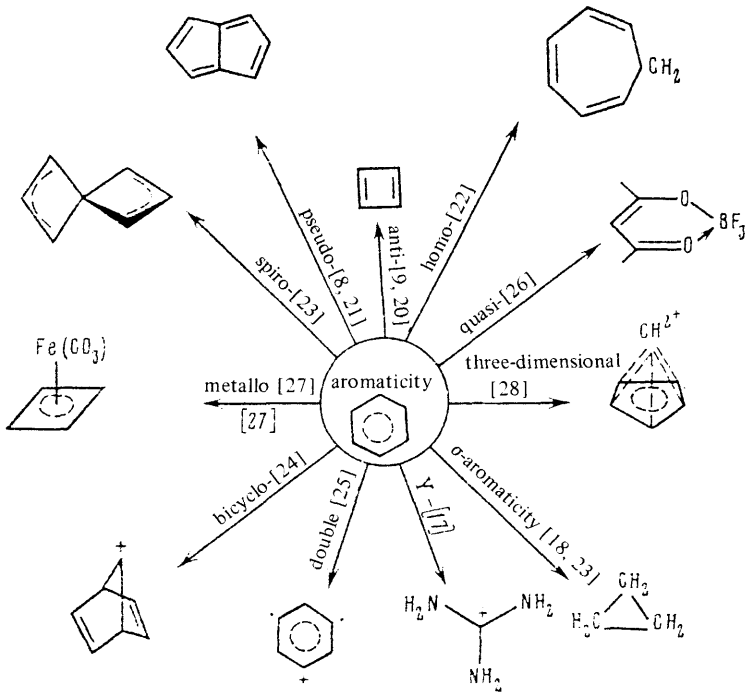


Figure 1. Illustration of the wide variety of aspects of the concept of aromaticity. Structures corresponding to a particular type of aromaticity are presented.

Note. Numbers in square brackets denote references (Ed. of Translation).

Because of this, the class of antiaromatic compounds constitutes a kind of "touchstone" for the estimation of the limited applicability of a particular theoretical method and makes it possible to elucidate its limitations and scope for further improvement.

1. Criteria of Aromaticity and Antiaromaticity

An unambiguous criterion which could be used to classify particular compounds—aromatic or antiaromatic—does not exist. The criteria based on reactivity data characterise the kinetic stability and are determined by the properties not only of the ground state of the molecule but also those of the transition state in the reaction considered. The capacity to undergo electrophilic substitution reactions, which is frequently regarded as the most characteristic feature of aromatic compounds,[13] cannot always be used as a sufficiently reliable sign of aromaticity.[33] In their monograph "Facts and Theories of Aromaticity", Lewis and Peters[16] concluded on the basis of a detailed discussion of various interpretations of the term "aromaticity" that the most general definition reduces to the following: "an aromatic molecule is a molecule which resembles benzene". Even in this definition, it is necessary to establish which feature of similarity is the most important. In the present reivew the structural-energetic criterion has been adopted for this purpose: a conjugated compound is aromatic if the delocalisation of π-electrons stabilises its cyclic structure relative to the corresponding acyclic polyene structure (for example, benzene and hexa-1,3,5-triene). On the other hand, in the case of a greater stability of the acyclic reference structure (cyclobutadiene and buta-1,3-diene) the given system is classified as antiaromatic.

Quantitative estimates of the degree of aromaticity or antiaromaticity are based on the concept of resonance energy.

(a) Energetic criteria of aromaticity and antiaromaticity. The resonance energy. Hückel[34] showed that the molecule or ion with a monocyclic structure is stabilised when the bonding π-orbitals are completely filled with electrons and the non-bonding and antibonding molecular orbitals (MO) are unoccupied. The fulfilment of these conditions leads to the familiar $(4n + 2)$ rule for the number of π-electrons in an aromatic monocyclic compound. On the other hand, annulenes with $4n$ π-electrons in the ring have an open π-electron shell. The cyclic delocalisation of π-electrons in these systems leads to the destabilisation of the structure. Consequently, [4*n*]-annulenes must be classified as antiaromatic systems.

The general concept—the requirement that all the bonding MO are completely filled and the remaining MO are unoccupied—proved to be fruitful also for three-dimensional systems [polyhedral carbaboranes,[35] pyramidal structures $(CH)^{n+}_{n+4}$,[36] and organometallic clusters,[37] for the determination of the stability of which specific electron count rules have been proposed[38,39]]. This concept has been extrapolated also to acyclic conjugated molecules. For example, the stable guanidinium cation, which contains six π-electrons, has been assigned to the class of so-called molecules with a centre of aromaticity (Y-aromaticity[17]), while trimethylenemethane (four π-electrons) can be regarded as an antiaromatic system in this sense.[31]

The contribution of conjugation to the energy of the molecules is characterised by the Hückel resonance energy (HRE), which is defined in terms of the Hückel approximation[40] as the difference between the total π-electron energies of the conjugated molecule and a system consisting of *m*

isolated double bonds present in the classical (Kekulé) structure of the conjugated molecule:

$$\mathrm{HRE} = E_\pi^m - mE_\pi(\mathrm{C{=}C}), \qquad (1)$$

where E_π^m is the π-electron energy of the conjugated molecule.

However, estimates of aromaticity with the aid of the HRE did not prove to be entirely satisfactory. Thus, in conformity with Eqn.(1), the degree of aromaticity should increase with increasing size of the π-electron system, which conflicts with certain experimental data. For example, the kinetic stability of polyacenes diminishes on successive linear annelation (pentacene and hexacene readily interact with atmospheric oxygen[43]). In a number of instances unduly high HRE correspond to antiaromatic molecules,[44] for example, the HRE of pentalene (2.46β) is higher than for benzene (2β).

Dewar[45,46] developed a more rigorous scheme for the estimation of the resonance energies of cyclic conjugated structures. He adopted as the reference structure a polyene in which the numbers of the σ- and π-bonds are equivalent to those in the cyclic compound and not the system of isolated π-bonds adopted when Eqn.(1) is used. Using the approximation assuming the additivity of the bond energies in acyclic polyenes,[47] it is possible to calculate the total energy of any acyclic or cyclic polyene with localised double bonds by adding together the energies of all the bonds. The Dewar resonance energy (DRE) is defined as the difference between the heat of formation of a given conjugated molecule and the heat of formation calculated for the classical (Kekulé) reference structure:

$$\mathrm{DRE} = -(\Delta H^m - \Delta H_{\mathrm{add}}), \qquad (2)$$

where ΔH_{add} is the heat of formation calculated for the model reference structure (the minus sign is included because the values of DRE for aromatic systems are assumed to be positive (see Dewar,[45] p.480). For example, for benzene we have $\Delta H_{\mathrm{add}} = 3E_1 + 3E_2 + 6E_{\mathrm{C-H}}$, where E_1 and E_2 are parameters representing the energies of the "polyene" single and double bonds. Thus DRE can be expressed in a form more convenient for comparison with the HRE:

$$\mathrm{DRE} = -(E_\pi^m - (n_1E_{1\pi} + n_2E_{2\pi})) \qquad (3)$$

where n_1 and n_2 are the numbers of single and double bonds in the Kekulé structure of the π-electron system considered and $E_{1\pi}$ and $E_{2\pi}$ are the π-electron energies of the "polyene" single and double bonds.

The method for the calculation of the resonance energies described above makes it possible to take into account more accurately the contribution of cyclic conjugation to E_π. Furthermore, since the calculation of the DRE is based on the scheme of the Pariser–Parr–Pople (PPP) method modified by Dewar and de Llano,[42] which makes it possible to take into account the contribution of σ-bonds, the values of DRE in Eqn.(2) contain a correction for the energy of the contraction (extension) of the σ-bonds in the cyclic conjugated compound relative to the model structure. The values of DRE are satisfactorily correlated with experimental stability data[44] (furthermore in the case of annulenes, for example, a series of correlations have been observed between the physicochemical properties and the resonance energy, in particular between the $\Delta G^{\neq}$ for the Diels–Alder reaction with maleic anhydride and the difference between the corresponding resonance energies).

On the basis of the Hückel method, Hess and Schaad developed a scheme for the calculation of the resonance energy (HSRE) in which account was taken of the differences between the immediate environments of the bonds (C–C and C=C).[45,46]

The sharp increase of the number of empirical parameters for heteroatomic molecules must be included among the disadvantages of the DRE and HSRE definitions. Furthermore, the values of DRE and HSRE can be found only for molecules for which it is possible to construct Kekulé structures and hence the above definitions are inapplicable to radicals, ions, and non-classical structures (see, however, Hess and Schaad[47]).

The definition of the topological resonance energy (TRE),[48–50] based on the employment of the Hückel theory and the methods of the theory of graphs,[51] is free from these disadvantages. The concept of the TRE is applicable to any conjugated system, including ions, radicals, and radical-ions.[52,53]

The TRE, defined by the formula

$$\mathrm{TRE} = \sum_j (g_j x_j - g_j^{\mathrm{acycl}} x_j^{\mathrm{acycl}}) \qquad (4)$$

(g_j are the filling numbers for the filling of π-orbitals by electrons in the ground state, x_j the roots of the characteristic polynomial for the conjugated system, and x_j^{acycl} and g_j^{acycl} refer to the acyclic polynomial[48–50] corresponding to the given molecular graph), characterises the cyclic conjugation energy in the given molecule or ion.

We emphasise that, in estimating the degree of aromaticity with the aid of the TRE, there is no need to select a suitable reference structure. Furthermore, the acyclic polynomial used in the definition of the TRE need not correspond to any real structure which can be represented in the traditional way. This is both an advantage and a disadvantage of the TRE as a criterion of aromaticity, since the concept of the TRE is not linked directly to the concepts of structural chemistry familiar to chemists. In a number of instances, the estimates of the TRE are nevertheless unsatisfactory.[54–56] Thus the TRE for cyclobutadiene (–1.226β) has been obtained on the assumption that $g_1 = g_2 = 2$. However, according to Hund's rule, it must be assumed that $g_1 = 2$ and $g_2 = g_3 = 1$; the TRE then obtained is +0.304β, i.e. cyclobutadiene then appears to be actually more aromatic than benzene.

Table 1. The values of HRE, DRE, HSRE, and TRE for certain annulenes, annulenoannulenes and monocyclic conjugated ions (all the resonance energies have been normalised per π-electron in the calculation).

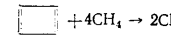
Compound	HRE, β units (Refs.34, 41)	DRE, eV (Refs.42, 44)	HSRE, β units (Refs.45–47)	TRE, β units (Refs. 48–50, 52, 53)
Cyclobutadiene	0.000	–0.1335	–0.268	–0.3065
Benzene	0.333	0.1450	0.065	0.046
Cyclo-octatetraene	—	0.0542	–0.0609	—
Propalene	—	—	–0.100	—
Pentalene	0.307	0.0008	–0.018	–0.027
Heptalene	0.302	0.0078	–0.004	–0.042
Butalene	—	–0.0457	–0.067	–0.1007
Octalene	—	–0.0007	0.007	—
Cyclopropenyl anion	—	—	–0.423	–0.366
Cyclopentadienyl cation	—	—	–0.114	–0.153

The values of DRE, HSRE, and TRE for benzene and certain antiaromatic compounds are listed in Table 1 (to facilitate comparison, the RE for different systems have been calculated per π-electron). The values of TRE normalised in this way are linked to the HSRE by the relation[57]

$$\mathrm{TRE} \cong \mathrm{HSRE} + (0.69/N)\ln K, \qquad (5)$$

where N is the number of π electrons, K the number of Kekulé structures; the values of TRE and HSRE are calculated per π electron.

The heats of isodesmic[58] reactions, characterising the stability of the given cyclic systems relative to the corresponding acyclic compounds with the same types of single and double bonds, have also been used to determine the resonance energy. Thus the heats of the given reactions can be used to estimate the energy of cyclic conjugation in the given system, reflecting thereby its aromatic or antiaromatic character,[60] for example (the values of ΔH are given in kJ mol^{-1}):



$$+4CH_4 \rightarrow 2CH_3{-}CH_3 + 2CH_2{=}CH_2 \qquad (6)$$

ΔH = —294.5 [MINDO/3 (Ref.59)]; —217.1 (MNDO); —268.6 [STO-3G (Ref.60)]; —278.2 [4-31G (Ref.60)]; —284.1 [6-31G//3-21G (Ref.61)]†;



$$+6CH_4 \rightarrow 3CH_3{-}CH_3 + 3CH_2{=}CH_2; \qquad (7)$$

ΔH = 30.4 (MINDO/3); 154.8 (MNDO).

(b) Magnetic criteria of aromaticity and antiaromaticity. It has been suggested that a compound be defined as aromatic if induced diamagnetic π-electron ring currents are maintained in its molecule (diatropic system). The ring current influences the chemical shifts in the ^{1}H NMR spectra and the current itself is used as a quantitative measure of the aromaticity of the compound. On the other hand, paramagnetic ring currents (paratropic systems) are characteristic of antiaromatic compounds, for example [4n]annulenes (see the relevant reviews[62,63]).

In the case of [4n + 2]annulenes there is a simple relation between the resonance energy per π-electron (RE/π-E in β units) and the system of π-electron ring currents I [64–66]:

$$RE/\pi\text{-}E = \frac{\pi^2 I}{kS}, \qquad (8)$$

where S is the area of the ring; for benzene, it has been assumed that $S = 1$, $k = 3$;[64] $k = 4$.[65]

In addition a linear correlation has been observed between the difference between the chemical shifts of the signals due to the external and internal protons for $\tau_{ext} - \tau_{int}$ in the ^{1}H NMR spectra of [n]annulenes and the value of RE/π-E:[67]

$$\frac{(\tau_{ext} - \tau_{int})}{S} = m(RE/\pi\text{-}E), \qquad (9)$$

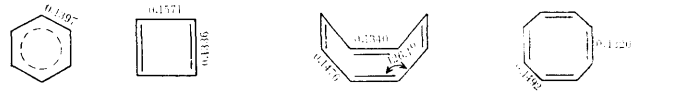
where m is a constant.

However, for non-alternate hydrocarbons and for heterocyclic systems, the relation between the resonance energy and the magnetic criteria is not sufficiently defined.[64] Furthermore, the results of calculations of ring currents for antiaromatic systems depend greatly on the method employed (see, for example, Mallion[62]).

The use of magnetic parameters as exhaustive criteria has been subjected to serious criticism.[16,62] We may point out, for example, that the manifestation of diatropism does not necessarily indicate a tendency towards electrophilic substitution reactions or even the stabilisation of the cyclic conjugated system.[66] In many cases the system may be diatropic and antiaromatic, for example, bicyclo[6.2.0]-decapentane.[68]

†Here and henceforth the abbreviations proposed by Pople are used; the numerals in brackets indicate that a non-empirical calculation has been carried out in terms of, for example, the 6-31G basis set, for the geometry optimised in terms of the 3-21G basis set.

(c) Structural criteria of aromaticity and antiaromaticity. The most distinctive structural characteristics of the benzene molecule are its planarity and complete equalisation of the C–C bond lengths. In conformity with the structural criterion, analogous properties are to be expected for aromatic molecules. On the other hand, for antiaromatic molecules, in which the cyclic conjugation destabilises the structure, one may expect a tendency towards the localisation of double bonds, i.e. towards the breakdown of the equalisation of the C–C bond lengths.



[according to results of *ab initio* calculations (Ref.69)] [according to electron diffraction data (Ref.70)] [according to results of *ab initio* calculations (Ref.71)]

It has been suggested that the molecule be regarded as aromatic when the lengths of the carbon–carbon bonds are in the range 0.136–0.143 nm, i.e. are close to the value of 0.1397 nm in benzene, and should be regarded as a polyene when the C=C bond length is in the range 0.134–0.135 nm, while the C–C bond length is 0.144–0.1475 nm.[16] A quantitative character has been given to this criterion. The degree of aromaticity has been estimated from the means square deviation of the carbon–carbon bond lengths:[72]

$$\delta = \frac{\sum_{rs} (d_{rs} - \bar{d})^2/\bar{d}^2}{n}, \qquad (10)$$

where d_{rS} is the length of the bond between the atoms r and s and $\bar{d}$ is the average length of n bonds (Å).

The aromaticity index A was then determined[72] from the formula

$$A = 1 - 225\delta. \qquad (11)$$

Subsequently the expression for A was modified in order to take into account the requirement for the equalisation of the distribution of electron density along the ring bonds of the aromatic molecule.[73] However, difficulties then arise in the case of molecules such as those of azulene owing to the considerable length of the transannular bond and in the case of heterocyclic conjugated molecules. Developing the criterion of bond length equalisation for the definition of aromaticity, Kruszewski and Krygowski[74] suggested that two aromaticity indices, based on the harmonic oscillator model (HOMA), be introduced. The value of HOMA$_d$ is determined by the length d(Å) of the carbon–carbon bonds:

$$HOMA_d = 1 - \frac{a}{n}\sum_{r=1}^{n}(X_r - 1.397)^2 \qquad (12)$$

where a = 98.89, X_r is the length of the rth bond, and n is the number of bonds. HOMA$_d$ = 1 has been obtained for the structure of benzene with D_{6h} symmetry and HOMA$_d$ = 0 has been found for the molecule with D_{3h} symmetry. Thus HOMA$_d$ reflects the increase of the energy of the π-electron system when the bond lengths deviate from the value in benzene (1.397 Å).

The index HOMA$_p$ is determined by the bond orders:

$$HOMA_p = 1 - \frac{3.66}{n}\sum_{rs}^{n}\left(\frac{2}{3} - P_{rs}\right)^2, \qquad (13)$$

where P_{rs} is the order of the bond between the atoms r and s.

The planarity of the molecule is usually regarded as a characteristic feature of aromatic systems.[13] However, the non-planar character of the structures of [4n]annulenes can

hardly be interpreted solely as a consequence of antiaromaticity,[75,76] because the strains in the σ-electron system can play a decisive role in the breakdown of planarity. Cyclooctatetraene has a non-planar structure with D_{2d} symmetry but its π-electron energy is a minimum for a planar configuration and the non-coplanar distortion leads to an increase of this energy.[75] The non-planar character of the carbon skeleton for cyclo-octatetraene and of its derivatives is due to angular strains which arise in the planar σ-electron system (their contribution to the enthalpy of the transition to the D_{2d} configuration is ~85%).[77,78]

Thus one should not completely identify antiaromaticity with the tendency towards the breakdown of the planar structure of the molecule. A molecule which can be classified as antiaromatic can deviate only slightly from a planar conformation, as, for example, for 1,5-bisdehydro[12]annulene,[76] and at the same time the properties of the σ-electron system can determine the non-planar structure also in the case of aromatic compounds. For example, non-empirical calculations for the cyclobutadiene dication (two π electrons) point to a non-planar structure with D_{2d} symmetry.[79,80] On the other hand, calculations by the MINDO/3 method have shown[81] that a saddle point and not a minimum on the potential energy surface of cyclobutadiene (C_4H_4) corresponds to the non-planar structure of its molecules, which have the same symmetry.

Thus the structural criterion of antiaromaticity is apparently most correctly treated as the energetic preference for a planar structure with alternating bond lengths as compared with a planar highly symmetrical structure with equalised carbon–carbon bond lengths. The generality of this structureal criterion is confirmed by the results of Nakajima and Binsch et al., who developed the theory of lattice instability in a series of studies (see the relevant reviews[82,83]).

In order to determine the stability of a highly symmetrical planar configuration of the molecule relative to distortions leading to planar structures of lower symmetry, it is necessary to estimate the force constant of the corresponding normal vibration Q_i which causes the deformation of the highly symmetrical configuration. A conjugated cyclic system is aromatic if the "fixation of double bonds" of the first or second order is not observed (in the first-order bond fixation, the symmetry of the σ-skeleton does not change in contrast to the second-order bond fixation).[83] The second-order double bond fixation is characterised by a minimum eigenvalue λ of the bond–bond polarisability matrix and the corresponding eigenvector determines the symmetry of the distortion. If λ_{max} (in units of β) is less than a critical value $\lambda_{cr} = 1.22$, then the system is stable in relation to distortions leading to the breakdown of the equalisation of bond lengths. For example, the minimum force constant for the in-plane vibrations of benzene corresponds to a distortion b_{2u} to give the D_{3h} structure, but $\lambda_{max} = 0.791 < \lambda_{cr}$ and a distortion of this kind is not realised. On the other hand, for pentalene and heptalene the calculated λ_{max} exceed λ_{cr} and a dynamic alternation of bond lengths,[83] analogous to the topomerisation of the D_{2h} structure of cyclobutadiene,[84,85] should obtain for such compounds, which makes it possible to classify pentalene and heptalene as antiaromatic systems.

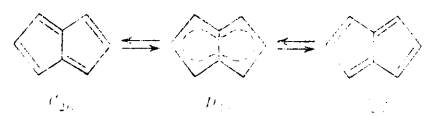
The criterion of the lattice instability is consistent with the criteria based on the resonance energies and magnetic properties.[64]

The degree of instability of the molecular configuration and the possibility of a reduction of symmetry are caused by the second-order Jahn–Teller effect, which depends on the difference $\Delta E = E_1 - E_0$ between the energies of the ground and first excited singlet states.[82] The following criterion of the instability of the geometrical configuration of the molecule has been formulated: if the quantity ΔE calculated for a given structure with equalised bond lengths is less than the empirically selected quantity 1.2 eV, then the force constant of the in-plane skeletal vibration will assume a negative value, giving rise thereby to a tendency towards a distortion resulting in a less symmetrical structure with alternating carbon–carbon bond lengths.[82,86,87] Thus $\Delta E = 0.35$ eV has been obtained for the pentalene structure with D_{2h} symmetry and this structure is unstable in relation to distortions giving rise to a structure with C_{2h} symmetry.

Thus a minimum on the potential energy surface does not correspond to a highly symmetrical configuration of the singlet state of antiaromatic molecules. On the other hand, there are minima on the potential energy surface corresponding to structures with reduced symmetries involving alternating bond lengths, which are interconverted via a multiplicity of valence isomerisation modes. The topomerisation of structures with alternating bond lengths is then the main process:



(14)



(15)

For benzene, the structure with D_{6h} symmetry corresponds to a minimum on the potential energy surface for the C_6H_6 system. For example, the structure of the singlet state of cyclobutadiene with D_{4h} symmetry is the transition state in the topomerisation reaction of the D_{2h} configuration (Fig. 2).[88–90]

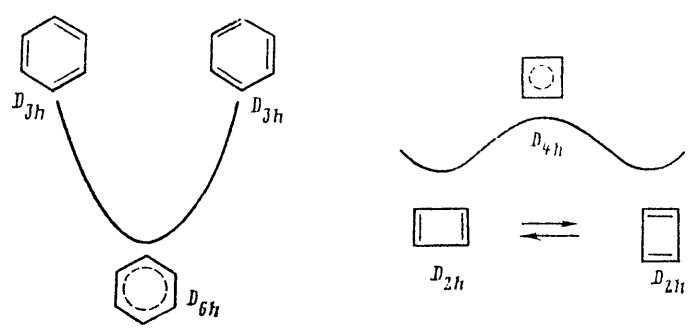


Figure 2. Potential curves for benzene and cyclobutadiene molecules along the coordinate corresponding to the shift of the double bonds.[3] In the case of benzene a skeletal vibration is observed in the Raman spectrum at 1585 cm^{-1}. For cyclobutadiene, the topomerisation of the D_{2h} structure takes place.

The multiplicity of other proposed aromaticity–antiaromaticity criteria,[12–16,91–96] and their interrelations[97] cannot be discussed within the framework of the present review. Furthermore, almost all the remaining definitions are to some extent derived from the fundamental criteria of aromaticity–antiaromaticity considered above.

We may note that the application of the concept of resonance energy and magnetic criteria to antiaromatic molecules does not in fact always lead to definite conclusions.[55,62]

2. Characteristic Features of the Calculation of the Electronic Structure of Antiaromatic Molecules

The complex relief of the potential energy surfaces of antiaromatic molecules and the closeness of the energy surfaces for the ground and lowest excited states, which in many instances leads to their touching and even intersecting, are all factors which impose more stringent requirements on the rigour of the quantum-chemical calculations of the electronic structures of antiaromatic molecules. When the SCF MO method is used, one encounters the problem of the stability and multiplicity of the Hartree–Fock (HF) solutions.[98–114]

In this connection it is necessary to note two aspects of the problem. The first involves the methodology of the correct selection of the computational scheme which can yield specific results for antiaromatic molecules. The second involves the interrelation between the so-called singlet instability of the HF solutions for antiaromatic molecules and the lattice instability, which we mentioned in the previous section as one of the structural criteria of aromaticity–antiaromaticity. The schemes for the calculation of the stabilities of solutions have been examined in a number of studies.[35,107–109] They reduce to the evaluation of the eigenvalues of the instability matrices, whose elements are determined from the familiar formulae for the matrix elements of the HF Hamiltonian between singly excited states and between the ground and doubly excited states.[35]

It is possible to discover a series of instability levels[106–111] which determine the concrete form of the instability matrix. In the case of a closed shell the singlet and triplet (non-singlet) instabilities are treated within the framework of the restricted Hartree–Fock method (RHF), which presupposes identical spatial wave functions for electrons with different spins. The singlet instability is the instability in the variations of the overall wavefunction with retention of the twofold occupation of the orbitals. The triplet instability is one corresponding to the abandonment of the restriction in the RHF method imposed by the requirement for the twofold occupation of the orbitals and to variations characteristic of the unrestricted Hartree–Fock method (UHF).

The triplet instability of the solutions obtained in the calculation by the RHF method is a sufficient (but not necessary) condition for the existence in the calculation by the UHF method of a solution with a lower energy.[99,108] This type of instability is much more common than the singlet instability. The instability of the relative occupation of the MO [the so-called filling up (FU) instability[107]] where the filling of the highest orbitals can lead to solutions with a lower total energy, to the breakdown of the Aufbau-principle of the filling of energy levels,[100] is of special interest.

If the solution by the RHF method is unstable, it is necessary to take into account correlations effects.[115] For a correct description of the electronic structures of antiaromatic molecules, there exist in this instance two alternative procedures.[116] Firstly, remaining within the framework of the one-determinant approach, one can employ MO of lower symmetry than that of the nuclear skeleton, while in the presence of triplet instability one can employ the UHF method. This procedure makes it possible to obtain results which agree well with experimental data, in contrast to those based on the use of fully symmetrical solutions (see, for example, Karpfen and Petkov[117] and Canuto et al.[118]). In the presence of triplet instability, the transition to the UHF approximation makes it possible to describe the multiplicity of the electronic state of the highly symmetrical configurations of antiaromatic molecules.[119–122] For example, analysis of the stability of the solution for cyclobutadiene obtained by the UHF method indicates a singlet ground state having a D_{4h} structure.[119,122] On the other hand, the cyclopropenyl anion (D_{3h}) and the cyclopentadienyl cation (D_{5h}) have a triplet ground state.[119] Thus the study of the character of the stability of the HF solution permits qualitative conclusions about the nature of the electronic ground states of the given molecules which are fully confirmed by non-empirical calculations taking into account the electronic correlation energy.[88–90]

Another procedure for taking into account correlation effects is also possible, involving the superposition of configurations made up of MO with corresponding symmetries or involving the use of multiconfiguration self-consistent field methods (MC SCF). Although this approach requires the allowance for a large number of configurations and involves a considerable consumption of computer time, nevertheless it is perhaps the most preferable. In relation to the cyclopropenyl anion, cyclobutadiene, the cyclopentadienyl cation, and other antiaromatic molecules, the multiconfiguration approximation was developed further by Borden and Davidson (see the relevant reviews[29,31] and the literature quoted therein).

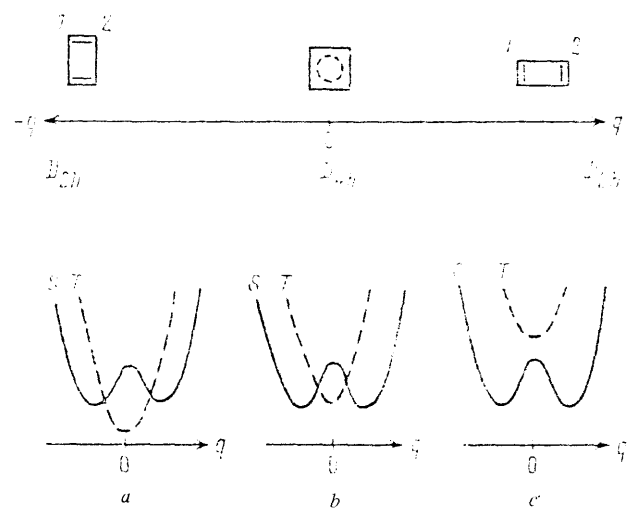


Figure 3. The forms of cross-sections through the potential energy surface for C_4H_4 along the locus of the minimum energy of the reaction (LMER) involving the topomerisation of the cyclobutadiene structure with D_{2h} symmetry (q is the reaction coordinate).

The second structural aspect of the problem of the instability of the HF solutions is determined by the relation between the singlet instability of solutions by the RHF method and lattice instability. The singlet instability has been revealed by the results of calculations by semiempirical methods of the PPP type for aromatic hydrocarbons only when unrealistic values of the resonance integral β were used.[123] However, for antiaromatic molecules the singlet instability of the RHF

solutions has been found even for values of the resonance integral β close to the standard values.[124,125] The singlet instability entails the existence of a solution with an electron distribution corresponding to a reduced symmetry, which gives rise to a tendency towards the distortion of the highly symmetrical geometrical configuration (lattice instability)[126-129] and determines the symmetry of this distortion.[129] The relation between the matrix of the singlet instability and the expression for the force constant when the molecular configuration is distorted as a consequence of the second-order Jahn–Teller effect has been demonstrated.[130]

Thus the singlet instability in the solutions by the RHF method for antiaromatic molecules is responsible for the possibility of the lattice instability, which is one of the structural criteria of aromaticity-antiaromaticity and makes it possible to predict a number of characteristics of the potential energy surface. The presence of the single instability should be regarded as an indication of the necessity to correct the initial hypothesis concerning the form of the nuclear configuration.[131] The possibility of a dynamic process involving the isomerisation of antiaromatic molecules is generally speaking an essential consequence under these conditions of the singlet instability and must be investigated in each specific case. The quantum-chemical calculation of the potential energy surfaces of antiaromatic compounds, to the results of which the next Section of this review is devoted, assumes particular importance in this connection.

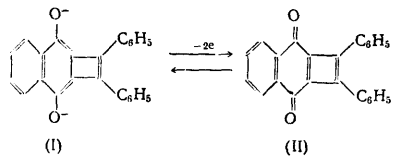
II. THE STRUCTURE AND VALENCE ISOMERISATION OF ANTIAROMATIC $(CH)_n$ POLYMETHINES AND THEIR HETERO-SUBSTITUTED DERIVATIVES

1. Cyclobutadiene

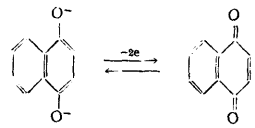
Cyclobutadiene (CBD) is the key structure in the theory of antiaromatic systems. Just as the benzene molecule is a prototype of an aromatic system, CBD is regarded as an example of a system which is antiaromatic not only on a relative scale (compared with the corresponding model system), but also on the absolute scale,[132] bearing in mind the degree of localisation of the molecular π orbitals. This implies that the electronic-structural properties of CBD are directly opposed to those of benzene. The bond conjugation in the four-membered ring of CBD causes a sharp destabilisation of the structure which is expressed in negative resonance energies for CBD (Table 1), the localisation of the double bonds in the ring, a tendency towards reactions involving addition to the double bonds, and the stereochemical non-rigidity of the CBD molecule associated with the fluctuations of the positions of the π bonds in the molecule.

Monographs and reviews have been devoted to CBD.[29,31,133-135] Here we shall briefly consider the principal manifestations of the antiaromaticity of CBD by comparing the thermodynamic stabilities of CBD and its derivatives, the tendencies towards isomerisation, and the structural characteristics.

The resonance energies of CBD calculated by different procedures (Table 1) may be compared with the experimental data. The latter are based on a comparision of the energy relations of isotypical reactions, some of which lead to the formation of the [4]annulene fragment, with other reactions in which this fragment does not arise. For example, a study has been made[9,136] of the reversible electrochemical oxidation-reduction of the quinones (II) and (IV):



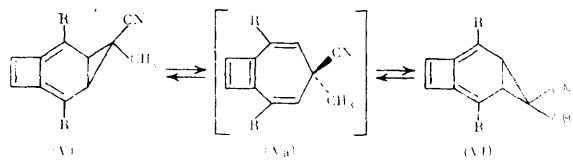
(I) (II) (16)



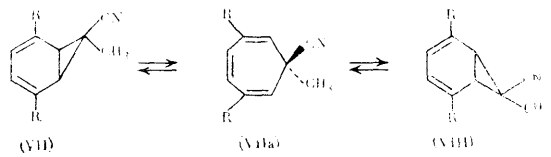
(III) (IV) (17)

The much higher oxidation potential of compound (I) compared with that of compound (III) has been interpreted[9,136] as the manifestation of the characteristic features of the antiaromaticity of compound (I), which contains an annelated cyclobutadiene fragment. The energy of the antiaromatic destabilisation of CBD after taking into account the influence of steric effects in the system of compound (I) (see also Herr[137]) has been estimated as 60–80 kJ mol^{-1}.

Another approach[138] is based on a comparison of the activation barriers to the topomerisation reactions (V) ⇌ (VI) and (VII) (VIII) determined by dynamic NMR.



(18)



(19)

The differences between these barriers are attributed to the formation in the first case of the destabilised structure (Va) containing the antiaromatic CBD ring. The resonance energy of the unsubstituted CBD has been estimated as approximately 88 kJ mol^{-1}.

As mentioned above in Section (I), calculations of the heat of the isodesmic reaction (6) also indicate the antiaromaticity of CBD.

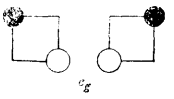
Paramagnetic ring currents have been observed[135] in an NMR study of tri-t-butylcyclobutadiene, which makes it possible to classify CBD as a paratropic system and, in conformity with the magnetic criteria, as an antiaromatic system.

(a) The geometrical structure of the type of the electronic ground state of CBD. The problems of the geometry and the multiplicity of the electronic ground state of CBD have found a reliable theoretical and experimental solution only recently (see the detailed review of Bally and Masamune[135]). Here we shall note only the most significant features.

Numerous calculations for CBD have led to three possible types of cross-sections through the potential energy surface for the C_4H_4 system corresponding to the locus of the minimum energy of the reaction involving the topomerisation of the CBD structure with D_{2h} symmetry via a structure having the D_{4h} symmetry (Fig.3).

The results of the majority of the calculations show that in the singlet ground state CBD has an equilibrium configuration with D_{2h} symmetry. The scheme in Fig. 3*a* corresponds to the results of Allinger et al.[139] (PPP method, the σ-skeleton is treated by the method of molecular mechanics). On the other hand, the conclusions concerning the energy of the lowest singlet and triplet states having a structure with D_{4h} symmetry have been contradictory. For the CBD structure having this symmetry, two electrons in the e_g orbitals can be accommodated in different ways, which leads to six degenerate configurations within the framework of the one-determinant approximation.

By considering their interactions and using the symmetry properties, it can be shown that in the given instance there is a possibility of the electronic states ^1A_1g, ^1B_1g, ^1B_2g and ^3A_2g (whose energies relative to that of the ^3A_2g state are 280, 251, and 29 kJ mol^{-1} according to the results of non-empirical calculations in terms of the 6-31G basis set[88]), differing in the ways the electrons are accommodated in the orbitals. Orbitals of the e_g type are localised at different carbon atoms:



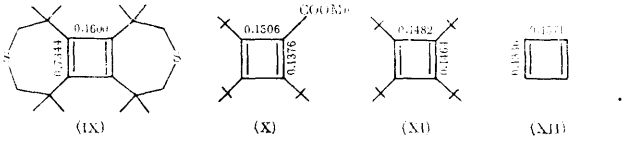
The corresponding exchange integral should be very small (it should be approximately zero in terms of the NDO approximation), which has two consequences. Firstly the energies of the ^3A_2g and ^1B_1g states are similar, because the electrons in the e_g orbitals are separated in space and the energy of the interelectron interaction depends less on whether the spins are parallel of not.[90] Secondly, as a result of the dynamic spin polarisation#, which is much more effective in the case of the singlet state, the energy of the ^1B_1g state is lower than that of the ^3A_2g state (see the scheme in Fig. 3*c*). Since this type of effect cannot be described in terms of the approximation of the RHF method without taking into account the configuration interaction, the energy of the ^1B_1g state is significantly too high.

The electronic structure of CBD with a nuclear configuration having the D_{4h} symmetry cannot be described satisfactorily in terms of the one-determinant approximation and, for example, non-empirical calculations in terms of the 4-31G basis set lead to the conclusion that the triple state of the CBD molecule with D_{4h} symmetry has an energy lower by 22.6 kJ mol^{-1} than that of the singlet state with a nuclear configuration with D_{2h} symmetry (Scheme *a* in Fig. 3).[141]

Non-empirical calculations with allowance for configuration interaction lead to differences between the energies of the ^3A_2g and ^1B_1g states of 30.5–58.2 kJ mol^{-1} depending on the basis set,[88–90] which confirms the results of the earlier study[142] (1968) which lead to the scheme in Fig. 3*c*. Analogous results have been obtained by the MC SCF calculations for CBD in the π-electron approximation,[143] and also by calculations based on the MNDOC method[144] (the corresponding energy differences are 29.7 and 39.3 kJ mol^{-1}).

The results of the calculations have been confirmed recently by experimental data. Using the technique of flash photolysis, it has been established that the T_1 state of the peralkylated CBD has an energy higher by 50 kJ mol^{-1} than that of the singlet ground state.[145]

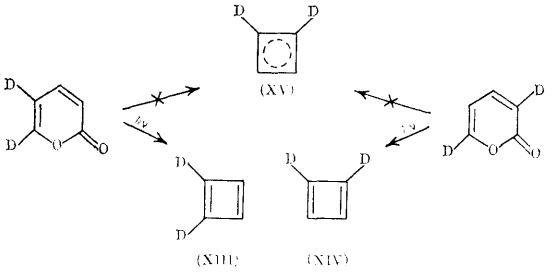
The most accurate calculated data for the geometry of CBD have been obtained by a non-empirical method in a study[67] employing an extended basis set including polarisation functions taking into account the electron correlation (see also, Clark and Harrison[146]). In the singlet ground state of CBD, the carbon σ-skeleton has the form of a rectangle with localised double bonds. It is striking that the C–C bond lengths actually exceed the usual values (the C–C bond length in ethane is 0.1537 nm) which can be accounted for by a tendency towards the decrease of the destabilising effect of conjugation [the results of *ab initio* calculations are quoted for structure (XII) [69]]:



(IX) (X) (XI) (XII)

The considerable differences in the C–C bond lengths are confirmed by the results of X-ray diffraction studies on CBD derivatives of the type of (IX)–(XI).[145,147–149] The equalisation of bond lengths in structure (XI) can be explained by steric causes.[150]

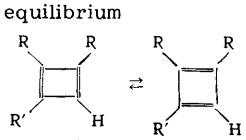
Although the results of earlier investigations[151,152] of the infrared spectra of CBD (isolated in matrices) were interpreted as evidence for a square configuration of the carbon skeleton of the molecule, it was shown subsequently that the presence in the IR spectrum of CBD of four bands due to the skeletal vibrations of the four-membered ring with frequencies below 2000 cm^{-1} [153] can be compatible only with a rectangular molecular structure. This conclusion was recently confirmed by experiments on the matrix isolation of two dideutero-substituted CBD derivatives (XIII) and (XIV) obtained by the photolysis of [5,6-D_2]- and [3,6-D_2]-α-pyrones respectively:[154]



(XV) (XIII) (XIV)

Earlier, it has been assumed erroneously that the reactions indicated lead to the formation of the same product having the square structure (XV). Calculation of the IR spectra of 1,2-dideuteriocyclobutadienes confirmed structures (XIII) and (XIV).[155]

The study of the equilibrium



(20)

R = t-C_4H_9, R′ = 1) t-C_4H_9, 2) t-C_4D_9

#Its essential feature is as follows.[140] The e_g orbitals are localised at different carbon atoms and the electrons present in them, which have opposed spins in the case of a singlet state, determine the disposition in space of the remaining electrons in the preceding, in terms of energy, CBD orbitals, since the repulsion between an electron in one of the e_g orbitals (for example with a spin α) and the electron in the preceding MO with the same spin is smaller, as a consequence of the exchange interaction, than the repulsion between the electrons with the opposite spins. Since the two electrons in the e_g orbital and their spin states are interchangeable, the spin polarisation is dynamic, in contrast to the similar statistical spin polarisation in radicals.

by dynamic ^{13}C NMR provided direct evidence for the existence of the valence isomers of CBD with alternating carbon–carbon bond lengths (in the ring), in contrast to the description of CBD in terms of resonance structures (cf. Fig.2).

Thus, whereas in the case of aromatic compounds, for example, benzene, structures with alternating bond lengths (the structures with $D_{3}h$ symmetry in Fig.2) cannot be observed experimentally, because the transition via the fully symmetrical $D_{6}h$ form does not involve the overcoming of an energy barrier and takes place at an electron oscillation frequency of approximately 10^{15} s^{-1},[152] in the case of CBD reaction (14) does in fact require the movement of nuclei. Thus in the ground state the geometry of CBD belongs to the $D_{2}h$ symmetry group with localised double bonds in the ring. Consequently both the structural criteria of aromaticity–antiaromaticity and the energetic (resonance energies, heats of isodesmic reactions) and magnetic criteria show that CBD is antiaromatic.

(b) Valence isomerisations of CBD. The closeness of the potential energy surfaces for the ground and lowest excited states of antiaromatic compounds leads to the possibility of low-barrier valence isomerisation reactions, in contrast to benzene and other aromatic molecules. Fig.4 illustrates schematically the valence isomerisation reactions of CBD based on calculations by the MINDO/3 method.[157–160]

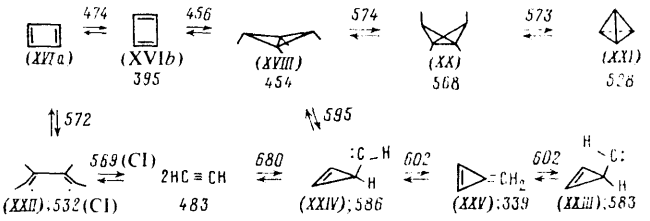
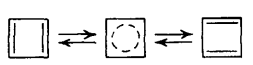
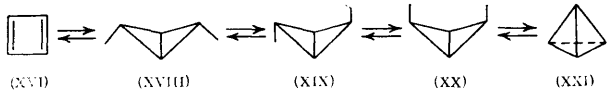


Figure 4. Schemes illustrating the principal valence isomerisations of CBD according to calculations by the MINDO/3 method.[157–160] The numerals under the numbers designating the structures represent the calculated heats of formation (in kJ mol^{-1}) and the numbers along the arrows represent the heats of formation of the structures of the transition state (in kJ mol^{-1}). The calculations for the cyclodimerisation of acetylene to CBD have been made taking into account the configuration interaction (CI).[159] The concerted cyclisation mechanism cannot be described satisfactorily within the framework of the one-determinant approximation because of the triplet instability of the RHF solutions.[160]

Two types of reactions are possible theoretically in principle: topomerisation occurring as a fluctuation of π-bonds in the ring [the bond shift process—see Eqn.(14)],



and the interconversion of CBD and the only theoretically permissible isomeric form—tetrahedrane:



(21)

The isomerisation reaction (14) can be regarded as the manifestation of a second-order Jahn–Teller effect. The lowest singlet $^{1}B_{1g}$ state of the structure with $D_{4}h$ symmetry can be mixed with the $^{1}A_{1g}$ state, which has a similar energy, as a result of vibrations with $b_{1}g$ symmetry corresponding to deformations which convert the CBD structure with $D_{4}h$ symmetry into the rectangular form.[89] The triplet $^{3}A_{2g}$ state of the $D_{4}h$ structure of CBD might be mixed, as a consequence of the b_{1g} vibration, with the $^{3}B_{2g}$ state, but the triplet state with a suitable symmetry has an unduly high energy. This in fact explains why the geometry with $D_{4}h$ symmetry corresponds to the $^{1}A_{2g}$ state of CBD.

It has been suggested[161] that the interconversion of the rectangular $D_{2}h$ topomers of CBD of the type of compounds (XVIa) and (XVIb) (Fig.4) can proceed via a rhombic and not quadratic transition state with $D_{2}d$ symmetry. However, in the case of the CBD structure having the $D_{4}h$ symmetry there are no excited singlet states whose interactions with the $^{1}B_{1}g$ state would lead to the rhombic distortion of the structure.[88,89]

It follows from the results of non-empirical calculations that the $^{1}B_{1}g$ state with a $D_{4}h$ structure of CBD has only one negative force constant corresponding to the $b_{1}g$ distortion, while the $^{1}A_{2}g$ state has no negative force constants. Thus the $D_{4}h$ structure of CBD in the $^{1}B_{1}g$ electronic state does indeed correspond to the transition state in the topomerisation of the $D_{2}h$ structure and the activation barrier has been estimated as 34.7–56.1 kJ mol^{-1} (*ab initio* calculations[88–90]).

We may note that Dewar and Kollmar[157] quote an energy difference between the lowest singlet and triplet states of the CBD structure with $D_{4}h$ symmetry amounting to 54.8 kJ mol^{-1} (MINDO/3 method). Correspondingly, the activation barrier to the topomerisation of $D_{2}h$ structures is 79.5 kJ mol^{-1}, but, in terms of the NDO approximation, the above energy difference between the lowest singlet and triplet states should be zero. Indeed the calculations for the CBD molecule by the MINDO/3 method, which we repeated, confirmed this. The activation barrier to the topomerisation of the $D_{2}h$ structures of CBD proved to be 24.7 kJ mol^{-1}, which agrees well with the results of non-empirical calculations,[88–90] in contrast to the results of Dewar and Kollmar.[157] The use by the latter workers of an initial density matrix corresponding to the double filling of one of the CBD molecular π orbitals with e_{g} symmetry led to an artefact solution.[125] This is yet another example demonstrating the complexity of the calculation of the electronic structure of antiaromatic molecules discussed above (Section I).

The experimental barrier to the topomerisation of tri-t-butylcyclobutadiene found by dynamic NMR is 10.5 kJ mol^{-1}.[162]

The direct thermal cyclisation of CBD to tetrahedrane [reaction (21): ($\pi 2a + \pi 2a$ – cycloaddition)] and the reverse reaction are forbidden by the Woodward–Hoffman rules,[163] which is the reason for the kinetic stability of tetrahedrane, whose energy is higher than that of CBD.[69,146,164–169] Indeed, the valence isomerisation of tetra-t-butyltetrahedrane to tetra-t-butylcyclobutadiene takes place only at 135 °C and above.[170,171] The reversibility of the isomerisation has been confirmed by low-temperature NMR data. In view of the prohibition of the concerted mechanism of the thermal isomerisation CBD ⇌ tetrahedrane, reaction (21) has been shown by calculations[69,166–168] to proceed in several stages involving the formation of the diradicaloid intermediates (XVIII) and (XX) (Fig.5).

The following values have been obtained for the total activation energy for the isomerisation reaction CBD → tetrahedrane: 179.5 kJ mol^{-1} (MINDO/3 [159]), 255.6 kJ mol^{-1} (MNDO – CI 2 × 2 [168]), and 143.4 kJ mol^{-1} (*ab initio*, DZ + P basis, with allowance for electronic correlation[69]). The diyl (XIX) is the transition state in the reaction (XVIII) → (XX),

which constitutes the rate-limiting stage. The activation barrier for this reaction has been estimated as 142 kJ mol^{-1} (*ab initio*, DZ + P basis, with allowance for correlation energy[69]), 120.9 kJ mol^{-1} (MINDO/3), or 125.1 kJ mol^{-1} (MINDO/3, with allowance for CI 3 × 3 [153]).

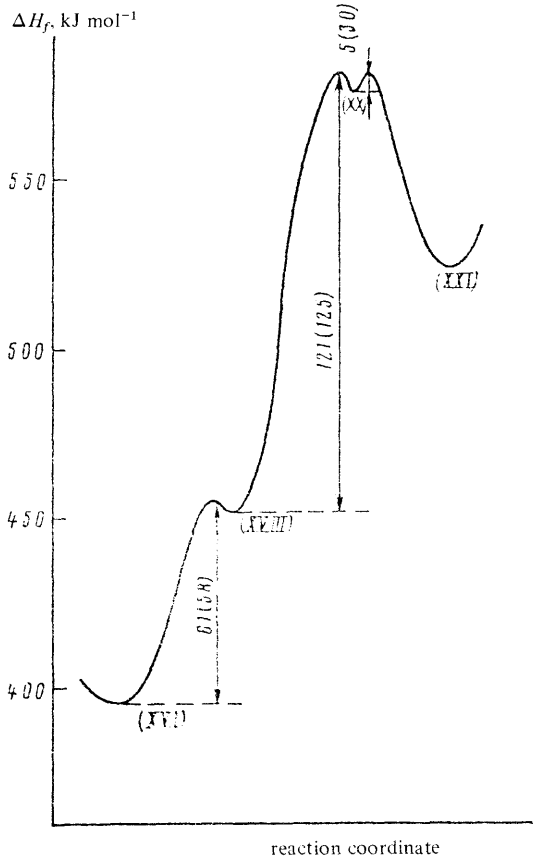
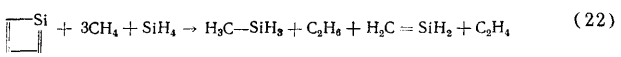


Figure 5. Cross-sections through the potential energy surface for the C_4H_4 structure along the locus of the minimum energy of the reaction involving the CBD → tetrahedrane isomerisation (calculation by the MINDO/3 method[153]). The activation barriers (in kJ mol^{-1}), calculated taking into account the 3 × 3 configuration interaction, are indicated in brackets.

2. Hetero-substituted Cyclobutadienes

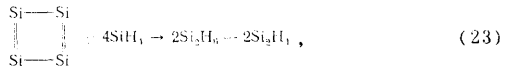
The analogues of cyclobutadiene have been studied to an incomparably lesser extent than cyclobutadiene itself. Calculations and individual experimental data are available only for sila- and aza-substituted derivatives.

Silacyclobutadiene. The results of the calculation of the heat of the isodesmic reaction (22) (*ab initio*, 6-31G/3-21G basis[61])



(22)

(ΔH = −223 kJ mol^{-1}), which is a characteristic of the stability of the conjugated cyclic system, indicate the antiaromaticity of silacyclobutadiene. On this scale, the degree of antiaromaticity of cyclobutadiene exceeds by 61.1 kJ mol^{-1} that of silacyclobutadiene [see reaction (6)]. This is caused mainly by the fact that the introduction of the silicon atom with its diffuse atomic orbitals into the ring decreases the destabilising effect of the conjugation in the four-membered ring. Indeed the degree of antiaromaticity of tetrasilacyclobutadiene, estimated from the heat of reaction (23) by the MINDO/3 method, is significantly lower than in the case of cyclobutadiene:[172]

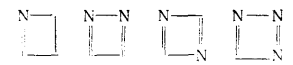


(23)

for which ΔH = −68.6 kJ mol^{-1}.

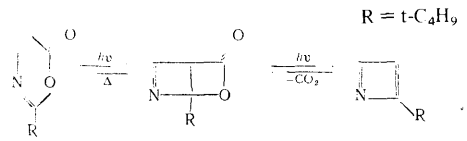
According to the results of non-empirical calculations (6-31G/3-21G basis),[61] silatetrahedrane has a total energy higher by 139.3 kJ mol^{-1} than silacyclobutadiene.

Azacyclobutadienes. The unsubstituted azacyclobutadiene (azet) (XXVI) has not so far been obtained, but there exist data demonstrating the experimental detection of a number of its derivatives.[173,174]



(XXVI) (XXVII) (XXVIII) (XXIX)

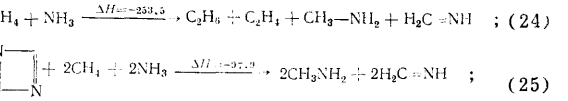
For example, when oxazinone was irradiated, t-butylazacyclobutadiene was obtained:



In order to compare the properties of cyclobutadiene and its aza-derivatives, we shall discuss the influence of aza-substitution on the e_g π orbitals of CBD with D_{4h} symmetry (Fig. 6).

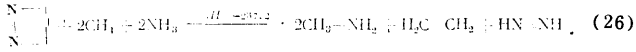
Monoaza-substitution leads to the removal of degeneracy from the e_g π orbital in the D_{4h} structure of CBD, stabilising the a_1 π orbital (the C_{2v} structure of azet)[54] (the change in the energies of the π orbitals of conjugated cyclic systems on aza substitution has been considered;[176] see also the aza-substitution of trimethylenemethane in the case of Y-antiaromaticity[177]). 1,3-Diaza-substitution leads to an even greater change in the relative energies of the e_g π orbitals, stabilising the b_{2g} orbital. This results in an increase of the energy difference between the ground ^1A_g and the first excited singlet $^1B_{1g}$ states of the structure of 1,3-diazet with D_{2h} symmetry, which promotes an increase of both the antiaromatic character and the lattice instability of the structure in conformity with the aromaticity-antiaromaticity criteria.[16,81] 1,2-Diaza-substitution should not lead to an appreciable stabilisation of any one of the e_g π orbitals of the D_{4h} structure of CBD relative to another.

Calculations by the MINDO/3 method of the heats of the isodesmic reactions (24)–(26) indicate a higher stability of 1,3-diazet compared with 1,2-diazet and of azet compared with cyclobutadiene[59] (the values of ΔH for the reaction are indicated in kJ mol^{-1}):



(24)

(25)



(26)

The results of non-empirical calculations (STO-3G basis) of the heats of reaction (25) also indicate a greater stability of 1,3-diazet ($\Delta H = -201.4$ kJ mol^{-1}) compared with CBD ($\Delta H = -268.6$ kJ mol^{-1}).[60]

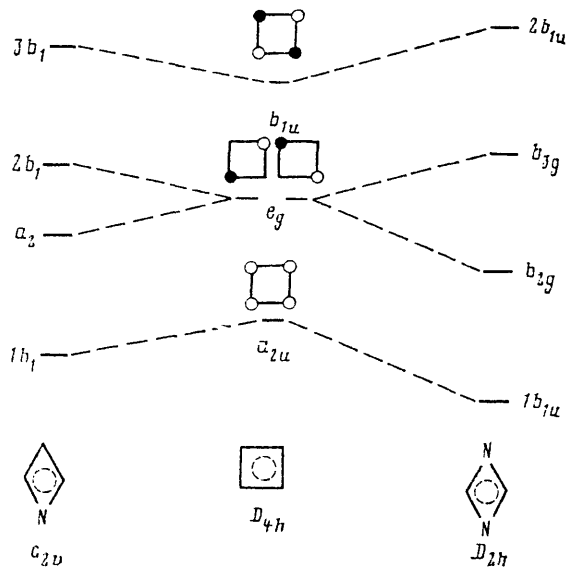


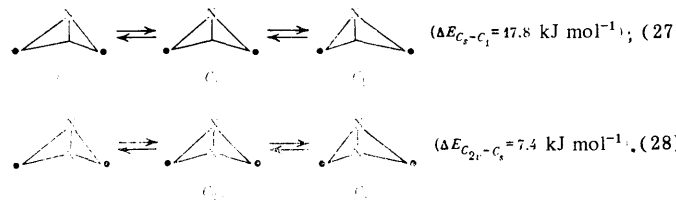
Figure 6. Correlation of the π MO for the cyclobutadiene structure, the azet structure with D_{2h} symmetry, and the 1,3-diazet structure with D_{2h} symmetry.

A decrease of the antiaromatic character of azet compared with CBD follows from the calculations of the Dewar resonance energy: −71.1 kJ mol^{-1} [44] and −64.8 kJ mol^{-1} [178] have been obtained for CBD and azet respectively. Despite the variation of the initial density matrix, calculations by the Pariser–Parr–Pople (PPP) method for 1,2-diazet cannot yield a solution corresponding to a structure with equalised bond lengths.[179,180]

The substitution of three carbon atoms must be treated as a special case because in this instance both e_g π orbitals of the CBD structure with D_{4h} symmetry are stabilised. The structure with alternating bond lengths having the C_S symmetry corresponds to a minimum on the potential energy surface for CN_3H and not the structure of triazet with C_{2v} symmetry (calculations by the MINDO/3 method[59]). Consequently, in contrast to the tendencies characteristic of mono- and 1,3-di-aza-substitution, 1,2-diaza-substitution and triaza-substitution do not stabilise the highly symmetrical configuration, which, by virtue of the small energy difference between the ground and first excited singlet states, involves lattice instability.[179,180]

Thus analysis of the transformations of the molecular orbitals of the CBD molecule with D_{4h} symmetry for different types of aza-substitution justifies the expectation of three different types of potential energy surface corresponding to reactions (14) and (21) for azacyclobutadienes. (The results of the calculations and of the valence isomerisations of azacyclobutadienes are presented in Fig.7).

Isomerisation to structures of lower symmetry is characteristic of the C_S structure of 1-azabicyclo[1.1.0]butane-2,4-diyl (XXXI) and the C_{2v} structure of 1,3-diazabicyclo[1.1.0]-butane-2,4-diyl (XXXVII) [59] (the energy differences calculated by the MINDO/3 method are indicated in brackets):



($\Delta E_{C_2-C_1} = 17.8$ kJ mol^{-1}); (27)

($\Delta E_{C_{2v}-C_s} = 7.4$ kJ mol^{-1}). (28)

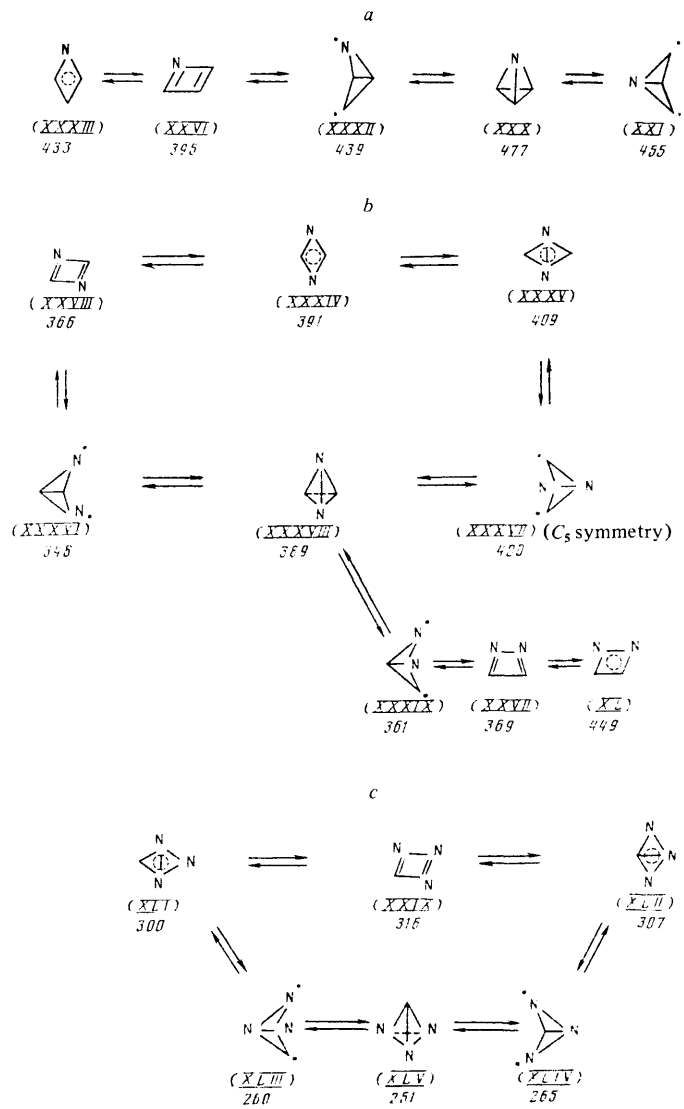


Figure 7. Schemes illustrating the valence isomerisations of azet (*a*), 1, 2- and 1,3-diazets (*b*), and triazet (*c*). The numerals under the numbers designating the structures represent the heats of formation (in kJ mol^{-1}) calculated by the MINDO/3 method.[59,179,181] Minima on the potential energy surface correspond to all the structures with the exception of structures (XXXIII), (XXXIV), and (XL), to which maxima correspond.

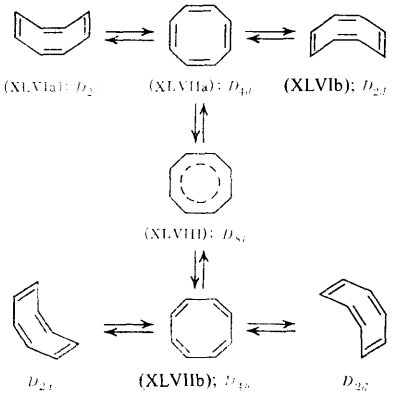
The reactions involving the cyclisation of azabicyclo[1.1.0]-butanediyls to the corresponding azatetrahedranes are prohibited by bond symmetry conservation rules[182] (see Glukhovtsev et al.[59] for the given reactions) and are characterised by high activation barriers, which is the reason for the kinetic stability of the corresponding azatetrahedranes.

3. Cyclo-octatetraene

The structure of cyclo-octatetraene (COT), which is the second member of the series of [4*n*]annulenes with $n = 2$, has been studied in extremely great detail.[183–185] This compound and some of its derivatives are stable substances and there exist fairly reliable experimental data for their geometry, the type of the electronic ground state, and the most characteristic chemical properties.

The boat configuration (XLVI) with D_{2d} symmetry corresponds to the COT molecule in the ground state. According to calculated data,[186–188] its energy is lower by 63–75 kJ mol^{-1} than that of the planar structure (XLVII) with $D_{4}h$ symmetry. Only one compound with a planar cyclo-octatetraene fragment is known, namely the cyclic perfluorotetracyclobutane derivative, in which there is a slight alternation of the bond lengths in the COT ring (0.1425 nm) according to X-ray diffraction data.[189]

The planar forms of COT with $D_{4}h$ and $D_{8}h$ symmetries are the transition states for the most important COT isomerisation reactions—the enantiomerisation (XLVIa) ⇌ (XLVIb) and the structural topomerisation (XLVIIa) ⇌ (XLVIIb) respectively. The latter process is isotypical with the topomerisation of the D_{2h} structure of CBD.



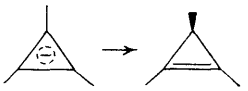
In the case of certain tri- and tetra-methyl-substituted COT the isomerisation, involving the formation of structure (XLVIII) with $D_{8}h$ symmetry (fluctuation of π-bonds), can compete with the ring inversion which proceeds via the $D_{4}h$ structure, although the barrier to ring inversion in COT is lower by 8.4–12.5 kJ mol^{-1} (see the relevant reviews[78–84]). Comparison of the activation energies for ring inversion and for the fluctuation of π-bonds makes it possible to estimate the COT delocalisation energy. The difference between these energies was found to be 14.2 kJ mol^{-1} in the case of 1,3-di-t-butylcyclo-octatetraene.[78] The antiaromatic character of COT is thus fairly weak.[77]

4. Antiaromatic Monocyclic Ions

The cyclic ions (XLIX)–(LII) containing $4n$ π-electrons and having a ring symmetry $D_{m}h$ ($m = 3$, 5, 6, and 7 respectively) have an unclosed electron shell. In the singlet state in such systems a second-order Jahn–Teller effect is observed, being manifested, as in the case of CBD and COT, by a transition to a geometrical structure with a reduced symmetry and involving alternating bond lengths.

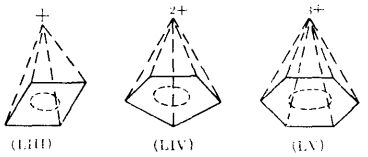


There is also a possibility of the formation of non-planar systems, which leads to the breakdown of cyclic conjugation as a result of the exclusion of one of the p_z orbitals from the conjugation system and to a decrease of the degree of antiaromaticity of the molecule, for example, in the case of the cyclopropenyl anion (CPA):

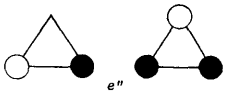


(29)

In addition the ions (L)–(LII) can have isomers in the form of non-classical polyhedral structures with $C_{(m-1)}$ symmetry provided that the latter satisfy the essential electronic requirements for three-dimensional aromaticity,[28] for example:

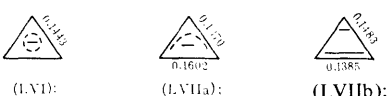


The cyclopropenyl anion. The unsubstituted CPA has not so far been obtained, but is triphenyl derivative is known. It has a strongly antiaromatic character, which is confirmed by the unusually high pK_a of its conjugate acid—triphenylcyclopropene (p$K_a \geq 51$).[9,20] Calculations[190–194] show that CPA has a triplet ground state and the $D_{3}h$ geometry. Since the π orbitals with e'' symmetry cannot be localised in such a way that they have no common carbon atom, the corresponding exchange integral is fairly high.



As a result, the dynamic spin polarisation is not any way significant, in contrast to CBD and Hund's rule holds.[140]

The degenerate character of the highest incompletely occupied e'' orbitals in the CPA structure with $D_{3}h$ symmetry [the π-electron configuration of the state is $(a_2'')^2(e'')^2$] leads, as for CBD, to a second-order Jahn–Teller effect and to a decrease of the energy of the singlet $^1A_1$ state§ by 48.9 kJ mol^{-1} as a result of the decrease of the symmetry of the nuclear configuration to C_{2v} [194] [structures (LVIIa) and (LVIIb) with unequal C–C bond lengths]:

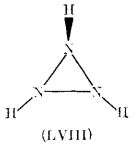


§ The designations for the electronic states of CPA and the cyclopentadienyl cation (CPC) correspond to the C_{2v} symmetry group (for further details, see the relevant literature[29,194–196].

The energies of the C_{2v} structures (LVIIa) and (LVIIb) (in kJ mol^{-1}) are indicated in brackets relative to the energy of the $^3A'_2$ state of the D_{3h} structure (LVI), found by a non-empirical method (STO-3G, CI basis);[194] the numerals opposite the bonds represent their lengths in nm.

However, in contrast to CBD, the singlet $^1A_1$ state is not the electronic ground state of CPA. This important conclusion must nevertheless be regarded as preliminary, because sufficiently reliable results can be obtained only by calculations where account is taken of the interaction of the configurations constructed not only on the basis of π orbitals but also σ orbitals.[195,196] Indeed, calculations carried out taking into account the configurations constructed on the basis of π orbitals describe incorrectly the form of the potential energy surface for the $^1A_1$ state.[196]

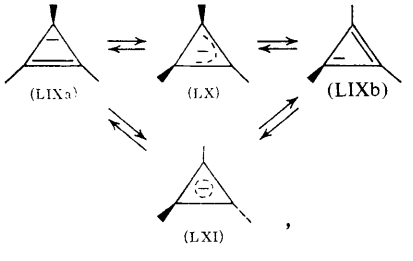
Non-empirical calculations[190] and calculations performed by the MINDO/3 and NDDO [193] methods have shown that additional stabilisation of the singlet state of CPA is achieved as a result of the displacement of the C–H bond in structures (LVIIa) and (LVIIb) from the plane of the three-membered ring. According to the results of non-empirical calculations (taking into account CI) for the $(NH)_3^{2+}$ system,[195] which is isoelectronic with respect to CPA, the electronic triplet state of the planar structure having the D_{3h} symmetry has a lower energy than the singlet state. However, the ground state of the ion $(NH)_3^{2+}$ is of the singlet type and a structure with displacement of the N–H bond from the plane of the ring in (LVIII) corresponds to it:



(LVIII)

The energy of the triplet state is also reduced in a structure of this type but to a lesser extent than that of the singlet state.

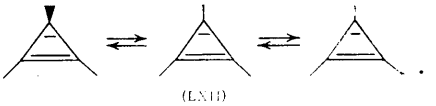
The valence isomerisations of CPA. The high symmetry (D_{3h}) of the CPA structures subjected to the Jahn–Teller effect is responsible for the formation of a multiplicity of local minima on the potential surface in the vicinity of the point corresponding to the given structure. According to the Murrell–Laidler theorem,[197] the singlet state of the structure with D_{3h} symmetry cannot be the transition state for the isomerisations of configurations having a lower symmetry, which has been confirmed by calculations.[192,194] Two types of isomerisations are possible, namely fluctuations in the position of the double bond [structures (LX) and (LXI) are the transition states]:



(LIXa) (LX) (LIXb) (30a)

(LXI) (30b)

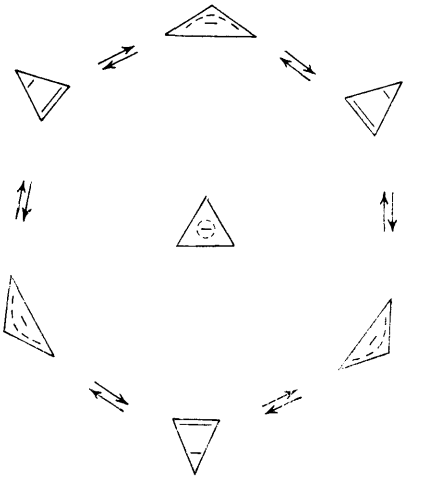
and the inversion of the carbanionic carbon [structure (LXII) is the transition state]:



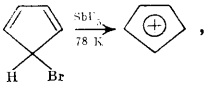
(LXII) (31)

The activation energies for reactions (30a) and (31) calculated by the CNDO/2 method[92] are 90 and 107 kJ mol^{-1}. An activation energy of 88.7 kJ mol^{-1} corresponds to the isomerisation reaction (30b), which proceeds via the transition state (LXI).[192]

The fluctuation of the double bond in planar structures (singlet state) of CPA of the type (LVIIa) and (LVIIb) can be represented by the following scheme, which shows that the reaction pathway runs in the "valley" encircling the "top of the hill" on the potential energy surface corresponding to the configuration with the D_{3h} symmetry:

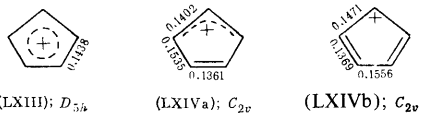


The cyclopentadienyl cation (CPC). Experimental studies, especially the EPR spectrum of CPC obtained by treating 5-bromocyclopentadiene with antimony pentafluoride at 78 K,[198]



(32)

confirmed the results of quantum-chemical calculations[199–204] showing that the electronic ground state of CPC (LXIII) is of a triplet type and has a geometry with D_{5h} symmetry. The energy of the singlet state corresponding to structure (LXIV) with C_{2v} symmetry is higher by only 30.5 kJ mol^{-1} (*ab initio* calculation, STO-3G, CI basis[204]).

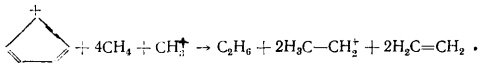


(LXIII); D_{5h} (LXIVa); C_{2v} (LXIVb); C_{2v}

The comparatively small difference between the energies of the singlet and ground states makes it possible to stabilise the former by introducing substituents into the ring.[205] In the case of the $^1A_1$ state of the structure with D_{5h} symmetry a second-order Jahn–Teller effect is observed.[29,204] The stabilisation energy on transition to the structure with C_{2v} symmetry is 56.1 kJ mol^{-1},[201] which is approximately three times greater than the analogous quantity calculated on the basis of the same scheme for CBD.[29] This can be accounted for by the greater similarity of the energies of the states, which can become mixed on distortion of the geometry of the nuclear skeleton of the CPC.

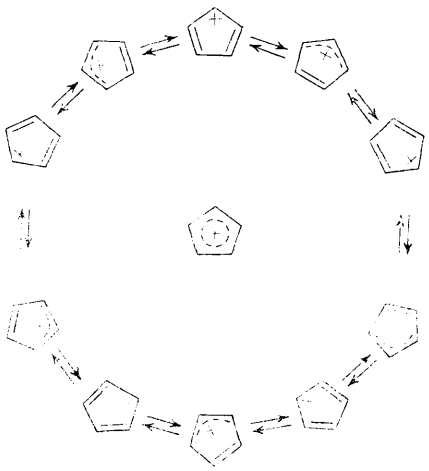
The antiaromaticity of CPC is confirmed both by the alternation of the bond lengths in structures of the singlet state and by the resonance energies (Table 1) and the heat of the

isodesmic reaction (33), which amounts to -12.6 kJ mol^{-1} (*ab initio* calculation, 4-31G basis).[202]

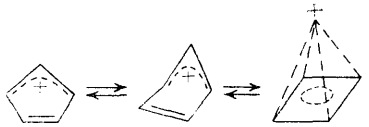


(33)

The valence isomerisations of CPC. Two main types of valence isomerisation are possible for CPC—the shift of the π-bonds in the planar structure described as pseudorotation of structures with C_{2v} symmetry:



and isomerisation to the classical square pyramidal structure (LIII), the possibility of the existence of which has been demonstrated by calculations using the extended Hückel method (EHM):[206]



(LXIVa) (LXV) (LIII) (34)

The pathway of the reaction involving bond shifts does not intersect the region corresponding to the D_{5h} configuration, which cannot be the transition state in the given reaction according to the Murrell–Laidler theorem.[197] Indeed, calculations have shown[204] that the symmetry-prohibited concerted isomerisation reaction $C_{2v} \rightarrow D_{5h} \rightarrow C_{2v}$ has a considerable activation barrier. The minimum energies for structures (LXIVa) and (LXIVb) differ by not more than 4.18 kJ mol^{-1}.[204]

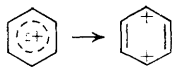
The activation barrier of reaction (34) involving isomerisation to the square pyramidal structure (LIII), having an energy higher by 58.6 kJ mol^{-1} than structure (LXV), is 238.6 kJ mol^{-1} (MINDO/3 method[200]). According to revised data,[203,207] structure (LXV) is in its turn more stable by only 2.9 kJ mol^{-1} than structure (LXIVa). An interconversion reaction, whose transition state is structure (LXVI), is possible for structure (LIII), the activation barrier amounting to 77.8 kJ mol^{-1} (calculation by the MINDO/3 method).[39]



(LXVI)

The existence of structure (LIII) has been confirmed experimentally (the dimethyl derivatives[208] and also the trimethyl derivative[209] have been obtained; see also the relevant reviews[210,211]).

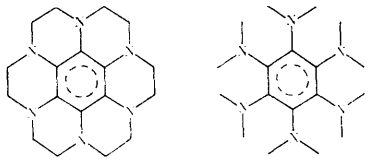
The benzene dication. The studies on the benzene dication and its fragmentation pathways have been the subject of numerous investigations.[212–214] Calculations by the MINDO/3 method have shown that the triplet state of the structure with D_{6h} symmetry is more stable by 40 kJ mol^{-1} than the singlet state,[214] which agrees with experimental data indicating a triplet ground state of the hexachlorobenzene dication.[215] When the limitations due to the D_{6h} symmetry were removed in the course of calculations on the structure of the singlet state of the benzene dication (LI), a distortion of the geometry was observed (without an activation barrier), resulting in the conversion into the less symmetrical structure (LXVII) with D_{2h} symmetry, whose energy is lower by ~320 kJ mol^{-1}.[214]



(LI: D_{6h}) (LXVII: D_{2h})

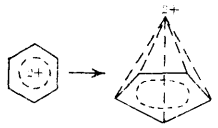
At the same time, structure (LXVII), which has four π electrons, is insufficiently well favoured by energy factors, which leads to the possibility of its fragmentation into acyclic structures.

A number of procedures have been proposed for stabilising the benzene dication by introducing substituents,[216,217] for example, as in systems (LXVIII)–(LXIX).



(LXVIII) (LXIX)

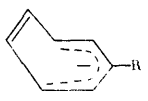
As in the case of CPC, one can assume that the antiaromatic character of the benzene dication promotes its isomerisation to the more stable non-classical pyramidal structure (LIV).



(LI) (LIV)

The hexamethyl derivative of the dication (LIV) is stable under the usual conditions.[218]

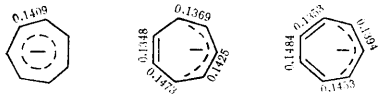
The cycloheptatrienyl anion. It has been suggested that the cycloheptatrienyl anion (CHA) is an intermediate in many reactions,[219,220] including the cycloheptatriene dimerisation reaction under the influence of bases.[221] Certain monosubstituted CHA, investigated by NMR which indicates a non-coplanar structure (LXX), are known.[222]



(LXX)

Here R = CO_2R^1, $CONR^2R^3$, or SO_2R^1, where R^1, R^2, and R^3 are aryl or alkyl. The planar structure of CHA with D_{7h} symmetry (eight π electrons) has a pair of e' orbitals (π4 and π5 orbitals), which are degenerate with respect to energy. In this case there is a possibility of the following electronic states: a triplet ($^3A'_2$) and two singlet ($^1A'_1$ and $^1E'_3$) states. As a consequence of a second-order Jahn–Teller effect, the state E'_3 is mixed with the low-lying singlet state $^1A_1$, which distorts structure (LII) to give structures (LXXI) and (LXXII) with C_{2v} symmetry. Calculations by the MINDO/3

and MNDO methods have shown that minima on the potential energy surface of the $(CH)_7^-$ ion correspond to the planar structures (LXXI) and (LXXII) having similar energies [the numerals under the numbers of the structures represent the energies relative to structure (LXXI) in kJ mol^{-1} found by the MINDO/3 method; the numerals in brackets have been found by the MNDO method;[222] the numbers opposite the bonds represent their length in nm calculated by the MINDO/3 method]:

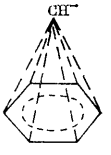


(LII); D_{7h} 36.6 (27.2) (LXXI); C_{2v} 0 (0) (LXXII); C_{2v} 0.04 (0.17) .

These results can be regarded as preliminary in view of the known tendency of the MINDO/3 and MNDO methods to "flatten" cyclic hydrocarbon structures.[223]

The energy of the triplet state of the structure with D_{7h} symmetry is higher by 9.8 kJ mol^{-1} than that of the singlet state of structure (LXXI) with C_{2v} symmetry (the MINDO/3 method).[222]

Isomerisation involving bond shifts may be expected for CHA, i.e. (LXXI) → (LXXII), which is analogous to that examined above for the cyclopentadienyl cation. The isomerisation to the pyramidal structure (LXXIII)

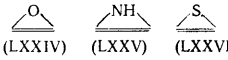


(LXXIII); C_{6v}

does not occur in this case because the electron count rules[39] do not hold for structure (LXXIII) and such a system must be unstable.

5. 4π-Electron Three-membered Heterocycles

Oxiren (LXXIV), 1H azirine (LXXV), and thi-iren (LXXVI) are known as extremely unstable compounds, which can be isolated only using the matrix isolation technique (see the review of Tores et al.[224]).



(LXXIV) (LXXV) (LXXVI)

Oxiren and its substituted derivatives have been proposed as intermediates in many reactions, in particular in the Wolff rearrangement of α-diazoketones. However, the experimental attempt to identify oxiren as an intermediate in this reaction were unsuccessful.[225] Indeed quantum-chemical calculations, including non-empirical calculations with allowance for electron correlation, have shown that a very shallow minimum on the potential energy surface of the C_2H_2O system corresponds to oxiren. Furthermore, oxiren has a much higher energy than isomers such as, for example, keten and hydroxyacetylene.[193, 226–233] The kientic stability of oxiren is extremely low. Thus the activation barrier to the isomerisation to formylmethylene has been estimated as only 3.3 kJ mol^{-1} (*ab initio* calculation, DZ + P basis, allowance for electron correlation),[230] while that for isomerisation to keten is about 32 kJ mol^{-1}.[231] Such instability of oxiren can be accounted for by the fact that in the series of systems (LXXIV)–(LXXVI) the mechanism of the reverse $p \rightarrow \pi^*$ donation, which stabilises the three-membered ring, is least evident for oxiren by virtue of the greater electronegativity of oxygen.[39]

III. NON-ALTERNANT[*n*]ANNULENO[*n*]ANNULENES CONTAINING INTERNAL OR PERIMETRIC 4*m*π-ELECTRON RINGS

The question of the aromatic or antiaromatic character of compounds of this series, namely propalene (LXXVII), pentalene (LXXVIII), and heptalene (LXXIX), has aroused a prolonged controversy.



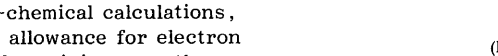
(LXXVII) (LXXVIII) (LXXIX)

The Hückel rule has been derived in the study of monocylic systems and its direct application to annulenoannulenes is incorrect (see also Section IV). Calculations by the HMO method yielded similar delocalisation energies for azulene and heptalene.[41,234] However, the conclusion that heptalene is aromatic, based on this finding, conflicts with experimental data indicating the absence of any manifestations of aromatic character by heptalene.[7]

Higher delocalisation energies have also been obtained for pentalene,[7,41] which serve as a basis for the conclusion concerning its stability.[235] At the same time, the unsuccessful attempts to synthesise pentalene (see the relevant reviews[236, 237]) contradict to this conclusion. All these factors stimulated much interest in detailed calculations of the electronic structures of non-alternant [*n*]annuleno-[*n*]annulenes.

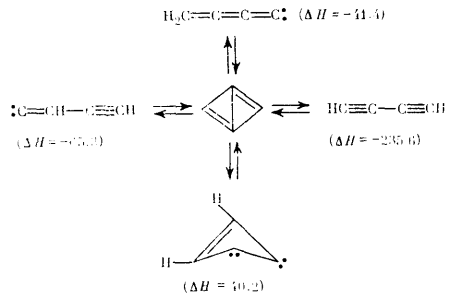
1. Propane

Propalene [bicyclobutadiene (LXXVII)] is stable, according to MINDO/1 calculations, relative to its valence isomer diacetylene, whose photochemical cyclisation is believed to be capable of resulting in the formation of propalene.[238] Calculations by the MINDO/1,[238] MINDO/3,[239] MNDO,[240] and *ab initio*[240] methods indicate a C_2h structure of the ground state, which is more stable than the orthorhombic D_{2h} structure with equalised lengths of the peripheral carbon–carbon bonds in the ring (Table 2). However, according to the results of calculations by the MNDO method,[240] diacetylene has a lower energy than propalene and the activation barrier to the isomerisation of propalene to the carbene (LXXX) has been estimated as only 3.8 kJ mol^{-1}:

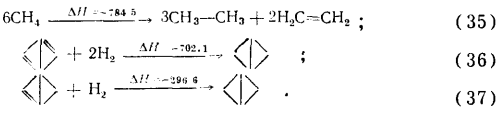


(LXXVII); C_{2h} (LXXX) .

Non-empirical calculations in terms of the 4-31G basis altogether failed to demonstrate the existence of a barrier, which, in combination with the data in Table 2, permitted the authors[240] to conclude that propalene is thermodynamically and kinetically unstable in contrast to the optimistic predictions of Baird and Dewar.[238] The relative stability of propalene can be estimated from the calculated heats (the ΔH are indicated in kJ mol^{-1}) of the isomerisation reactions (the MINDO/3 method):[239]



The propalene ring strain energy has been estimated [using the isodesmic reaction (35)] as 784.5 kJ mol^{-1} (the MNDO method).[240] Calculation of the resonance energies by the method of Hess and Schaad indicates the antiaromaticity of propalene,[241] which is greater than that of pentalene (Table 1). At the same time the energy of the antiaromatic destabilisation, determined from the heats of the hydrogenation reactions of propalene [reaction (35)] and 1-bicyclobutene [reaction (36)] has been estimated as only 108.9 kJ mol^{-1}, which is much less than the strain energy (the ΔH for the reactions are indicated in kJ mol^{-1}):



(35)

(36)

(37)

Table 2. The relative energies (in kJ mol^{-1}) of the C_4H_2 valence isomers.

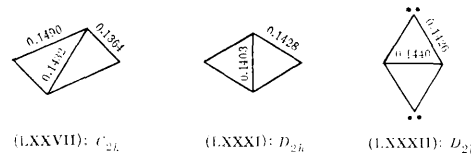
Structure	Method of calculation							
	MINDO/3 (Ref.239)	MNDO (Ref.240)	STO/3G (Ref.239)	4-31G// STO-3G (Ref.239)	4-31G (Ref.240)	MP2[a]/4-31G (Ref.240)	6-31G*// 4-31G (Ref.240)	MP2[a]/ /6-31G* (Ref.240)
(LXXVII)	0	0	0	0	0	0	0	0
(LXXX)	−65.3	−247.3	—	—	−236.4	−123.0	−137 2	−23.8
(LXXXI)	32.2	56.4	63.6	42.7	64.9	—	—	—
(LXXXII)	163.2	—	82.8	87.4	—	—	—	—
(LXXXIII)	38.9	—	−98.7	−28.8	—	—	—	—
(LXXXIV)	211.7	—	128.9	128.4	—	—	—	—
(LXXXV)	−235.6	−536.4	—	—	−421.3	−384.5	−306.3	−269.4

[a] An estimate of the electron correlation energy in terms of the Meller–Plesset perturbation theory taking into account second-order terms.

The minimum on the potential energy surface for the C_4H_2 system does not correspond to the propalene structure with D_{2h} symmetry and the latter is converted via a barrier-free process into a structure with C_{2h} symmetry and alternation of bond lengths.[239,240]

Calculations in terms of the π-electron approximation have led to the conclusion that propalene with the D_{2h} configuration is subject to lattice instability.[242] The employment of the UHF approximation does not result in a qualitative change in the conclusions.[243]

Calculations for propalene by the PPP method revealed a multiplicity of solutions of the Hartree–Fock equations with the initial density matrix varied,[125] which is a characteristic feature of calculations for conjugated systems containing internal or perimetric $4n\pi$-electron rings. Indeed, with the exception of instances of an anomolously distorted geometry,[244] calculation by the PPP method leads to the same solution regardless of the initial density matrix or the initial geometry.[245] For example, for an initial benzene geometry with D_{3h} symmetry, calculation by the PPP method in terms of the Dewar σ,π parametrisation[42] (optimisation of bond lengths) leads to a D_{6h} structure (cf. Fig.2). However, depending on the initial density matrix, three different solutions have been obtained for propalene corresponding to a structure with C_{2h} symmetry and different bond lengths [structure (LXXVII)], structure (LXXXI) with D_{2h} symmetry [the $(b_{1u})^2(b_{2g})^2$ π-electron configuration], and the D_{2h} structure (LXXXII) of the dicarbene type [the $(b_{1u})^2(b_{3g})^2$ π-electron configuration], i.e. the structural data differ in the order of the frontier MO (Fig.8).



(LXXVII): C_{2h} (LXXXI): D_{2h} (LXXXII): D_{2h}

(The numerals along the bonds represent their lengths in nm.)

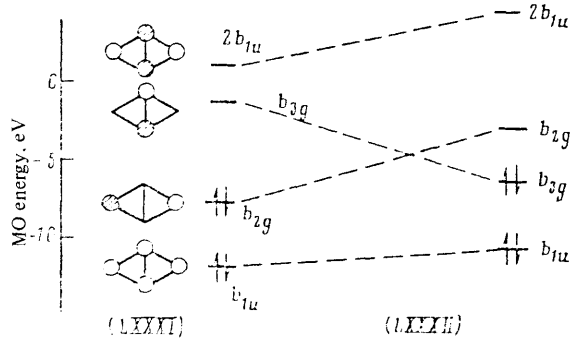
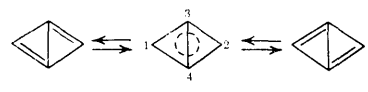


Figure 8. Correlation of the π MO of structures (LXXXI) and (LXXXII) with D_{2h} symmetry (PPP method).[239]

The solution of the Hartree–Fock equations corresponding to structure (XXXII) is unstable with respect to the filling of the MO in order of their increasing energies[107,125,264] (see Section 1).

We shall consider the valence isomerisations of propalene. Together with the topomerisation [reaction (38)] of the propalene structure with C_{2h} symmetry, there is a possibility of another non-coplanar mode of isomerisation.

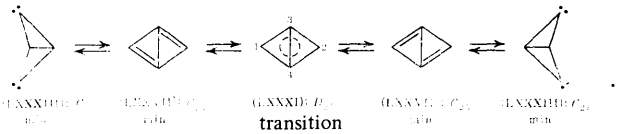


(38)

C_{2h} D_{2h} C_{2h}

Indeed, when the length of the transannular bond is altered, the b_{2g} orbital is destabilised, and the b_{3g} orbital is stabilised (Fig.8), there is a possibility of the formation of structure (LXXXII) of the dicarbene type. The instability of the wave function of this structure with respect to the filling of the MO justifies the expectation that propalene can isomerise via the extension of the transannular bond (isomerism involving bond extension[206]). Calculations by the MINDO/3 method confirmed the above hypothesis, as can be seen from the schematic illustration of the valence isomerisation of

propalene (the type of stationary point on the potential energy surface for the C_4H_2 system is indicated under the numbers designating the structures):[239]

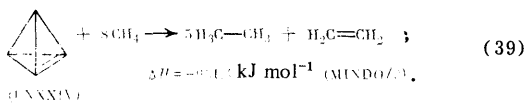


However, the planar structure of the dicarbene type having D_{2h} symmetry, analogous to that obtained in PPP calculations, was converted by a barrier-free process into the non-planar dicarbene structure (LXXXIII) with C_{2v} symmetry.

The relative energies of the valence isomers of C_4H_2, found by semiempirical[239] and non-empirical[240] methods, are presented in Table 2. Evidently, the results obtained in terms of the MINDO/3 approximation are in fact satisfactorily correlated with the results of non-empirical calculations, in which account was taken of the correlation energy by the Meller–Plesset method.

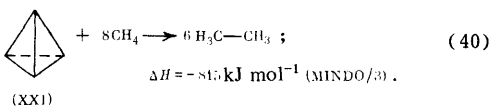
The activation barrier in the isomerisation of propalene (LXXVII) to the non-planar dicarbene C_{2v} structure (LXXXIII) is 72.4 kJ mol^{-1} (MINDO/3) [239] (Fig.9). In contrast to butalene (six π electrons), whose isomerisation on bond extension leads to the formation of *p*-benzyne,[247] the propalene (four π electrons) isomer analogous to 1,3-dehydrocyclobutadiene is not formed. The structure with C_{2v} symmetry, corresponding to the dicarbene structure (LXXXII) found in calculations by the PPP method, is energetically more favourable.

Structures (LXXXIII) can isomerise to dehydrotetrahedrane (LXXXIV), but this compound must be extremely strained:



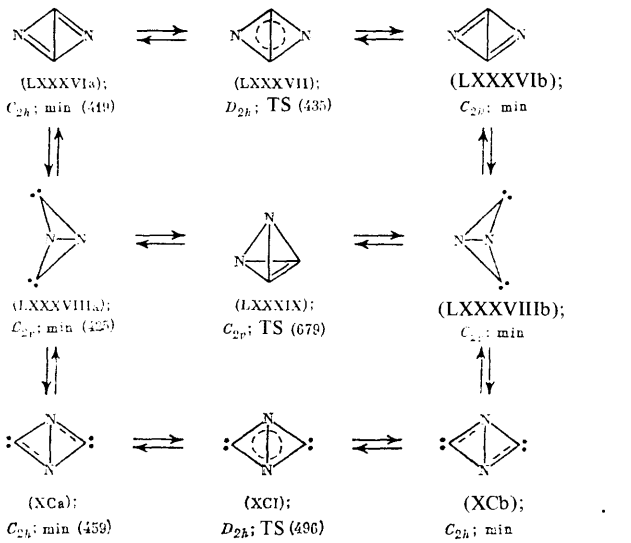
(39)

Analogous data for tetrahedrane (XXI) are presented in the following scheme:



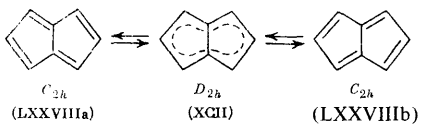
(40)

Diaza-substitution, which stabilises tetrahedrane,[59] does not lead in this instance to the stabilisation of dehydrotetrahedrane, which follows from the results of calculations of the structure of 1,2-diazapropalene and calculations for its valence isomers. Together with the type of symmetry of the structures, the scheme below indicates the character of the stationary point (TS denotes the transition state) on the potential energy surface of the C_2N_2 system, the heats of formation calculated by the MINDO/3 method (in kJ mol^{-1}) being indicated in brackets [we may note that structure (LXXXIX) corresponds, as in the case of dehydrotetrahedrane (LXXXIV), to a transition state; however, the latter is not that of the isomerisation reaction (LXXXVIIIa) ⇌ (LXXXVIIIb) but of another reaction[239]].



2. Pentalene

Unsubstituted pentalene has not so far been obtained, but many of its substituted derivatives are known (see the relevant reviews[236,237]). In particular, 2-methylpentalene, which is extremely unstable and shows a very great tendency towards dimerisation, has been obtained at −195 °C under the conditions of matrix isolation.[248] Comparison of the electronic spectra of methylpentalene,[248,249] 1,3-dimethylpentalene,[250] as well as the electronic and photoelectron spectra of 1,3,5-tri-t-butylpentalene[251–255] with the results of quantum-chemical calculations[252–255] supports the formation of a structure of type (LXXVIII) with unequal bond lengths. X-Ray diffraction study of 1,3,5-tri-t-butylpentalene led to the same conclusion.[256] The pentalene structure (XCII) with D_{2h} symmetry is subject to lattice instability[129] and has a higher energy than the C_{2h} structure by 25.9 kJ mol^{-1} (NDDO method[252]), by 14.6 kJ mol^{-1} (PPP method[255]), by 46.0 kJ mol^{-1} (CNDO/2 method[86]), but 56.1 kJ mol^{-1} (MINDO/3 method[255]), but 46.4 kJ mol^{-1} (MNDO method[240]), and by 56.9 kJ mol^{-1} (non-empirical calculation, 4-31G//STO-3G basis[254]) and is the transition state in the topomerisation of the latter:



(41)

The experimental barrier to the topomerisation of 1,3,5-tri-t-butylpentalene is 21 kJ mol^{-1} (dynamic NMR [254]). 2,5-Diaza-substitution decreases the barrier to 14.6 kJ mol^{-1} (MINDO/3 method[255]). We may not that the activation energy for the topomerisation of the heptalene structure with C_{2h} symmetry is 108.3 kJ mol^{-1} (MNDO method[240]), which is twice as high as the corresponding value for pentalene.

In the calculations for pentalene by the PPP method, solutions corresponding to structures with C_{2h} and D_{2h} symmetry as well as one with D_{2h} symmetry but with a very long transannular bond (HOMO) having a_u symmetry have been obtained depending on the initial density matrix.[125] The inversion of the frontier π MO is characteristic of solutions corresponding to structures with D_{2h} symmetry. According

to the results of non-empirical calculations in terms of the 4-31G basis (the UHF approximation),[254] the energy of the T_1 state of the pentalene structure with D_{2h} symmetry is lower by 7.1 kJ mol^{-1} than the energy of the electronic singlet state. Here one must bear in mind that an unduly low energy of states with higher multiplicity is usually obtained in terms of the UHF approximation.

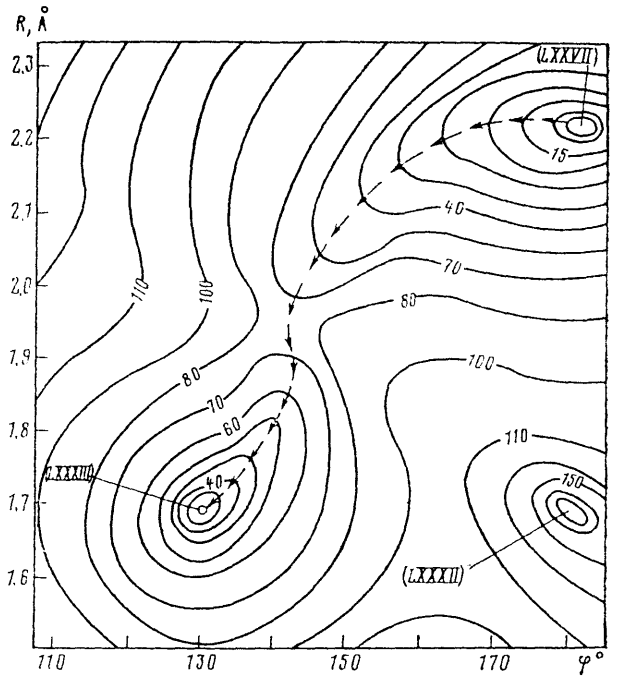
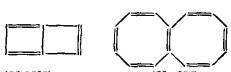


Figure 9. Potential energy surface for the isomerisation reaction of propalene with C_{2h} symmetry [(LXXVII) → (LXXXIII)]; the pathway corresponding to the minimum energy of the reaction is indicated by arrows. The numbers in the gaps in the lines represent the energies (in kJ mol^{-1}) relative to that of the propalene C_{2h} structure; ϕ is the dihedral angle between the C(1)C(2)C(4) and C(1)C(2)C(3) planes [for the significance of the numbering, see reaction (38)]; R is the distance between the C(1) and C(2) atoms.[239]

IV. ALTERNANT [*n*]ANNULENO-[*n*]ANNULENES CONTAINING INTERNAL OR PERIMETRIC 4*k*π-ELECTRON RINGS

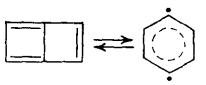
Naphthalene can be regarded as a bridged (transannular bond) analogue of [10]annulene [a(4*n* + 2)π-electron system]. We shall consider the cause of the lability of butalene (XCIII) and octalene (XCIV), whose analogues are also (4*n* + 2)π-electron systems, namely benzene and [14]-annulene, but they contain internal 4*k*π-electron rings.



(XCIII) (XCIV)

The study of these cyclic compounds is of interest because it makes it possible to discover the rules governing the influence of the internal rings on the properties of the system as a whole.

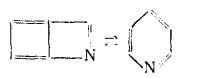
Despite the presence of six π electrons, butalene is nevertheless extremely unstable and its formation only as an intermediate is postulated.[257,258] Calculation of the resonance energy indicates the antiaromaticity of butalene, which contains two cyclobutadiene fragments (Table 1), although its extent is smaller than for cyclobutadiene. Consequently, in this instance the influence of the individual rings prevails over the cyclic conjugation effect along the periphery of the system (six π electrons). At the same time, the contribution of the six-membered (4*n* + 2)π-electron butalene ring to the overall exaltation of the diamagnetic susceptibility determines the diatronic character of the antiaromatic system under consideration.[66] Calculations by the MINDO/3 method have shown that the butalene structure corresponds to a minimum on the potential energy surface for the C_6H_4 system.[247] The isomerisation of butalene to *p*-benzyne (XCV) (isomerism involving bond extension) is allowed by the orbital symmetry conservation rules:[259]



(XCIII) (XCV) (42)

The activation barrier in the given reaction has been estimated as 19.2 kJ mol^{-1}.[247] The difference between the energies of butalene and *p*-benzyne is 150.2 kJ mol^{-1} according to the results of calculation by the MINDO/3 method. It also follows from the results of non-empirical calculations in terms of the 4-31G basis that butalene corresponds to a minimum on the potential energy surface, but the above energy difference between structures (XCIII) and (XCV) amounted to 323 kJ mol^{-1}.[260]

Monoaza-substitution of butalene does not result in a significant stabilisation of the molecule. The energy difference between 2-azabicyclo[2.2.0]hexa-1,3,5-triene (XCVI) and 2,5-bisdehydropyridine (XCVII) has been estimated as 172 kJ mol^{-1} (by the MNDO method).[261] The activation barrier in the extremely exothermic isomerisation reaction (43) (ΔH = −172 kJ mol^{-1}) is 15.9 kJ mol^{-1}.



(XCVI) (XCVII) (43)

Detailed calculations for octalene (XCIV), which has a nonplanar structure,[262] have not been made.

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The advances achieved in the theory of the chemical structure of antiaromatic systems have promoted further progress in the experimental and theoretical methods for the investigation of molecules. As a result, antiaromatic compounds which had not existed earlier, such as, for example, cyclobutadiene, have become entirely real objects for experimental study.

Bearing in mind the position occupied by the theory of aromaticity–antiaromaticity in the conceptual system of organic chemistry and the multiplicity of ways in which the essential feature of this concept is reflected in various theoretical ideas, it is to be expected that further study of antiaromatic molecules will deepen our understanding of the structure of conjugated organic molecules and will help in the solution of the key problem of the relation between the structures and properties of compounds.

During the preparation of the review for the press, two studies which in our view are of significant interest were published. On the basis of a model calculation of the tunnelling rate constant, Carpenter[263] showed that the contribution of the tunnel mechanism to the automerisation of cyclobutadiene ($D_{2h} \rightleftharpoons D_{4h} \rightleftharpoons D_{2h}$) at temperatures below 0 °C may be more than 97%, determining the low activation entropy, in agreement with experimental data.

Jug[264] proposed a method for the estimation of aromaticity based on the calculation of the total ($\pi + \sigma$) bond order as a weighted sum of the eigenvalues of the two-centre components of the density matrix and demonstrated its relation with π-electron ring currents, which constitute a magnetic criterion. This approach makes it possible, in principle, to consider any compounds, avoiding the limitations of the schemes considered above (DRE, HSRE, TRE). At the same time, the necessity for the preliminary calculation of the optimised molecular geometry undoubtedly significantly complicates the application of this criterion of aromaticity–antiaromaticity.

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