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# Polyhedral Organic Molecules and Ions—Structural Analogues of Organometallic Clusters

V.I.Minkin and R.M.Minyaev

The results of experimental and theoretical studies are considered and the principles of the stabilisation of non-classical and highly strained polyhedral structures of organic molecules and ions are formulated. The electron count rules regulating the stability of definite polyhedral forms are analysed. The analogy between the electronic structures of organic and organometallic clusters is demonstrated.
The bibliography includes 189 references.

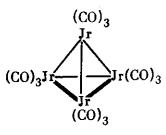
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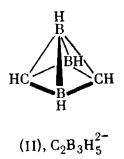
## I. ORGANOMETALLIC AND HYDROCARBON CLUSTERS

Hydrocarbon chains and rings incorporating heteroatoms (oxygen, nitrogen, sulphur, etc.) as individual units make up the skeletons of organic molecules. The usual method of joining together several rings in a molecule is annelation, i.e. fusion in one plane via a common edge, while the formation of three-dimensional structures in which planar rings would correspond to individual faces of polyhedra is not characteristic of organic compounds.

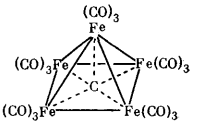
In contrast to organic chemistry, inorganic, coordination, and organometallic chemistry abound in examples of polyhedral structures: boranes, carbaboranes, transition metal carbonyl clusters, etc. Compounds (I)–(VI), chosen for illustration, comprise some of the smallest polyhedra: the tetrahedron, the tetragonal and pentagonal pyramids, the pentagonal bipyramid, and the cube.



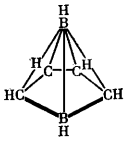
(I), $Ir_4(CO)_{12}$



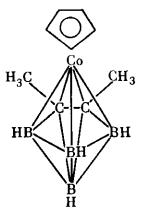
(II), $C_2B_3H_5^{2-}$



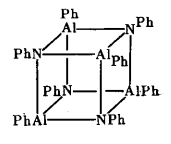
(III), $CFe_5(CO)_{15}$



(IV), $C_4B_2H_6$



(V)



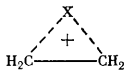
(VI)

The causes of the above difference consist in the characteristics of the electronic structures of organic and organometallic compounds. In a hydrocarbon chain or ring of an organic molecule each individual bond can be described as a two-centre two-electron bond and the number of bonding electron pairs is equal to the number of bonds, in complete agreement with the requirements of the classical theory of valence. On the other hand, in the above structures of carbaboranes and clusters the total number of valence electrons is insufficient for the formation of "normal" two-centre two-electron bonds between all the atomic centres in close proximity, which determines their classification as electron-deficient or excess-orbital compounds. However, the geometrical configurations of these compounds ensure the maximum filling of all the bonding many-centre orbitals by electrons[1–5], enabling at the same time each atom to retain around itself the number of electrons corresponding to the inert gas electronic configuration[6].

Thus, in essence, the three-dimensional structure of the molecular skeleton in electron-deficient compounds, the deviations from the standard valence angles [the bonds between carbon atoms in compounds (II)–(V)], and the unusually high coordination numbers [ranging from 5 for the carbon atom in the carbido-carbonyl cluster (III) and in the series of closo-carbaboranes[5,7] to 8 for the carbon atoms in the carbido-carbonyl clusters of cobalt and osmium[8]] are due to the necessity to observe the principal requirement of the stability of the molecular structure—the maximum utilisation of all the valence electrons for bonding. The latter becomes possible for a geometrical structure of the molecule which ensures the most effective interaction between the orbitals and its constituent fragments. The conditions for the maximum overlap of such orbitals are in general different from the requirements of the standard geometry and the usual valence limitations. The classical theory of structure and classical stereochemistry therefore lose their predictive power and the ability to describe such structures.

This fairly rare situation is encountered in organic chemistry mainly in two fields: the chemistry of non-classical ions[9] and strained structures[10]. Non-classical ions are usually understood as organic cations (electron-deficient species) containing one or more σ-bridges[9,11,12], as in the cation (VII)

or in the norbornyl cation (VIII).



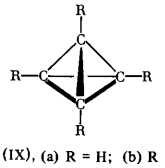
(VII), X = H, Hal, or $CH_3$



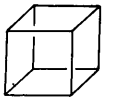
(VIII)

The enforced departure from the classical description of the cations of this type places them among the most controversial structures in organic chemistry. Thus, according to Dewar's count[13], more than 500 studies were devoted to the theoretical and experimental investigation of the norbornyl cation (VIII) as early as 1977.

In contrast to the non-classical ions, in the strained molecules, starting from cyclopropane, the standard rules of valence hold, but the valence angles are highly distorted. The compensation of the angular and bond strain necessary to ensure stability is achieved by concentrating the electron cloud within the molecular skeleton and not along the lines of individual skeletal bonds[14]. Examples of compounds of this type with regular polyhedral structures (platonic bodies) are provided by tetrahedrane (IX)[15] and cubane (X)[16].

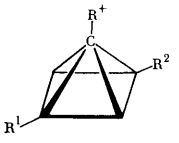


(IX), (a) R = H; (b) R = t-$C_4H_9$

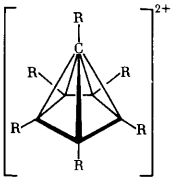


(X)

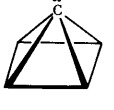
Compounds (IX) and (X) are organic analogues of clusters (I) and (VI) respectively and, like the pyramidal non-classical cations of types (XI) and (XII) obtained recently[18-20], have the same polyhedral structure as the isoelectronic *nido*-carbaboranes (II) and (IV). A pyramidal structure has been predicted by calculations[17] also for the metastable isomer of the neutral hydrocarbon $C_5H_4$ (XIII), whose electron deficiency is caused by the removal of the electron pair of the apical carbon from involvement in the formation of skeletal bonds.



(XI), (a) R = $R^1$ = $R^2$ = H;
(b) R = $R^1$ = $CH_3$; $R^2$ = H (Ref.18)
(c) R = $R^1$ = $R^2$ = $CH_3$ (Ref.19)



(XII), (a) R = H;
(b) R = $CH_3$ (Ref.20).



(XIII)

Evidently the structural similarity of the two series of compounds (I)–(IV) and (VI), on the one hand, and (IX)–(XIII) on the other, examined above, is not fortuitous and is determined by analogies between their electronic structures. Nevertheless the synthesis of compounds (IXb), (X), (XIb), and (XIIb) was treated by organic chemists as a sensation. Increasing amounts of experimental and calculated data are being accumulated nowadays on the unusual polyhedral structures of organic molecules and ions and it is becoming increasingly clear that there are common factors governing the structures of these and structurally analogous organometallic and inorganic compounds.

There is reason to believe that, from the standpoint of the nature of the chemical bond, the field of polyhedral compounds in organic chemistry is closest to organometallic and inorganic chemistry. The aims of the present review are as follows: (a) to elucidate the causes of this analogy, (b) to examine the experimental and theoretical data on polyhedral organic structures which have already accumulated, and (c) to examine the descriptive and predictive possibilities of a general qualitative approach to the study of the causes of the stabilisation of the non-classical polyhedral organic molecules and ions based on the so-called reconstruction or fragment analysis.

## II. RECONSTRUCTION ANALYSIS OF THE MOLECULAR ORBITALS OF COMPLEX MOLECULES

The principal idea of reconstruction analysis is to reproduce the molecular orbitals (MO) of the entire molecule A–B–C–D–... from data for the energies and forms of the molecular orbitals of its individual fragments. This physically clear idea, which combines the simplicity and logic of classical structural representations with the quantum-mechanical description of many-centre interactions, has been used in a whole series of theoretical investigations, starting with Dewar's work[21], but has been developed most logically by Hoffmann[22,23]. His two brief reviews contain an extremely valuable bibliography on this topic.

In essence, the above problem is one of perturbation theory. Its solution at different levels of approximation has been analysed in detail[24-28]. We shall consider here briefly the most important relations for the simplest case of the interaction of two molecular fragments in terms of the one-electron approximation where the overall result of the interaction of the fragments is determined by the sum of the orbital interactions.

### 1. The Interaction of Fragment Orbitals

When two non-degenerate orbitals $\phi_a$ and $\phi_b$ having the energies $\varepsilon_a$ and $\varepsilon_b$ and belonging to fragments A and B respectively interact, two new orbitals of the overall system A–B are formed ($\phi'_a$ and $\phi'_b$, Fig.1). The lower orbital $\phi'_a$ is then stabilised by the amount

$$\Delta\varepsilon_a = \frac{(H_{ab} - \varepsilon_a S_{ab})^2}{\varepsilon_a - \varepsilon_b} \quad , \qquad (1)$$

while the upper orbital $\phi'_b$ is destabilised by the amount

$$\Delta\varepsilon_b = \frac{(H_{ab} - \varepsilon_b S_{ab})^2}{\varepsilon_b - \varepsilon_a} \quad , \qquad (2)$$

where $H_{ab}$ is the matrix element of the interaction operator $\langle\phi_a|H'|\phi_b\rangle$ and $S_{ab} = \langle\phi_a|\phi_b\rangle$ is the overlap integral of the orbitals $\phi_a$ and $\phi_b$.

Like the orbital energies of the occupied and lowest unoccupied molecular orbitals, the quantity $H_{ab}$ is negative. Since $\varepsilon_a < \varepsilon_b$ (Fig.1a), it is seen from Eqns.(1) and (2) that, in terms of absolute magnitudes, $\Delta\varepsilon_a < \Delta\varepsilon_b$. Consequently if the two orbitals of the fragments $\phi_a$ and $\phi_b$ are occupied by pairs of electrons which are transferred to the MO of the A–B system, then the overall effect of such interaction is destabilisation. The effect of the four-electron destabilisation is none other than the well known exchange repulsion of occupied electron shells. The possibility of describing this effect by Eqns.(1) and (2) depends on being able to take into account the overlap integral $S_{ab}$ between the interacting orbitals.

A simple relation is usually postulated between $H_{ab}$ and $S_{ab}$[26-28]:

$$H_{ab} = kS_{ab} \quad , \qquad (3)$$

where $k$ varies within wide limits as a function of the method of calculation: from −8.55 eV (the Hückel molecular orbital method[26]) to −39.7 eV (the SCF MO methods[28]), etc.

Taking into account Eqn.(3), it is easy to determine which factors influence the orbital interactions. The main factor is the overlap integral between the orbitals, which is determined by the symmetry of the orbitals and their mutual orientation. The second factor is the proximity of the energy levels of the fragment orbitals. The strongest interaction corresponds to degenerate ($\varepsilon_a = \varepsilon_b = \varepsilon$) orbitals $\phi_a$ and $\phi_b$ (Fig.1*b*). In this case the stabilisation energy of the lower orbital $\phi'_a$ and the destabilisation energy of the upper orbital $\phi'_b$ of the A–B system are calculated in terms of the first-order perturbation theory with the aid of the relations

$$\Delta\varepsilon_a = \frac{H_{ab} - \varepsilon S_{ab}}{1 + S_{ab}} \quad ; \qquad (4)$$

$$\Delta\varepsilon_b = \frac{-H_{ab} + \varepsilon S_{ab}}{1 - S_{ab}} \quad . \qquad (5)$$

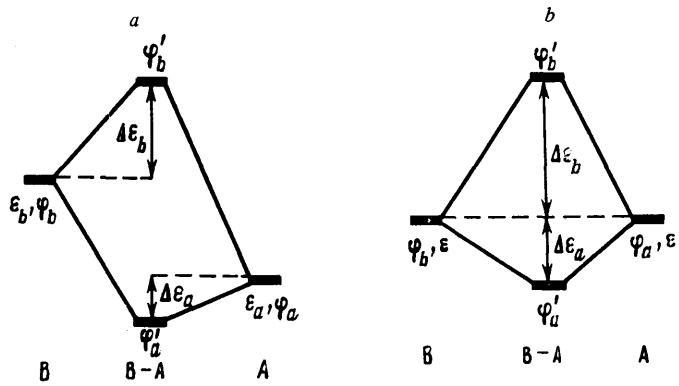



**Figure 1.** The formation of the MO of the A–B system ($\phi'_a$, $\phi'_b$) from the orbitals of the fragments A and B ($\phi_a$ and $\phi_b$): *a*) interaction of non-degenerate orbitals; *b*) interaction of degenerate orbitals.

The orbitals of the A–B system ($\phi'_a$ and $\phi'_b$) can be represented as a linear combination of the orbitals of the fragments A and B:

$$\varphi_a' = \varphi_a + \lambda\varphi_b \quad , \qquad (6)$$

$$\varphi_b' = \varphi_b + \mu\varphi_a \quad , \qquad (7)$$

and in absolute magnitude the coefficients $\lambda$ and $\mu$ are less than unity, i.e. the orbital $\phi'_a$ involves a greater contribution of $\phi_a$ and the orbital $\phi'_b$ involves a greater contribution of $\phi_b$. The interactions of the orbitals are additive in pairs, so that the above scheme can be readily extended to the interaction of a large number of orbitals belonging to additional fragments.

## 2. Fragmentation of the System. Group and Bond Orbitals

An important problem is how to isolate most effectively the fragments the interaction of the orbitals of which is most important for the determination of the stability (or instability) of the system as a whole. In the language of the LCAO-MO method, the problem is reformulated into one involving the determination of the delocalised MO of a complex system in the form of a linear combination of localised MO of its fragments, i.e. in the form of Eqns.(6) and (7).

Analysis of the wave functions and the electron distributions for a wide range of organic and inorganic compounds[29–31] has shown that, for both saturated and unsaturated and conjugated compounds, the delocalised MO can be constructed from a small number of localised group orbitals, which can be transferred from one system to another (transferable orbitals). For hydrocarbon systems, such groups are CH, $CH_2$, and $CH_3$; in the molecules with heteroatoms these are their isoelectronic fragments. Even in molecules with many-centre bonds—boranes and their derivatives[32], transition metal clusters[2,5], and π-complexes[22]—it is possible to isolate the group orbitals of several main fragments—the "building blocks" of the delocalised MO of a wide variety of compounds.

Fig.2 presents the group orbitals of the hydrocarbon fragments $CH_n$ constructed in the form of linear combinations of the atomic orbitals of carbon ($2s$, $2p_x$, $2p_y$, $2p_z$) and hydrogen ($1s$). All the orbitals can be divided into two groups. The first includes the σ-orbitals ($\sigma_{CH}$, $\sigma_{CH_2}$, $\sigma_{CH_3}$), whose form ensures the accumulation of electron density in the region of C–H bonds. On formation of the molecule from the CH groups, these orbitals interact weakly with one another, since the overlap between them is insignificant [see Eqns.(1), (2), (4), and (5)]. Such orbitals are regarded as bonding[29]. In contrast to the group σ-orbitals, a considerable proportion of the electron density in the orbitals of the π- and *n*-types is distributed outside the range of the bonds within the groups. The interaction of such group orbitals determines the formation of new bonds and the stabilisation or destabilisation of the structure made up of several groups. The conditions for the maximum overlap of the group π- and *n*-orbitals, which depend on the relative positions of the groups, dictate the resultant geometry of the system.

We shall illustrate these postulates by analysing the MO of molecules of the type $A_2H_4$ formed from the group orbitals of the $AH_2$ fragments (Fig.3). Only group orbitals with suitable symmetry properties are combined. The nature of the stabilisation of the planar structure of $C_2H_4$ is related to the interaction of boundary group orbitals (*n* and *p*), leading to the formation of bonding $\sigma_{CC}$ and $\pi_{CC}$ orbitals of ethylene. By virtue of the considerable overlap, the interaction of the *n*- and *p*-orbitals leads to a greater splitting of their levels, the stabilisation of the bonding combination of *n*-orbitals, and the formation of bonding $\pi(1b_{1u})$-MO (lying below the atomic *p*-level).

The $C_2H_4$ molecule is an example of a fully occupied system of bonding MO, which is the reason for its stability in the $D_{2h}$ configuration. For the hydrazine molecule $N_2H_4$, having two electrons more than the ethylene molecule, the additional electrons in the $D_{2h}$ structure should occupy the antibonding $\pi^*(1b_{2g})$-MO. Because of this, the stable conformation of the molecule does not consist of the planar $D_{2h}$-form but is represented by a skewed structure (the angle of rotation about the N–N bond is ~ 90°), pyramidalised at the nitrogen atoms, in which the energetically unfavourable π*-MO is not formed[34,36].

Analysis of the scheme of orbital interactions leads to a series of general and important postulates[28,29,34,37,38], which will be used in the subsequent discussion.

(1) The main type of orbital interactions of fragments, which determines the stability of the system, is the interaction of boundary and immediately adjoining orbitals of the *n*- and π-types. The interaction of the σ-orbitals lying below is of the repulsion type but, by virtue of the small overlap of such orbitals belonging to different fragments, the repulsion effect is comparatively weak.

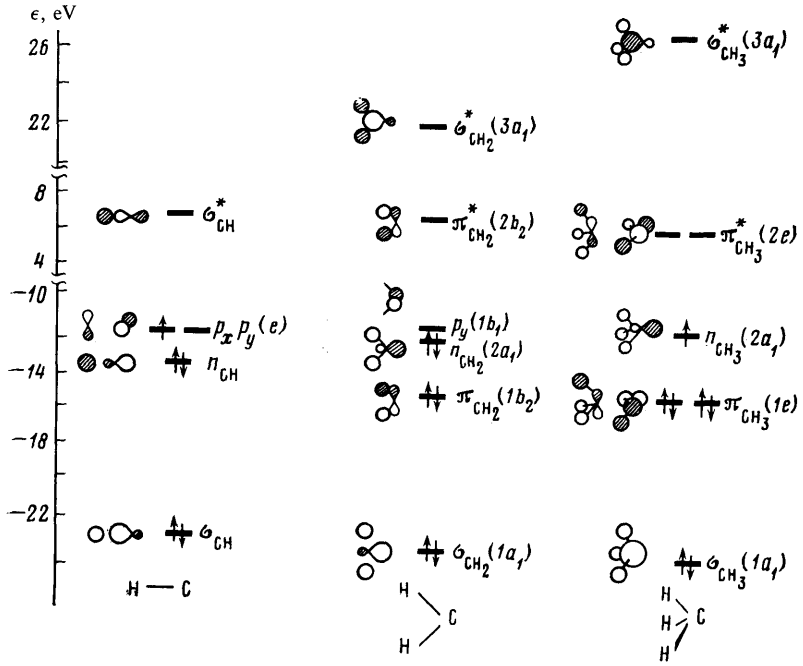



**Figure 2.** Group orbitals of the hydrocarbon fragments CH, $CH_2$, and $CH_3$.[29,33,34] The orbital energies have been calculated by the extended Hückel method[35].

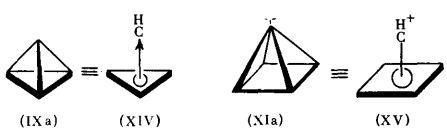
(2) Systems where the number of electrons does not exceed twice the number of bonding orbitals correspond to stable structures. This postulate constitutes the basis of all the electron count rules describing the stability of typical structures.

(3) Within the framework of the MO methods neglecting direct allowance for electron repulsions, there are no special limitations imposed on the method of fragmentation of the complex molecule or ion. However, for a qualitatively clear analysis, it is better to isolate fragments reflecting to the maximum extent the symmetry of the system and having valence orbitals of the $n$- and $\pi$-types.

### 3. Fragmentation of the Polyhedra

The last postulate is particularly important when the method of reconstruction analysis is applied to the determination of the MO of polyhedral structures. The structural units of the polyhedron are the vertices, edges, and faces; in a molecular system atoms or $\sigma$-linked groups, $\pi$-bonds, and conjugated cyclic fragments correspond to them. In relation to hydrocarbons, on which attention is concentrated in the present review, the vertices are C, CH, $CH_2$, $CH_3$, the edges are HC≡CH, while the faces are the $(CH)_n$ rings, where $n \geq 3$.

Pyramidal forms can be made up of these structural units by adding vertices to the basal plane, for example, via scheme (XIV) for tetrahedrane and (XV) for the cation $(CH)_5^+$.



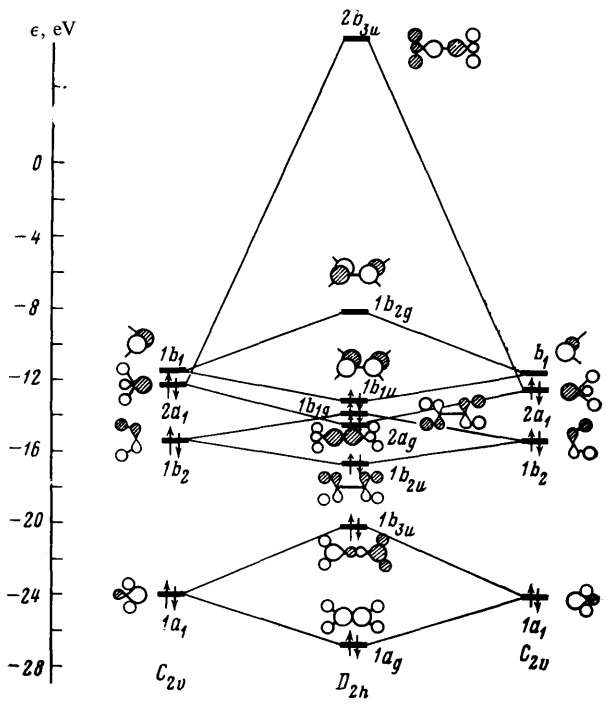
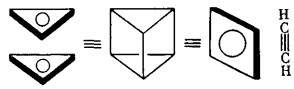




**Figure 3.** The formation of the MO of a molecule of the type $A_2H_4$ from the group MO of the $AH_2$ fragments. The filling with electrons for $C_2H_4$ and $CH_2$ is illustrated (calculation by the extended Hückel method).

More complex polyhedral molecules can be fragmented in several ways, using the above structural elements. Thus the prismane molecule can be made up either by the parallel superposition of two cyclopropenyl rings or by adding the acetylene edge to the cyclobutadiene ring.



This fragmentation scheme originated from the topological classification of the interactions of chains into *peri-*, *spiro-*, *longi-*, and *lati*-cyclic types developed by Goldstein and Hoffmann[39]. Indeed, although rings are absent from this scheme, they are obtained by the pericyclic combination of two or several conjugated chains (ribbons).

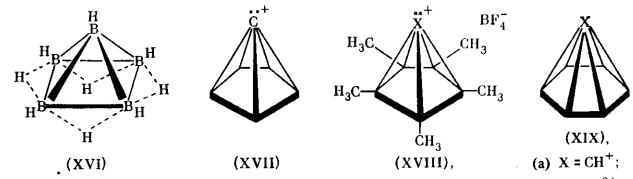
Thus, apart from the orbitals of the $CH_n$ groups (Fig.2), the orbitals of the π-bonds (Fig.3) and those of conjugated rings $(CH)_n$ are required for the construction of the MO of polyhedral hydrocarbon structures on the basis of reconstruction analysis. The conjugated rings can be readily obtained by combining $n$ group orbitals of CH, the full analogy between the schemes for the formation of delocalised σ- and π-MO being retained[29,30]. The different versions of the combination of the above fragments (as well as the isoelectronic heteroatomic groups) into polyhedral structures will be examined below in succession and the electronic requirements for their stability will be analysed. The results of the theoretical analysis will be compared with the results of experimental investigations.

## III. PYRAMIDAL STRUCTURES

### 1. Pyramidal Hydrocarbons and Their Heteroanalogues

The simplest pyramidal structure is that of the tetrahedrane molecule (IXa). The problem of the synthesis of tetrahedrane was formulated more than half a century ago and stimulated a vigorous investigation of methods for the synthesis and reactions of its possible precursors[10,40]. Nevertheless the tetra-t-butyltetrahedrane (IXb) obtained recently still remains the only fairly completely characterised compound with a carbon skeleton of type (IX).[15,41] The strain energy $E_{str}$ of the tetrahedrane molecule is 148.8 kcal $mol^{-1}$ according to latest estimates[42], i.e. ~ 25 kcal $mol^{-1}$ for each C–C bond, which is the upper known limit for strained organic compounds. The reason for the high value of $E_{str}$ is evidently high angular strain.

The next member of the series of pyramidal hydrocarbons $(CH)_n$, namely the cation $(CH)_5^+$ (XIa)≡(XV) is not only a strained but also a non-classical structure with a pentacoordinate carbon atom at the vertex. The possibility of the existence of such a cation was first postulated by Williams[43], who emphasised the fact that it is isoelectronic with the pyramidal pentaborane $B_5H_9$ (XVI). Analysis and calculations by the extended Hückel method by Stohrer and Hoffmann[44] explained the nature of the stabilisation of this non-classical structure and almost simultaneously Masamune et al.[18] reported the experimental discovery of the dimethyl derivative (XIb), which is stable in acid media. Reactions leading to derivatives of the first pyramidal cation (XI) have been studied in detail (see the reviews[45,46] and a communication[19]) and the stability of the $C_{4v}$ structure of the cation has been confirmed by a whole series of semiempirical[44,45,47–50] and non-empirical[51,52] calculations.

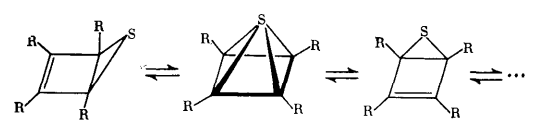


(XVI) (XVII) (XVIII), (a) X = Ge; (b) X = Sn (XIX), (a) $X = CH^+$; (b) $X = Sn^{2+}$; (c) $X = Pb^{2+}$.

In 1973 Hogeveen and Kwant[20,53] reported a new pyramidal $C_{5v}$ hydrocarbon—the hexamethyl derivative of the dication $(CH)_6^{2+}$ (XIIb). An analogous pyramidal $C_{5v}$ structure has been predicted by MINDO/3 calculations also for the metastable isomer of the cationic phenylcarbene (XVII)[54] and quite recently Jutzi et al.[55] synthesised the extremely stable germanium and tin analogues of the cationic carbene (XVIII) and demonstrated their $C_{5v}$ structure by direct X-ray diffraction study. However, it was found that the pyramidal $C_{6v}$ structure (XIXa), discussed as long as 20 years ago as one of the possible structures of the norbornadienyl cation[56], does not correspond to a minimum on the potential energy surface (PES) for the cation $(CH)_7^+$,[57] while the tin dication (XIXb)[58] and the lead dication (XIXc)[59] have the $C_{6v}$ symmetry in the crystal.

The pyramidal $C_{4v}$ structure of the hydrocarbon $C_5H_4$ (XIII) (pyramidane) has been shown by MINDO/3[17,60] and non-empirical[61] calculations to correspond to a fairly deep local minimum on the PES. Despite the fact that the tetracoordinate carbon atom at the apex has an extremely strained pyramidal bond configuration[62,63] (approximately $sp^6$ [sic.cf.Ref.62 (Ed. of Translation)] hybridisation), the strain energy per C–C bond corresponds to only 19 kcal $mol^{-1}$, which makes it possible to regard the synthesis of compound (XIII) as a realistic task.

The hypothesis of the formation of a pyramidal structure of type (XX) has also been put forward to account for the mechanism of the isomerisation of 2-phenylthiophen to 3-phenylthiophen[64] and of the peripheral migration of the sulphur atom in Dewar thiophen (XXI, R = $CF_3$)[65]:



(XXIa) (XX) (XXIb)

However calculations have shown[66] that the structure (XX, R = H) corresponds to a maximum and not a minimum on the PES for the model reaction.

The data presented make it necessary to seek an answer to the question why the existence of organic pyramidal structures (IX), (XI), (XII), (XVIII), and (XIX, b and c) is possible, while others, which should formally be formed in accordance with the same principle, cannot be realised.

### 2. The Eight Electron Rule

The causes of the stability of some and of the instability of other $C_{nv}$ pyramidal structures become clear in the reconstruction analysis of the MO. Compounds with a pyramidal structure can be regarded as organic π-complexes of type (XXII) formed by the [$n$]annulene conjugated fragment and the apical X atom or X–R group.

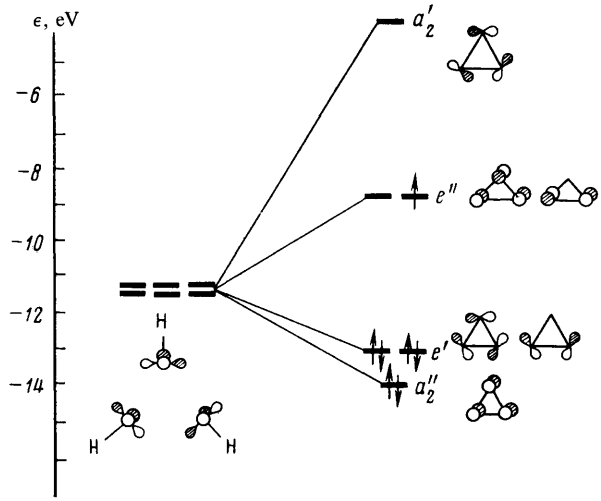
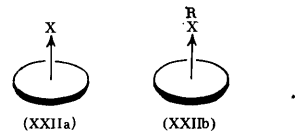



**Figure 4.** The formation of the MO of [3]annulene from the orbitals of three CH groups. The three $p_z$-orbitals of CH constitute a Hückel system and form the π-MO ($a_2''$, $e''$). The three $p_y$-orbitals constitute the Möbius system and form the σ-MO of the system of levels which is the inverse of that of π-MO.[67] For the complete $(CH)_3$ system, an admixture of the MO formed by the bonding CH orbitals to the molecular orbitals $e'$ and $a_2'$ is observed. The energies of the levels have been obtained by a calculation using the extended Hückel method.




The MO for such structures are usually constructed from the atomic or group [in the case of compound (XXIIb)] orbitals of the apical centre and the orbitals of the basal ring. The latter can be formed from the orbitals of the CH group (Fig.2) and only the MO produced by combining $p$-AO are capable of significant interaction with the orbitals of the apical centre, i.e. have energies close to the latter and there is adequate overlap.

Fig.4 illustrates the formation of the MO of [3]annulene from the $p$-AO of three CH groups. Analogous systems of π-MO and Walsh σ-MO are characteristic of any [$n$]annulene ring. The MO obtained by mixing the bonding $\sigma_{CH}$ orbitals lie outside the valence band and their electron density is concentrated in the band of the C–H bonds[29].

Calculations have shown that, as the X, XH, or XR vertex approaches the basal ring, the overlap integrals of the valence orbitals of the above groups with the π-MO of the [$n$]annulene ring are greater by a factor of 3–5 than the integrals for the overlap with the Walsh σ-MO. Since the energy of the interaction of orbitals is proportional, according to Eqns.(1) and (2), to the square of the overlap integral $S_{ab}^2$, it follows that in a qualitative study it is sufficient to take into account only the interaction between π-MO of the basal ring.

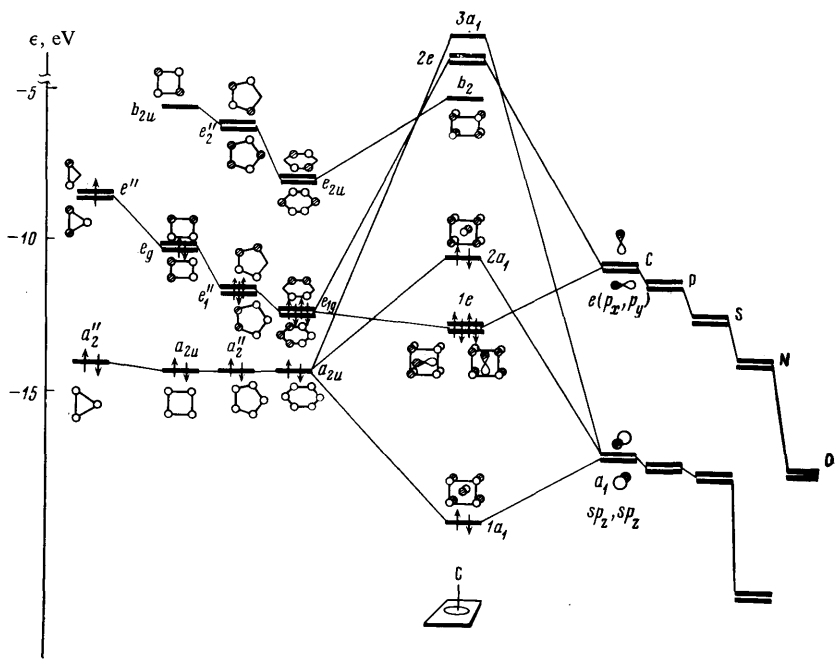
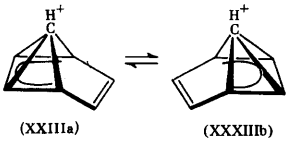



**Figure 5.** The reconstruction analysis of the MO of $C_{nv}$ pyramidal systems formed by the [$n$]annulene ring and the apical atomic centre. The molecule of pyramidane has been chosen as an example. The MO energies have been calculated by the extended Hückel method; the energies of the hybrid orbitals were taken from Hinze and Jaffé.[68] For the $C_{4v}$ and $C_{5v}$ structures with an apical atom more electronegative than phosphorus and for all $C_{3v}$ structures, an inversion of the $1e$ and $2a_1$ levels is observed.

We shall consider initially pyramidal structures of type (XXIIa) to which compounds (XIII), (XVII), (XVIII), and (XX) belong. The valence orbitals of the apical atom can be conveniently regarded as a pair of hybrid $sp_z$-orbitals and a pair of $p_x$- and $p_y$-orbitals. Fig.5 presents a generalised[17, 54,55,66,69] correlation diagram for the $C_{nv}$ pyramidal system (XXIIa). The interaction of the lowest $\pi$-orbital of annulene with a pair of hybrid orbitals of the apical atom, having identical symmetry properties, leads to the formation of the bonding ($1a_1$), non-bonding ($2a_1$), and antibonding ($3a_1$) MO. Since the initial fragment orbitals are completely filled with electrons, the resulting effect of this orbital interaction is destabilisation. The fragments are bound together as a consequence of the mixing of the lowest $e$-MO of the ring with the $p$-AO of the apical atom and the formation of the bonding $1e$-level of the $C_{nv}$ pyramidal system.

Thus the orbital interactions of the fragments of any $C_{nv}$ pyramidal structure described above give rise to three bonding and one non-bonding MO, which can accommodate eight electrons. If the number of $\pi$-electrons of the basal ring and of the valence electrons of the apical centre (it has been suggested[70] that these electrons be referred to as "inner") exceeds eight, the antibonding MO is filled, which destabilises the structure. Indeed the hypothetical structures of pyramidane (XIII), the cationic carbene (XVII), as well as compounds (XVIII) and (XIX, b and c) meet the above requirement, whereas the $C_{4v}$ structure (XX) and the $C_{6v}$ structure (XIXa) each contain 10 inner electrons and do not actually occur. In order to become adapted to the requirement of an eight-electron shell, such structures are distorted to give less symmetrical forms: (XXIa) for thiophen and (XXIII) for the norbornadienyl cation, for which the fluctuating conformation with a single "disconnected" $\pi$-bond is stable[71,72].




(XXIIIa) (XXXIIIb)

The correlation diagrams for pyramidal structures of type (XXIIb)[44,46,70] are analogous to that presented in Fig.5, which is due to the similarity of the fragment orbitals. Fig.6 illustrates the relation between the structure of the MO of the (XXIIa) and (XXIIb) systems. The significant difference is that the non-bonding $2a_1$ level in structures (XXIIa) is transformed into the low-lying $1a_1$ level of the X–R bond, which stabilises the structure. Like structure (XXIIa), structures (XXIIb) contain four bonding MO, which can be filled by not more than eight electrons, including the $\pi$-electrons of the basal ring, the valence electrons of the atom X, and one additional electron from the group R involved in the formation of the electron pair of the X–R $\sigma$-bond.

In combination with the analogous conclusion for compounds (XXIIa), the above conclusion can be regarded as the formulation of the eight electron ($8e$) rule for the stability of $C_{nv}$ pyramidal structures. The $8e$ rule can be understood as the tendency of the apical atom of the non-transition element to build up its electron shell to that of the corresponding inert gas. In this sense, it is analogous to the familiar 18 electron rule for transition elements.

Taking into account the $8e$ rule, it is possible to postulate the capacity for the existence of pyramidal organic molecules and ions of types (XXIV) and (XXV).

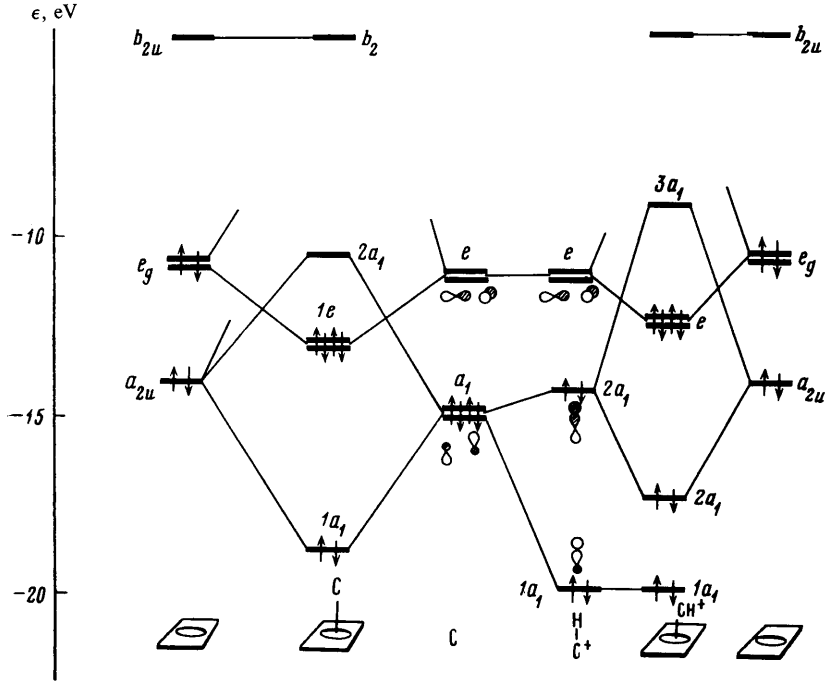
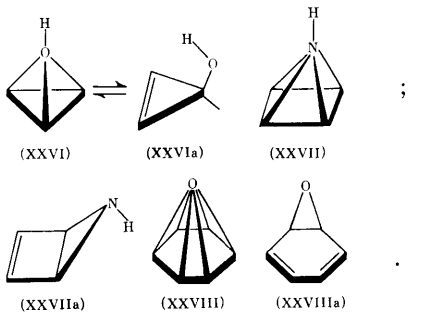



**Figure 6.** Relation between the correlation diagrams for the MO of the pyramidal structures (XXIIa) and (XXIIb). Pyramidane and the $(CH)_5^+$ cation have been chosen as examples.



(XXIV), X = $C^-$, CH, N, P, $O^+$, or $S^+$ (XXV), Y = C, $CH^+$, Si, $SiH^+$, $N^+$, $P^+$, $O^{2+}$, or $S^{2+}$ .

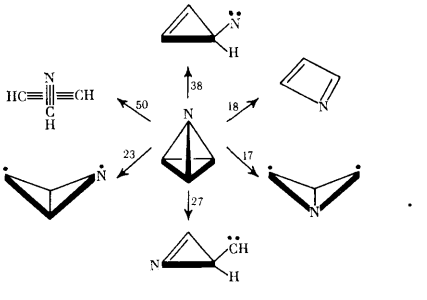
Calculations[69,73] by the MINDO/3 method with complete optimisation of all the geometrical parameters have indeed shown that all the structures quoted above for the $C_{3v}$ and $C_{4v}$ symmetry correspond to local minima on the PES. On the other hand, the non-classical structures (XXVI)–(XXVIII), which do not satisfy the 8*e* rule, correspond to maxima on the PES and relax to the stable forms (XXVIa)–(XXVIIIa):



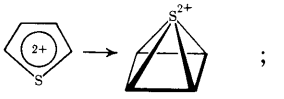
(XXVI) (XXVIa) (XXVII) ;

(XXVIIa) (XXVIII) (XXVIIIa) .

The validity of the 8*e* rule implies merely that the structure corresponds to a minimum on the PES for a molecule or ion. In order that such a structure should have a sufficiently long lifetime, it is necessary that it should have adequate kinetic stability in relation to different possible isomerisation and ring decomposition reactions. Detailed non-empirical[74] and MINDO/3[75] calculations on such transformations have been made for the tetrahedrane molecule, which is kinetically stable despite its strain. The pyramidane molecule has analogous properties[76]. The above schematic formulation[69] of the ring decomposition and isomerisation reactions involving another hitherto unknown pyramidal structure, namely that of azatetrahedrane (XXIV, X = N), where the numerals above the arrows indicate the activation barriers (kcal $mol^{-1}$) calculated by the MINDO/3 method, also indicates the kinetic stability of this compound even in relation to more stable isomers {azacyclobutadiene, 3-azabicyclobutane[1.1.0]diyl} and the decomposition products:



On the basis of the rule formulated above, it is possible to predict transformations which should lead to non-classical pyramidal structures. Non-empirical and MINDO/3 calculations[77] suggest that the thiophen dication (XXIX) is unstable and relaxes without an activation barrier to the pyramidal dication (XXV, Y = $S^{2+}$):

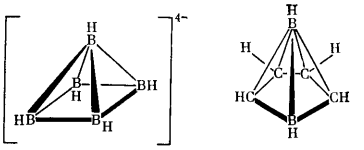


(XXIX) (XXV), Y = $S^{2+}$ .

### 3. Pyramidal Structures in a Series of Boranes and Organometallic Compounds of Non-transition Metals

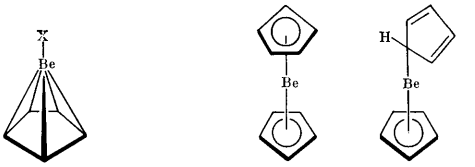
In contrast to organic compounds, the pyramidal (*nido*) structures are not an exception but the rule in the series of boranes and carbaboranes[1,4,7,78]. Electron count rules, taking into account the so-called skeletal electrons of all the groups[2-5], which are discussed above (see Section VI) have also been developed for these compounds. The 8*e* rule constitutes an equivalent formulation.

On the basis of the fragmentation scheme examined above, Lipscomb[1] predicted that the $B_nH_n^{4-}$ anions should have the pyramidal *nido*-structure, for example, compound (XXX, $n = 5$). Indeed the sum of the $\pi$-electrons of the basal ring (0) and the electrons of the apical group (8) is 8. The pyramidal structure (II) is expected[4] for the dianion $C_2B_3H_5^{2-}$ (2 + 6 inner electrons), isoelectronic with compound (XXX). For the stable *nido*-carbaborane $C_4B_2H_6$ (XXXI), this structure has been established experimentally[7,79] (4 + 4 inner electrons). In general any carbaboranes $C_4B_{n-4}H_n$ and the dianions $C_2B_{n-2}H_n$ should have the $C_{(n-1)v}$ pyramidal *nido*-structure:



(XXX) (XXXI) .

Numerous pyramidal $C_{5v}$ structures have been found for derivatives of cyclopentadienylberyllium hydride (XXXII). Data on the structures of and theoretical calculations for these compounds have been described[70,80]. The beryllocene molecule (XXIII), whose structure has been investigated by all possible experimental methods, including electron diffraction and low-temperature X-ray diffraction measurements[31,81-83], is of special interest in this series. The sandwich structure (XXXIIIa) and the half-sandwich structure (XXXIIIb) are believed to be most probable. The latter belongs to type (XXIIb) and corresponds to the 8*e* rule, to which Jemmis et al.[80] relate the results of their calculations (STO-3G basis set), indicating that structure (XXXIIIb) is preferable. Recent more complete calculations[82] using an extended basis set led to an analogous conclusion. It is of interest that the structure of the MO of the valence band obtained in this calculation is exactly consistent with the qualitative scheme in Fig. 6.



(XXXII), (a) X = H, (b) X = $CH_3$, (c) X = $BH_4$, (d) X = Cl, (e) X = Br (XXXIIIa) (XXXIIIb) .

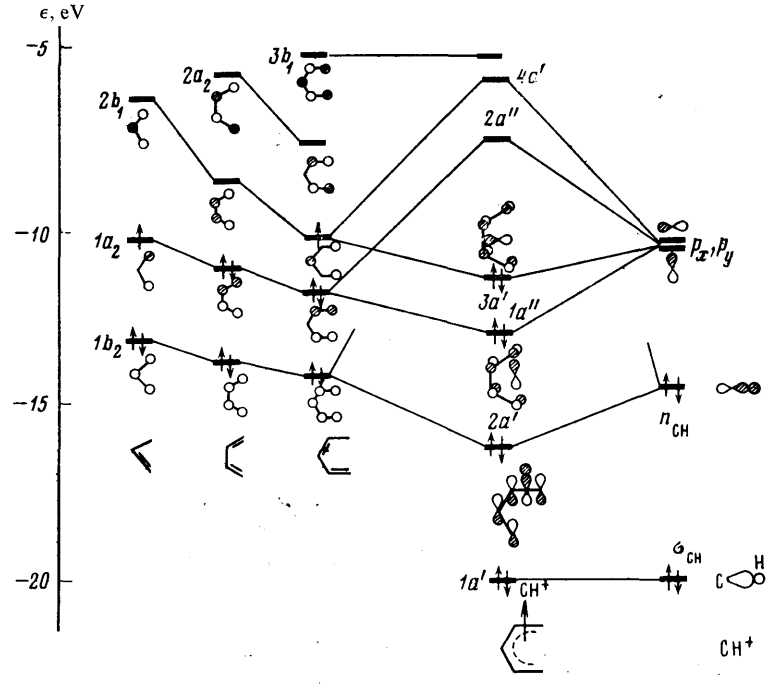
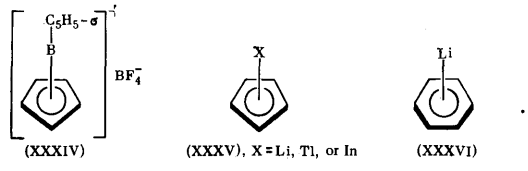



Figure 7. Reconstruction analysis of the MO of the non-classical cations formed by a polyene chain and a $CH^+$ vertex. The cation (XXXVIII) has been taken as an example. The MO energies have been calculated by the extended Hückel method.

A pyramidal structure has been established by X-ray diffraction for the cation (XXXIV), which is isoelectronic with beryllocene[84]. Cyclopentadienylthallium[85] and cyclopentadienylindium[86] have analogous structures in the gas phase (8 inner electrons). According to calculations[87,88], cyclopentadienyl-lithium also has the $C_{5v}$ structure (XXXV). The number of inner electrons in this compound is 6, which leads to additional stabilisation, since the non-bonding $2a_1$ MO (Fig.5) remains unoccupied. Presumably, in conformity with the 8*e* rule, the stable form of cycloheptatrienyl-lithium has the pyramidal $C_{7v}$ structure (XXXVI):

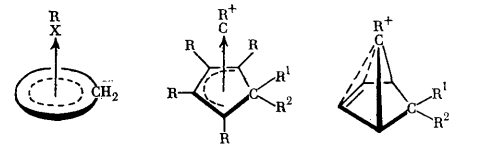



(XXXIV) (XXXV), X = Li, Tl, or In (XXXVI)

## 4. Homoconjugated Rings in the Basal Plane

Cyclic groups produced by the insertion of methylene and isoelectronic groups in one or several bonds of the [*n*]annulene ring also have a system of π-orbitals suitable for effective binding to the apical group. Such substitution diminishes but does not abolish the endocyclic orbital interactions and, according to a theorem[39], the symmetry of the π-orbitals in such a ring does not change compared with the initial conjugated ring. Consequently the type of interaction of these orbitals with those of the apical fragment does not change and the 8*e* rule can be extended to pyramidal structures, in the basal plane of which there is a polyene group, isolated π-bonds, and individual π-centres, the relative disposition of which is close to that of a closed ring.

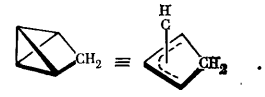
Fig.7 illustrates the formation of four bonding MO in structures of type (XXXVII) in relation to the homo-$(CH)_5^+$ cation (XXXVIII):




(XXXVII) (XXXVIII) (XXXVIIIa)

In contrast to the $C_{nv}$ pyramidal systems (XXIIb), the structures (XXXVII) have only a plane of symmetry and the apical centre is not equidistant from all the π-centres coordinated to it. The latter follows from $^{13}C$ NMR data for a series of hexamethylbicyclo[2.1.1]hexenyl cations (XXXVIII, R = $CH_3$)[45,46] and has been confirmed by MINDO/3 calculations[19].

The structure of the molecule of homotetrahedrane (XXXIX), which has been recently synthesised[40], can also be represented by analogy with scheme (XXXVII) as one involving the stabilising interaction of the 3π-electron allyl fragment with a 5-electron group CH [structure (XXXIXa)]:

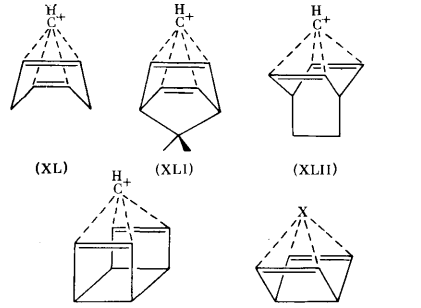



(XXXIX) (XXXIXa)

The form of the MO of the polyene chain (Fig.7) explained satisfactorily the asymmetrical orientation of the apical group X. Thus the displacement of this group towards the centre of the allyl fragment in compound (XXXIXa) and conversely towards the terminal atoms of the butadiene fragment in

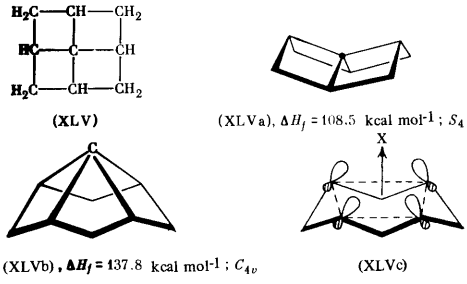
compound (XXXVIII) is determined by the conditions for the maximum overlap of the interacting orbitals of the polyene and apical centre.

The bishomo-$(CH)_5$ cation (XL)[45,89] and a series of derivatives of the cations (XLI)[90–92] and (XLII)[93] have been synthesised from suitable precursors and have been studied in detail. Calculations on compounds (XL)[45] by the MINDO/2 method and on compounds (XLI)[50] and (XLIII)[94] by the MINDO/3 method demonstrated their high kinetic stability in relation to various rearrangements. It has been shown by the same computational procedure that structures (XL)–(XLIII), containing at their vertices other four-electron groups instead of $CH^+$, as well as structure (XLIV) correspond to the minima on their PES.[95]



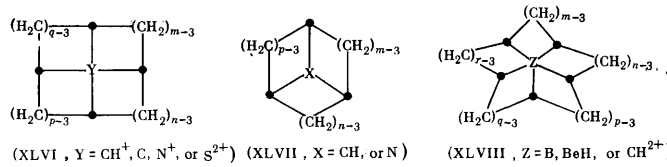
(XL) (XLI) (XLII) (XLIII) (XLIV), X = $CH^+$, C, or $N^+$

The polyhomopyramidal structures are unusual. Compound (XLV), which has been called[96] fenestrane (from the latin fenestra = window), containing the tetrahomocyclobutadiene ring on the periphery, has attracted special attention in connection with the possibility of a sterically constrained planar configuration, or a configuration flattened to the maximum extent, of its central tetracoordinate carbon atom[10,97,98]. MINDO/3 calculations[99] have shown that two conformations of fenestrane, with flattened tetrahedral (XLVa) and pyramidal (XLVb) configurations of the central carbon, are possible. The basis set of orbitals in the pyramidal conformation (XLVc) is topologically equivalent to that of pyramidane.



(XLV) (XLVa), $\Delta H_f$ = 108.5 kcal mol$^{-1}$; $S_4$ (XLVb), $\Delta H_f$ = 137.8 kcal mol$^{-1}$; $C_{4v}$ (XLVc)

According to Greenberg and Liebman[10,100], compounds (XLV) can be regarded as members of the general series of [*m.n.p.q*] fenestranes (XLVI), i.e. [4.4.4.4]fenestranes. It has been suggested[99] that the definition of fenestranes be extended to *n*-gonal "windows" in such a way that compounds of types (XLVII) and (XLVIII) can be defined as [*m.n.p*]fenestranes and [*m.n.p.q.r*]fenestranes:

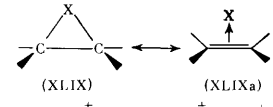


(XLVI, Y = $CH^+$, C, $N^+$, or $S^{2+}$) (XLVII, X = CH, or N) (XLVIII, Z = B, BeH, or $CH^{2+}$)

The validity of the 8*e* rule for the (XLVI)–(XLVIII) system has been confirmed by direct MINDO/3 calculations with optimisation of the geometry[99,101]. It is noteworthy that the series of fenestranes defined in the above manner includes as the initial members tetrahedrane as [3.3.3]fenestrane, pyramidane as [3.3.3.3]fenestrane, and the dication (XII) as [3.3.3.3.3]fenestrane, which were discussed above.

## 5. Three-membered Rings–Apex above the π-Bond

When the size of the polyene chain in compound (XXXVII) or of the basal ring in compound (XXII) is reduced to the limiting extent, it is possible to arrive at a two-dimensional version of the interaction of the apex and the π-bond, i.e. the three-membered ring (XLIX). In view of the large deviations from the normal valence angles, structures of this type are highly strained and the usual ideas concerning the nature of the bonding reflect inadequately the characteristics of their electronic structure:



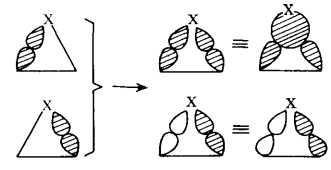
(XLIX) (XLIXa)

X = $CH_2$, $CH_3^+$, $BH_3$, NH, $NH_2^+$, O, $OH^+$, S, $SH^+$, $F^+$, Cl, or $Ag^+$.

In this connection Walsh[102] stated as early as 1947 that the structures of cyclopropane (X = $CH_2$), oxiran (X = O), and other compounds of type (XLIX) correspond to the π-complexes (XLIXa). The MO of these compounds were first described by Dewar[103], who recently examined in detail the genesis and evolution of the ideas in this field[104].

The correlation diagrams in Fig.8 illustrate the mechanism of the binding of the fragments of the molecules of compounds (XLIX) in relation to oxiran and thi-iran (X = O or S). The stabilisation is due to the effect of the $\pi \rightarrow p_z$ and $p_x \rightarrow \pi^*$ interactions, referred to respectively as direct and reverse donation. The ratio of the contributions of these interactions depends on the relative positions of the levels of these orbitals, i.e. on the electronegativity of the atom X. When the electronegativity of X is high, as in the case where X = O, the difference between the energies of the *p*- and π*-orbitals is large and the orbital interaction is weak [see Eqns.(1) and (2)]. In Fig.8 this is reflected by the slight changes in the form of the fragment orbitals in the oxiran MO $1b_2$ and $2b_2$, in conformity with Eqns.(6) and (7). In three-membered rings of this type the reverse donation effect is small and these structures qualify, in terms of the adopted terminology, as π-complexes. In the case of thi-iran the lower electronegativity of the sulphur atom is responsible for the comparable magnitudes of the direct and reverse donation effects. It has been suggested that such compounds be regarded as[104] normal three-membered rings.

Such subdivision is naturally extremely arbitrary, which is clear from a simple argument[105]. Symmetrised combinations (Lb) of the orbitals of two X–C σ-bonds of structure (XLIX) (normal three-membered ring) constitute none other than two bonding MO $2a_1$ and $1b_2$ (Lc), corresponding to the forward and reverse donation in the π-complex model (Fig.8):



(La) (Lb) (Lc)

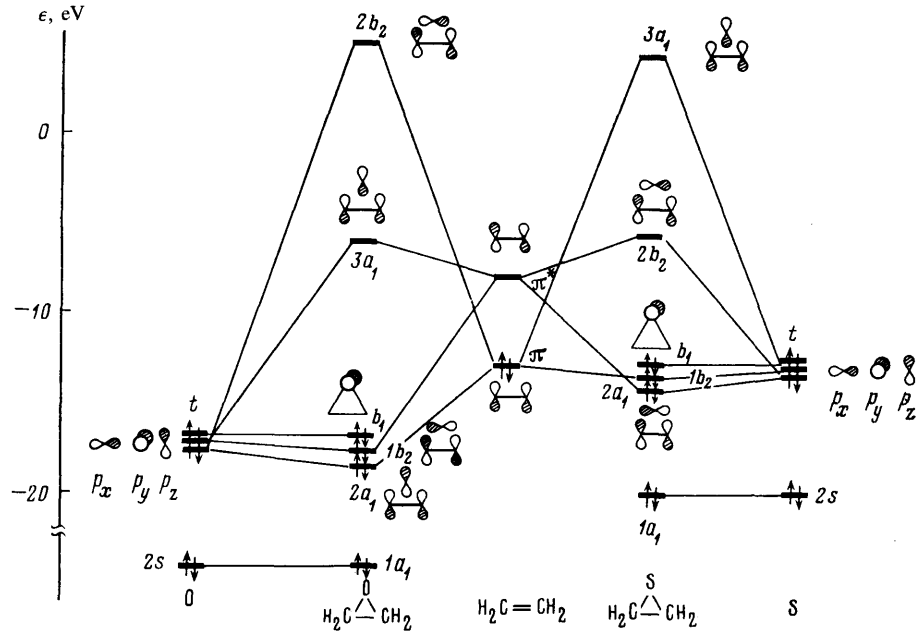


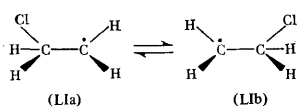

Figure 8. Correlation diagram for the MO of compounds (XLIX, X = O or S). In view of the high electronegativity of oxygen the $p \rightarrow \pi^*$ back-donation in epoxyethane is insignificant.

The significance of the above subdivision consists in the fact that it emphasises the ratio of the contributions of the forward and reverse donation, i.e. the stabilisations of the MO $2a_1$ and $1b_2$, and makes it possible to relate this ratio to the geometrical features and the reactivities of compounds (XLIX). The following series of groups X, in which the $\pi$-complex character of compounds (XLIX) diminishes, has been proposed[104]:

$$H^+ > SiH_3^+ > P^+ > CH_3^+ > Cl^+ > OH^+ \sim SH^+ \sim$$
$$\sim O \sim NH_2^+ \sim NH \sim PH_2^+ \sim S > CH_2 \sim PH > SiH_2 .$$

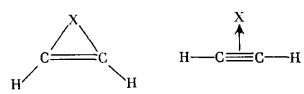
It follows from the correlation diagram in Fig.8 that the 8*e* rule should hold for the "pyramidal" structures (XLIX). Consequently, local minima on the PES should correspond to structures satisfying this rule. Indeed the stable cyclic cations (XLIX) with X = $RS^+$,[106,107] $Cl^+$,[108,109] and $RO^+$[110] have been discovered experimentally. A whole series of studies have been made[104,111–115] on calculations of their electronic and steric structures. The cation (XLIX, X = $F^+$), in which the $p \rightarrow \pi^*$ interaction is very weak, has aroused particular controversy. Nevertheless non-empirical calculations[111] and MINDO calculations with a detailed specification of the location of the stationary points on the PES[114] demonstrated the presence of a minimum for the cyclic form, located 10.3 kcal $mol^{-1}$ (STO-3G) or 18.7 kcal $mol^{-1}$ (MINDO) above the minimum for the 2-fluoroethyl cation $FCH_2CH_2^+$.

The introduction of additional electrons into the highly antibonding MO $2b_2$ (Fig.8) destabilises sharply the cyclic structure. Thus the radical (LI) is incapable of existing in the cyclic form (XLIX, X = Cl)[116] and the corresponding anion totally decomposes into ethylene and the chloride ion[117]:



(LIa) (LIb)

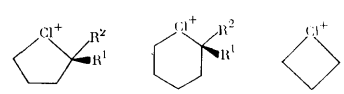
On the basis of the orbital interactions of the fragments of compound (XLIXa), it is possible to understand also the secondary characteristics of the structure: the rehybridisation of the basal atoms and the displacement of the O–H, B–H, and N–H bonds from the plane of the ring. The $\sigma$-orbitals of the above bond are then included in the interaction with the non-bonding MO $b_1$ of the ring (Fig.8). This orbital forms an overall closed $\pi$-system with the $\pi_4$-MO of the acetylenic fragment in the three-membered rings (LII):



(LII) (LIIa)

For X = O or S, this system is antiaromatic, which constitutes a powerful destabilising factor. Nevertheless, the extremely unstable compounds oxirene (X = O)[118,119] and thi-irene (X = S)[120] have been discovered experimentally.

The separation of the $\pi$-centres of the basal bond, i.e. transition to groups of the type $H_2C-(CH_2)_n-CH_2$, does not alter the form of the boundary orbitals. Olah[121,122] demonstrated the existence in solution of the stable cyclic halogenonium ions (LIII, *a* and *b*):



(LIIIa) (LIIIb) (LIIIc)

Theoretical and experimental study of the ion (LIIIa) demonstrated the high stability of the cyclic form relative to the classical open-chain isomer[123]. An analogous result has been obtained in calculations[124] for chloronium ions (LIII, *b* and *c*).

## IV. SANDWICH STRUCTURES

Compounds of the sandwich type (LIV), the first representative of which was ferrocene (LV, M = Fe), discovered in 1951, constitute the most important type of organometallic compounds of transition elements[125]. However, analogous compounds of the non-transition elements in Periods II and III are unknown.

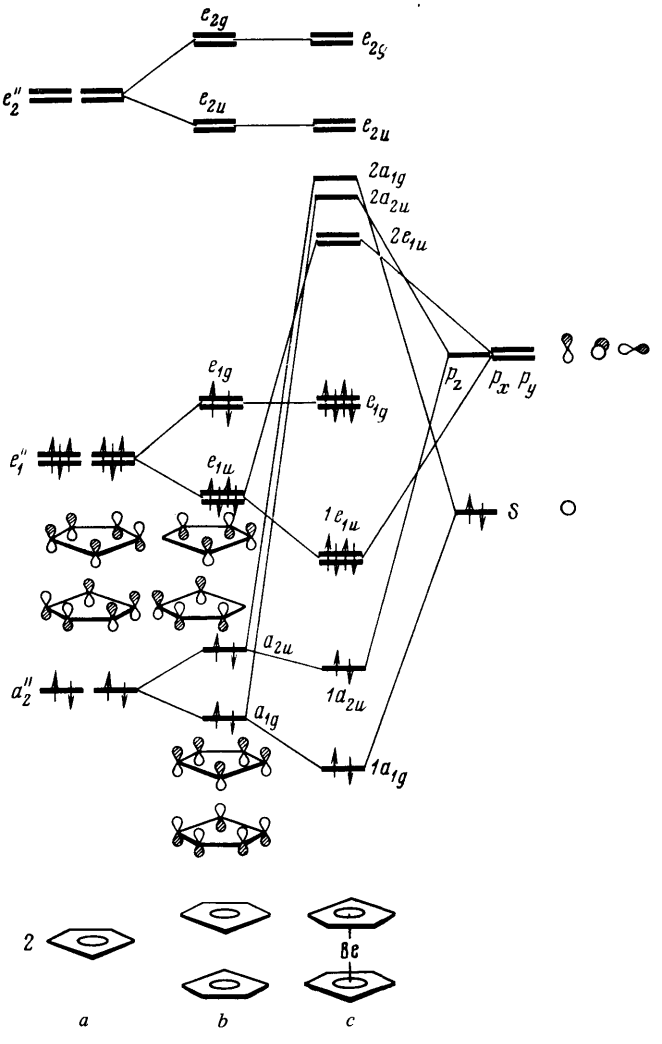
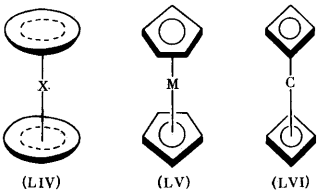



**Figure 9.** Correlation diagram for the MO of the beryllocene molecule in the sandwich form ($D_{5d}$ symmetry) according to Jemmis et al.[80]: *a*) MO of two non-interacting cyclopentadienyl fragments; *b*) the splitting of the MO of the cyclopentadienyl rings which have approached one another to the equilibrium distance; *c*) MO of the structure (XXXIIa). Only the bonding combinations of the orbitals of the two cyclopentadienyl rings which have approached one another are shown.

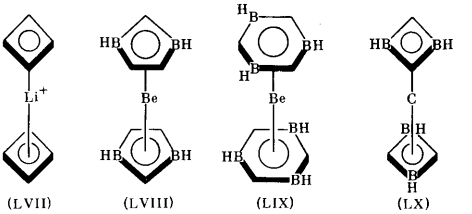
As already mentioned, the sandwich structure (XXXIIa) ≡ (LV) has not been confirmed for beryllocene (M = Be) in the light of the latest investigations:




(LIV) (LV) (LVI)

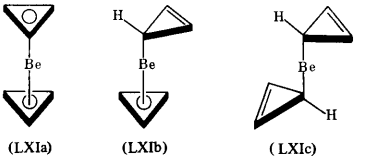
The causes of this are the rigid electronic limitations for structures (LIV): the sandwich structures of compounds of non-transition elements must contain in the π-orbitals of the cyclic fragments and in the valence orbitals of the central atom not more than eight electrons[70]. This conclusion can be clarified by the reconstruction analysis of the MO of the sandwich compound (LV) (Fig.9).

Only four bonding MO orbitals can be formed by the fragment orbitals of compound (LIV) in both $D_{nd}$ and $D_{nn}$ geometry. Since there are 12 "inner" electrons in the biscyclopentadienylberyllium sandwich, this structure is unstable. For another 12-electron structure, namely that of the hypothetical hydrocarbon bis($\eta^4$-cyclobutadienyl)carbon (LVI), the strain energy calculated by the MINDO/3 method is 31 kcal mol$^{-1}$ for each C–C bond[126], which is much higher than the values for tetrahedrane and pyramidane. On the other hand, structures (LVII)–(LIX)[70] and (LX)[126], which satisfy the requirement of the 8*e* rule for sandwich structures, can be stable. Thus the calculated heat of formation of compound (LX) is −7 kcal mol$^{-1}$ against 476 kcal mol$^{-1}$ for compound (LVI).




(LVII) (LVIII) (LIX) (LX)

When the approaches to sandwich structures (LIV) are considered, one must bear in mind that, even when the requirements of the 8*e* rule are met, an alternative to the pyramidal form exists for the majority of them, as in the case of biscyclopropylideneberyllium (LXI). Calculations[70] have shown that structure (LXIb) is preferable to structure (LXIa), but the bis($\eta'$-cyclopropylidene) form (LXIc) is energetically most favourable. The cause of this tendency is determined by the fact that, although the *e*″-MO of [3]annulenes are in fact stabilised by the interactions with the central atom in the π-complex, nevertheless a strong antibonding character is retained within the ring (Fig.5), which is eliminated in structure (LXIc). The important role of this factor in the analysis of the stability of sandwich structures in relation to various fragmentations was pointed out for the first time by Lopatko et al.[127]




(LXIa) (LXIb) (LXIc)

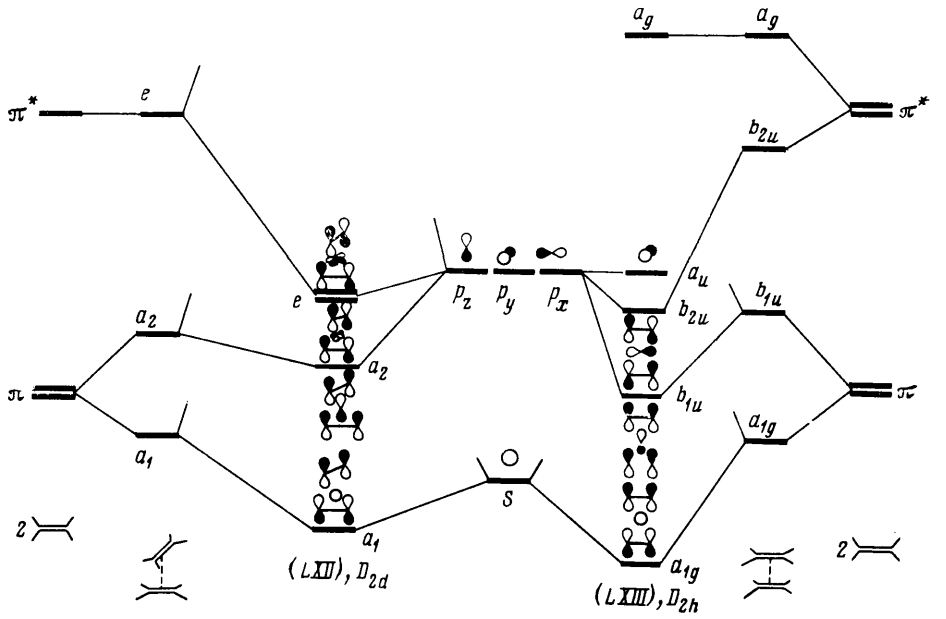
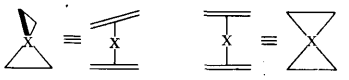



Figure 10. Correlation diagram for the MO of the orthogonal and planar spirorings (LXII) and (LXIII). The bonding MO are shown.

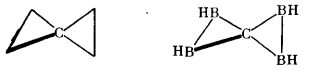
The spirocyclic compounds (LXII) can be regarded as a special case of sandwich structures. The structural alternatives—$D_{nd}$ or $D_{nh}$ symmetry[125,128]—usual for sandwich compounds (LIV) reduce in the given instance to a choice between orthogonal and coplanar dispositions of the multiple bonds of the fragments:



(LXII) (LXIIa) (LXIIIa) (LXIII)

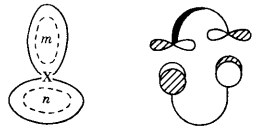
It is clear from the correlation diagram in Fig.10 that the orthogonal structure (LXII) is preferable, since the $p_y$-orbital of the central atom in compound (LXIII) remains isolated. The structure of the MO in compound (LXII) is analogous to that of compound (LIV) (Figs.9 and 10). The bonding MO of structure (LXII) accommodate 8 electrons, i.e. spirans with a four-electron central atom (C, $N^+$) are stable, whereas the stabilisation of the planar structure (LXIII) requires a two-electron centre (Be, $B^+$).

Another version of the stabilisation of a planar spiran involves the replacement of the carbon atoms and the nodes of the ethylene fragments by boron atoms. This approach to the problem of the stabilisation of a planar tetracoordinate carbon atom was put forward by Hoffmann[129] and developed by Schleyer, Pople, and coworkers[98,130]. As an example, we present the differences between the energies of the planar and orthogonal conformations of spiropentane (LXIV) and tetraboraspiropentane (LXV) obtained in non-empirical calculations (STO-3G and 4-31G basis sets):




(LXIV), $\Delta E$ = 167 kcal mol$^{-1}$ (LXV), $\Delta E$ = 6 kcal mol$^{-1}$

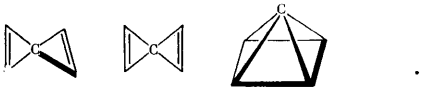
The spirans (LXII) can be formally regarded as the first members of the series of spirarenes (LXVI) with even $m$ and $n$[131,132]. The main type of orbital interaction in such systems involves the overlap of antisymmetric orbitals (LXVII).




(LXVI) (LXVII)

The stabilisation of [$m,n$]spirarenes with odd $m$ and $n$ is achieved if the following electron count rule is obeyed: $m$ and $n$ must be equal to $4q + 3$, where $q = 0,1,2,...$ [39,132]. The theory of spiro-conjugation and the experimental consequences of this effect have been examined in reviews[132,133].

Orbital interactions of type (LXVII) occur in addition to $p-\pi$ interactions in spirans of type (LXII) where the double bonds have been replaced by triple bonds. The spiropentadiene (LXVIII), for which the isomerisation PES has been investigated by the MINDO/3 and extended Hückel methods, constitutes an interesting case[17]. It has been found that the planar $D_{2h}$ form (LXVIIIa) corresponds to the transition state (57 kcal mol$^{-1}$) in topomerisation via a diagonal twist mechanism; PES contains a second minimum, whose depth is smaller than that of the minimum corresponding to structure (LXVIII) by only 14 kcal mol$^{-1}$ and which corresponds to the structure of pyramidane (LXVIIIb) = (XIII).



(LXVIII) (LXVIIIa) (LXVIIIb) ≡ (XIII)

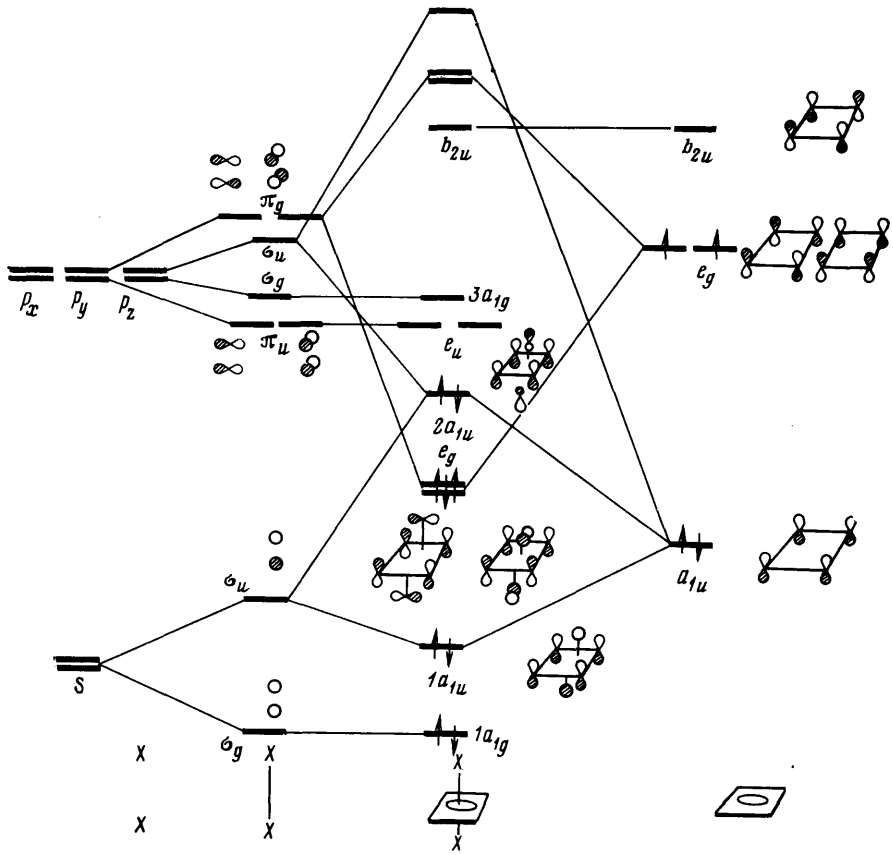
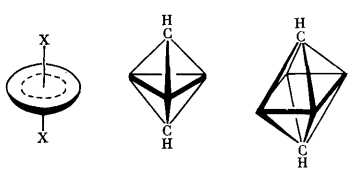



Figure 11. Correlation diagram for the MO of bipyramidal $D_{nh}$ structures (LXIX)[69]. The $D_{4h}$ structure has been adopted as an example.

## V. BIPYRAMIDAL STRUCTURES

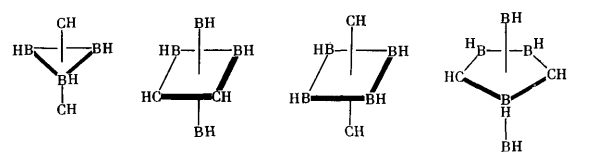
The addition of yet another vertex to the pyramid entails the formation of bipyramidal structures (LXIX) (inverted sandwiches).



(LXIX) (LXX) (LXXI)

In their study of the cation $(CH)_5^+$, Stohrer and Hoffmann[44] already discussed the trigonally bipyramidal $D_{3h}$ form (LXX) and found it to be less favourable than the pyramidal $C_{4v}$ structure (XIa). MINDO/3 calculations[46] showed that the energy difference reached is 100 kcal mol$^{-1}$ and, what is most important, structure (LXX) does not have the properties of a local minimum in the PES of $(CH)_5^+$. The $D_{3h}$ form of the anion $(CH)_5^-$ does not have these properties either[134]. Formally the $D_{4h}$ structure (LXXI) of $(CH)_6$, isomeric with benzene, contains six pentacoordinate carbon atoms. Non-empirical calculations[135,136] indicate an extreme instability.

The unusual valence states of the carbon atoms in compounds (LXX) and (LXXI) are not, however, the main reason for their instability, since the replacement of some of their CH vertices by BH gives rise to stable bipyramidal *closo*-carbaboranes $C_2B_{n-2}H_n$,[2,4,7] for example:



(LXII) (LXXIII) (LXXIV) (LXXV)

We shall consider the electronic requirements which must be met by the stable bipyramidal structure. Fig.11 shows that only those combinations of the orbitals of apical centres can interact with the π-MO of the central ring which are antisymmetric in relation to its plane. The lowest π-MO $a_{1u}$ produces on interaction with $\sigma_u(s)$- and $\sigma_u(p_z)$-orbitals the bonding ($1a_{1u}$), non-bonding ($2a_{1u}$), and antibonding molecular orbitals of the pyramidal structure, of which the first two are stabilised. Two $\pi_g$-orbitals of the apical centres give rise to a further two stabilised MO on interaction with the $e_g$-MO of the ring. Instead of the $\sigma_g(s)$-combination, it is possible to isolate five stabilised MO, which ensure bonding between the central ring and the pair of apical centres. They can be populated by not more than 10 electrons (counting the π-electrons in the ring and the valence electrons of both apices), which constitutes the 10*e* rule for the stability of bipyramidal structures (LXIX)[69].

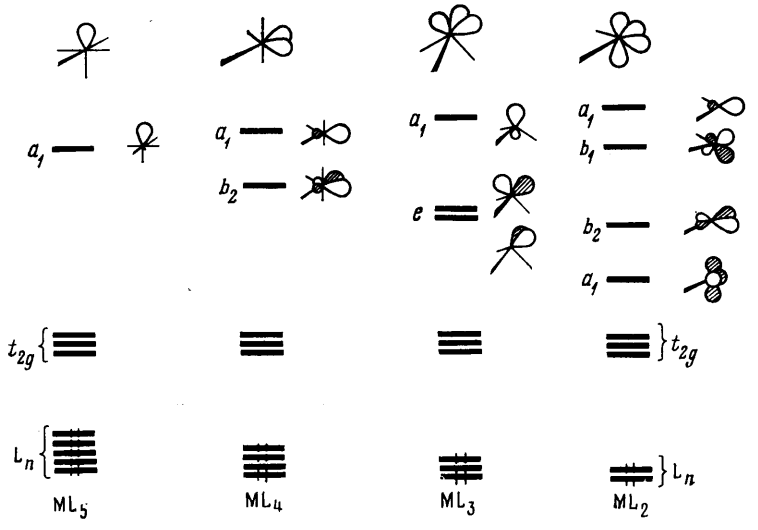



Figure 12. The group orbitals of the $ML_n$ fragments in which M is an atom of a transition element and L are two-electron ligands (CO, Cl, $PX_3$, etc.). The analytical functions of the MO have been published[144,145]. The $a_1$ and $b_2$ levels for $ML_n$ and $a_1$ and $e$ for $ML_3$ are inverted relative to the corresponding levels of the $CH_2$ and CH groups (Fig.2) owing to the contributions of the $d$-orbitals to the group MO of $ML_n$ and the changes in the nodal properties of their orbitals[67]. The assignment of the energy levels of the $ML_n$ groups to the $\pi$-MO of polyenes and annulenes has been published[145].

It is clear from this rule that the probability of observing bipyramidal organic molecules or ions is small. Each $CH^+$ group contributes its 4 electrons. Consequently the central ring must add not more than two $\pi$-electrons, i.e. the system must have a high positive charge: +3 for (LXX) and +4 for (LXXI). Such a high electron deficit is impossible simply for electrostatic reasons[137].

On the other hand all the carbaboranes (LXXII)–(LXXV) as well as the bipyramidal (*closo*)dianions of the boranes $B_nH_n^{2-}$ ($n$ = 5–7)[1,138] satisfy the 10$e$ rule. The bipyramidal $D_{4h}$ structure has been predicted by calculations[139] for the $Li_6$ cluster.

## VI. THE PRINCIPLE OF THE ISOLOBAL ANALOGY AND THE ELECTRON COUNT RULES FOR POLYHEDRAL ORGANOMETALLIC COMPOUNDS AND CLUSTERS OF TRANSITION METALS

Despite the fact that the atoms of transition elements use not only the valence $s$- and $p$-orbitals in the formation of bonds but also the close $d$-orbitals, the development of ideas concerning the nature of the chemical bond in organometallic compounds and clusters of transition metals has led recently to the discovery of profound analogies between the electronic structures of these compounds and the structurally isotypical compounds of non-transition elements.

### 1. Isolobal Analogy

An important step towards the discovery of the above analogy was the introduction of the concept of electronically equivalent groups, i.e. groups whose central atoms lack the same number of electrons for the complete filling of the valence electron shell[140,141]. In this sense the Cl atom and the radicals $CH_3$ and $Mn(CO)_5$, which give rise to the stable dimers $Cl_2$, $C_2H_6$, and $Mn_2(CO)_{10}$, are electronically equivalent.

A more exact correspondence between the valence possibilities of groups formed by non-transition and transition elements has been established by the definition by Hoffmann and coworkers[22,142–144] of isolobal (from the English word lobe) groups, i.e. groups for which the number, symmetry properties, forms, and energies of the boundary orbitals are approximately the same. By generating the groups $ML_n$ ($n$ = 2–5) from the $ML_6$ octahedron as a result of the successive abstraction of two-electron ligands L, Hoffmann and coworkers obtained the MO of the above groups (Fig.12).

The transition metal atom participates in the formation of bonds via nine orbitals: five $md$-orbitals, one $(m+1)s$-orbital, and three $(m+1)p$-orbitals. The three $d$-orbitals of the axially symmetrical fragment $ML_n$ do not mix with the ligand orbitals and give rise to a low-lying weakly split level, which corresponds closely to the $t_{2g}$ level in octahedral complexes. The interaction of $n$ orbitals of $n$ two-electron ligands with the remaining orbitals of the central atom gives rise to $n$ bonding and $n$ antibonding (not shown in Fig.12) MO of the group $ML_n$, localised at the M–L bonds. Thus $6-n$ orbitals of the group $ML_n$ remain in the valence band and are filled with $x-2(6-n)$ electrons, where $x$ is the number of valence electrons of the metal.

The group $ML_n$ utilises the above $6-n$ valence orbitals for bonding to other ligands or similar groups. Although these group orbitals involve considerable contributions from the $d$-orbitals in the metal atoms[22,142–145], their form and symmetry properties are analogous to those of the orbitals of the CH, $CH_2$, and $CH_3$ groups examined above (Fig.2). We shall compare the CH and $Co(CO)_3$ groups; the similarity between their boundary $a_1$- and $e$-orbitals is readily seen, the cobalt atom in $Co(CO)_3$, like the carbon atom in CH, having three electrons ($x$ = 9 for Co) to fill them. Such

electrons, consumed in the formation of bonds between groups when the latter are combined into skeletal and polyhedral structures, are referred to as skeletal electrons[2-5]. Atomic groups typical for organic structures are compared in the Table with the isolobal and electronically equivalent groups of transition metals.

Isolobal electronically equivalent groups*.

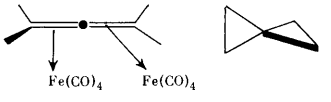
| Group | $v$ | $N_{s.e.}$ | Group $ML_n$ |
|---|---|---|---|
| CH, N, O+ | 5 | 3 | $Co(CO)_3$, Ni-(Cp-$\eta^5$), $Ir(CO)_3$ |
| CH+, C, BH | 4 | 2 | $Fe(CO)_3$, $Os(CO)_3$, Co-(Cp-$\eta^5$) |
| $CH^{2+}$, C+, BeH | 3 | 1 | $Mn(CO)_3$, Fe-(Cp-$\eta^5$) |
| $CH^{3+}$ | 2 | 0 | $Cr(CO)_3$, $Fe(CO)_2$, Cr-($C_6H_6$-$\eta^6$) |
| $CH_2$ | 6 | 4 | $Fe(CO)_4$ |
| $CH_3$ | 7 | 5 | $Mn(CO)_5$ |

* Here $\nu$ is the number of valence electrons and $N_{s.e.}$ is the number of skeletal electrons.

Chain, cyclic, skeletal, and cluster structures, obtained by combining isolobal groups, also possess analogous systems of valence orbitals and their structural possibilities are therefore similar. Thus the orbitals of the cyclic clusters $Fe_3(CO)_{12}$ and $Fe_3(CO)_9$ are analogous to the MO of cyclopropane and cyclopropenyl[146] (Fig.4), while the orbitals of the tetrahedral cluster (I) and their filling with valence electrons are analogous to those of tetrahedrane. Using the idea of the isolobal nature of the $\eta^5$-cyclopentadienyl and $CH^+$ groups, it is easy to show by calculation that the bipyramidal structure (V) meets the requirements of the 10*e* rule [two $\pi$-electrons from the five-membered ring and four electrons from each of the BH and Co-(Cp-$\eta^5$) groups].

We shall quote some further examples of pyramidal and bipyramidal organometallic structures together with the corresponding non-classical hydrocarbon structures made up of isolobal fragments. Detailed data concerning the structures of the above and other similar organometallic structures are contained in reviews[2-5,125,128,147-149].

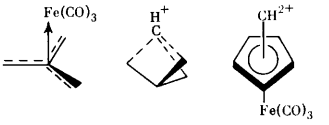
The importance of the concept of isolobal properties is that it constitutes a direct bridge linking the structural ideas of organic chemistry with the involved structural images of the chemistry of transition elements. It makes it possible to discover the analogy between the electronic structures of outwardly completely different classes of organic and organometallic compounds—for example it can be seen that the $\pi$-complex (LXXVI) is an organometallic spiropentane:




(LXXVI) (LXIV)

Isolobal analogy ensures a new methodological approach to the search for new non-classical organic structures which can be deduced by replacing the organometallic residues in the structures of $\pi$-complexes and clusters by isolobal organic groups (see Table). Thus the structure (XI) of the cation $(CH)_5^+$ might have been predicted on the basis of the structure of the $\eta^4$-cyclobutadiene complex of iron tricarbonyl established as early as 1960,[150] while the structure of the dication $(CH)_6^{2+}$ follows from the structure of ferrocene (LV, M = Fe), which became known as early as 1952.[125]

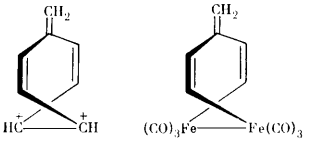
Bearing in mind the stability of the trimethylenemethane complex (XXVII) and the fact that the $CH^+$ and $Fe(CO)_3$ groups are isolobal, Chandrasekhar et al.[151] suggested the possibility of the existence of the 1-bicyclo[1,1,1]pentyl cation (LXXVIII) and confirmed this hypothesis by a direct MINDO/3 calculation:




(LXXVII) (LXXVIII) (LXXIX)

Although structure (LXXVIII) represents a local minimum on the PES, calculations predict an extremely low energy barrier (1.8 kcal $mol^{-1}$) in the rearrangement to the 1-methylene-3-cyclobutyl cation. This explains the finding that the intermediate formation of structure (LXXVIII) was not detected in experiments[152] on the distribution of an isotope label in the spiropentyl cation.

At the same time the suggestion that one should seek the bipyramidal dication (LXXIX), put forward by Hogeveen and Kwant[46], is not fruitful, since this structure does not satisfy the 10*e* rule. It must also be emphasised that, in connection with the method of constructing the valence orbitals of the organometallic residues, isolobal analogy should hold most completely for symmetrical compounds where the local symmetry axis of the group coincides with the symmetry axis of the molecule or ion as a whole. Otherwise the correspondence of the non-classical structure generated from a $\pi$-complex to a local minimum on the PES must be specially tested. Thus the hypothesis[153] that the dication (LXXX)—an analogue of the bisiron tricarbonyl complex (LXXXI)—can exist was not confirmed by detailed calculations[154], which failed to reveal the corresponding local minimum on the PES of $(CH)_8^{2+}$.




(LXXX) (LXXXI)

## 2. The Stability of Polyhedral Structures and the Skeletal Electron Count Rules

The stability of the non-classical polyhedral structures of organic molecules and ions examined above can be understood in the context of the general electron count rules developed for skeletal and cluster structures of boranes and heteroboranes and extended, taking into account the ideas of electronically equivalent groups, to the analogous organometallic compounds[2-5,155-157].

These rules are based on the count of skeletal electrons accommodated in the endocyclic orbitals of the skeletal bonds of skeletal and cluster compounds. The number of such electrons is $\nu + x - 2$, where $\nu$ is the number of valence electrons of the central atom of a non-transition element occupying one of the vertices and $x$ is the number of one-electron ligands (the unshared electron pair behaves as a phantom ligand). For groups formed by transition metals, the number of skeletal electrons is defined as $\nu + x - 12$. A relation involving electronic equivalence with groups of non-transition elements is then established (see Table). Naturally the difference of 10*e* is in essence the difference

between the requirements for the filling of 8- and 18-electron shells for atoms of non-transition and transition elements.

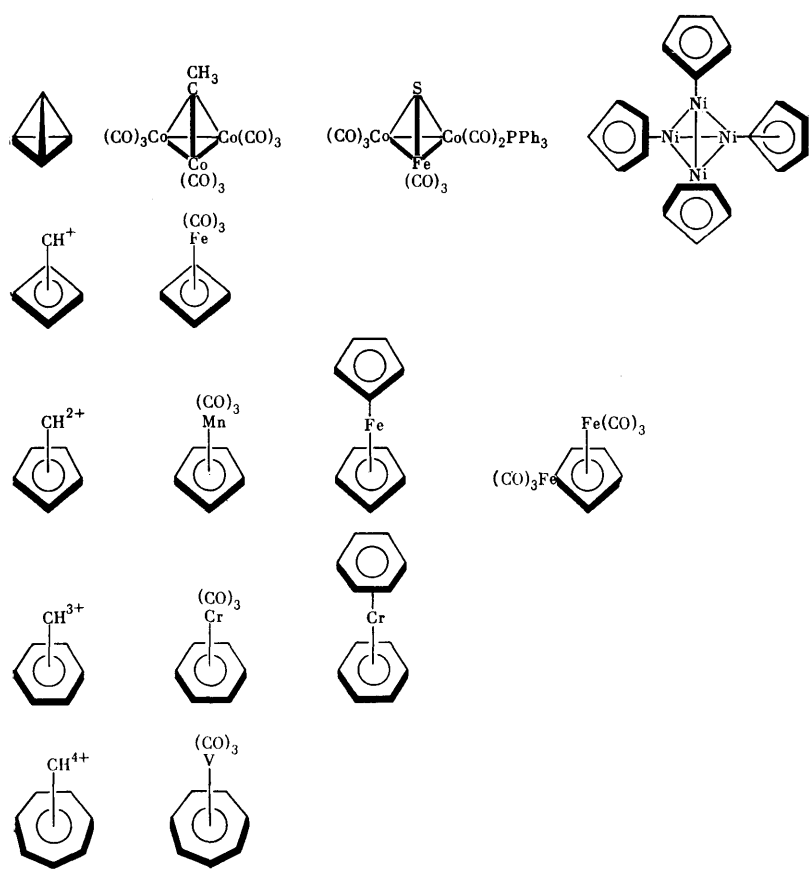
All the polyhedral structures formed by boranes, carbaboranes, heteroboranes, and organometallic compounds, differing by the presence of trigonal faces (deltahedra), can be generated[2-5,40] from the so-called *closo*(closed)-structures of a bipyramidal type for 5–7 vertices, from a trigonal dodecahedron for 8 vertices, etc., *nido*(nest)-structures are obtained from the *closo*-forms by truncating one vertex (for example, pyramids can be obtained from bipyramids). *arachno*(spider-like)-Structures are obtained similarly from *nido*-structures.

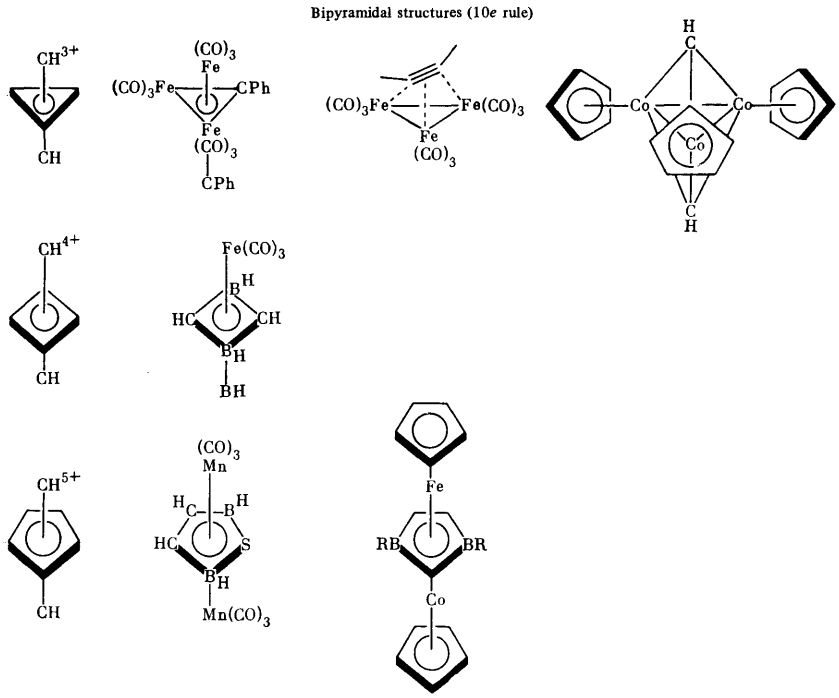
Qualitative analysis[1,2-5,155-158] and direct calculations on *closo*-structures lead to the conclusion that there are $n + 1$ bonding MO for the boranes $B_nH_n$, in which it is possible to accommodate $2n + 2$ skeletal electrons, i.e. the *closo*-structures of the dianions $B_nH_n^{2-}$ and of the isoelectronic carbaboranes $C_2B_{n-2}H_n$ are stable. The validity of this rule can be readily tested in relation to the bipyramidal compounds (LXXII)–(LXXV). At the same time the hydrocarbons (LXX) and (LXXI) contain respectively 3 and 4 excess electrons, which follows from both the $2n + 2$ and the 10*e* rules.

The $2n + 4$ rule holds for *nido*-structures. The tetraanions $B_nH_n^{4-}$, for example, (XXX), should be stable pyramidal boron hydrides. Finally, for the *arachno*-structure $B_nH_n$, the number of electrons which can be accommodated in the bonding MO is $2n + 6$, i.e. the hexa-anions $B_nH_n^{6-}$ are stable. For the *arachno*-structures of the hydrocarbons $(CH)_n$, generated by the truncation of the two vertices of bipyramids, i.e. for planar rings, this implies the stability of $(CH)_4^{2-}$, $(CH)_5^-$, $(CH)_6$, and $(CH)_7^+$, which is one of the consequences of the $4n + 2$ Hückel rule.

It is easy to show that the 8*e* and 10*e* rules obtained by reconstruction analysis are equivalent to the $2n + 4$ and $2n + 2$ rules for the skeletal electron count. Indeed in the pyramidal *nido*-structure of type (XXII), which has $n$ vertices, $2(n-1)$ electrons of the $2n + 4$ skeletal electrons form the endocyclic σ-bonds in the basal ring and 2 electrons are used in the exocyclic bond (in the electron pair) of the apical group. The number of electrons binding the above fragments is thus $(2n + 4) - 2(n-1) + 2 = 8$ (the 8*e* rule). For the bipyramidal (*closo*) structure, we obtain analogously $(2n + 2) - 2(n - 2) + 2 + 2 = 10$ (the 10*e* rule).

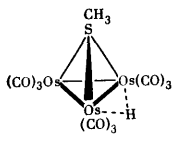
Pyramidal structures (8*e* rule)



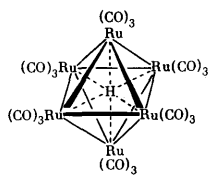



The rules for the counting of skeletal electrons can be readily extended to organometallic compounds, which can be done using the relations in the Table presented above. Other general formulations taking into account not only skeletal but also all valence electrons of skeletal and cluster structures, which are applicable to a wide range of metallic and organometallic structures with between 5 and 15 vertices[159,160] and also to skeletal and cluster electron-excess structures of the chalcogenides[161], have also been proposed.

Bridging groups, for example hydrogen atoms, can play the role of suppliers of skeletal and inner electrons. Thus the neutral *closo*-boranes $B_nH_{n+2}$ correspond to the *closo*-dianions $B_nH_n^{2-}$, while the *nido*-borane $B_nH_{n+4}$ [for example, $B_5H_9$ (XVI)] corresponds to the *nido*-tetra-anion $B_nH_n^{4-}$. In cluster (III) the carbon atom incorporated in the pyramidal skeleton contributes four additional electrons, with the aid of which the 8*e* requirement is met. We shall present further examples of the pyramidal [compound (LXXXII)][162] and bipyramidal [compound (LXXXIII)][163] clusters in which the bridging and endocyclic hydrogen atoms build up the inner electron shells to 8*e* and 10*e*:



(LXXXII)



(LXXXIII) $[H \cdot Ru_6(CO)_{18}]^-$

Using the technique of reconstruction analysis, it is possible to show that the bridging groups do not in fact alter the fundamental bonding pattern in polyhedral structures (Figs. 5 and 11). Analysis of the structures of the MO of a series of organometallic compounds with bridging hydrogen atoms has been described[164-166].

The importance of the electron count rules examined above is that they bring into direct correspondence the number of bonding MO and the type of polyhedral structure regardless of the nature of its constituent apical groups. These rules are topological in nature and clearly demonstrate the fact that inorganic and organic chemistry have common structural principles. This is confirmed also by the possibility of extending the relation

$$closo \underset{-2e}{\overset{+2e}{\rightleftharpoons}} nido \underset{-2e}{\overset{+2e}{\rightleftharpoons}} arachno \qquad (8)$$

which is familiar for boranes and carbaboranes, to polyhedral organic structures in the form

$$(n-2)\text{-gonal bipyramid } (10e) \underset{-2e}{\overset{+2e}{\rightleftharpoons}} (n-1)\text{-gonal pyramid}$$
$$(8e) \underset{-2e}{\overset{+2e}{\rightleftharpoons}} n\text{-gonal ring } (6e) \qquad (9)$$

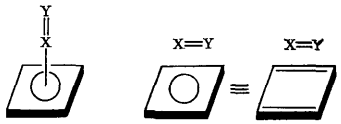
The reaction whereby the dication (XIIb) is obtained from Dewar hexamethylbenzene[46] as well as the reaction (XXIX)⇌(XXV, Y = $S^{2+}$) are examples where Eqn. (9) holds.

## VII. [n]PRISMANES AND OTHER POLYHEDRA

Apart from the combinations of structural units of polyhedra described above, there is also a possibility of edge–edge, edge–face, and face–face fusion.

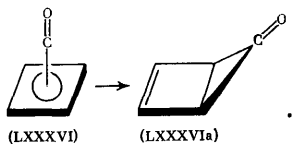
The interactions of π-bonds and conjugated chains, which correspond to the type of edge–edge interaction, have been analysed[38,39]. Two topologically different perpendicular [structure (LXXXIV)] and parallel [structure (LXXXV)] orientations of the face and edge, ensuring the interaction of the entire system of ring orbitals with the orbitals of the π-bond, are illustrated below in relation to a four-membered

ring:



(LXXXIV) (LXXXV) (LXXXVa)

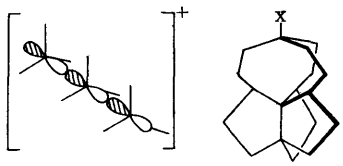
The valence orbitals of the groups X = Y (C≡O, N≡CH, N=O, S=O, O=O)[34,37] are similar in form to the CH group orbitals (Fig.2), the antibonding $\pi_x^*$- and $\pi_y^*$-orbitals of the group XY corresponding to the pair of $p_x$- and $p_y$-orbitals. Since the *e*-level of these orbitals lies high above the *e*-level of the π-orbitals of the ring, this main type of interaction stabilising the pyramidal structures (LXXXIV) is weakened. Therefore, even in the most favourable case with XY=CO,[167] the above orbital interactions are sufficiently strong for the overall stabilisation of the (LXXXIV) system. Thus non-empirical (STO-3G)[168] and MINDO[169] calculations have shown that a local minimum in the PES of $C_4H_4CO$ does not correspond to the $C_{4v}$ structure (LXXXVI)[44] and the latter relaxes to the structure of bicyclo[2,1,0]pentenone (LXXXVIa):



(LXXXVI) (LXXXVIa)

The hypothesis[65,171,172] of the intermediate structure (LXXXIV, XY=SO) in the topomerisation reaction of Dewar thiophen oxide, analogous to the rearrangement (XXIa) ⇌ (XXIb), has not been confirmed by calculations[170].

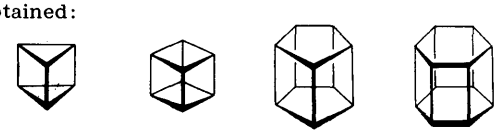
A more favourable orientation of the orbitals of the [*n*]-annulene ring and of the π-bond is attained in the configuration (LXXXV) predicted by calculations[168] for complexes of cyclobutadiene with C≡O, HC≡N, and $CO_2$. Discussion of the structures of these complexes has attracted considerable attention in connection with their intermediate formation in the photolysis and thermolysis of the precursors of cyclobutadiene derivatives[173–175]. The main type of orbital interactions in this configuration, namely $\pi_\sigma-\pi_\sigma$ interactions, has been considered recently with the aid of six different semi-empirical and non-empirical computational methods[176] in relation to the simple but structurally important model of the non-classical σ-allyl cation $(CH_3)_3^+$ (LXXXVII), in which the three methyl groups are bound together by the $p_\sigma-p_\sigma$ interactions of three *p*-orbitals:



(LXXXVII) (LXXXVIIa)

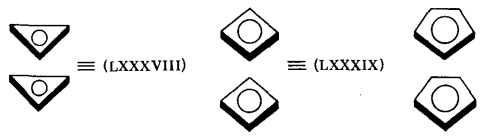
Since this type of interaction results in the formation of bonding, non-bonding, and antibonding MO, this configuration is stabilised in the two-electron case (cation). This suggests that fairly stable cations—analogues of the σ-allyl cation (LXXXVII)—can be generated from a suitable precursor, for example, propellane (LXXXVIIa).

The considerable role of the $\pi_\sigma-\pi_\sigma$ interactions between the orbitals of [*n*]annulene rings in the stabilisation of the polyhedral structure can be traced[177] in relation to [*n*]prismanes. The $(CH)_{2n}$ clusters with $D_{nh}$ symmetry belong to this series. The first member of the series, namely [3]prismane (LXXXVIII) (triprismane according to Schultz's nomenclature[180] for compounds of this type) and tetraprismane (LXXXIX), also known as cubane, have been synthesised and studied in detail theoretically[14,37,100,178,179]. The higher representatives of the series of [*n*]prismanes, namely pentaprismane (XC), hexaprismane (XCI), etc., have not so far been obtained:



(LXXXVIII) (LXXXIX) (XC) (XCI)

The structures and the MO of prismanes can be formed by the parallel superposition of two identical [*n*]annulene rings (face–face interactions):



≡ (LXXXVIII) ≡ (LXXXIX) ≡ (XC)

Two main types of interactions of the fragment orbitals can then be distinguished: π-overlap of a σ-MO of the Walsh type ($\sigma_\pi-\sigma_\pi$ interaction) and the σ-overlap of the π-MO ($\pi_\sigma-\pi_\sigma$ interaction). The above orbitals are illustrated in Fig.4 in relation to [3]annulene. The interaction between the completely filled σ-MO are of the repulsive, destabilising type. However, the magnitude of this effect is comparatively small, since it is approximately proportional to the square of the overlap integral [see Eqns.(4) and (5)]. The $p_\pi-p_\pi$ overlap integral does not exceed 0.15 for equilibrium distances, while the $p_\sigma-p_\sigma$ overlap integral reaches 0.35. Because of this, the interaction (splitting) of the π-MO is significantly stronger. The main cause of stabilisation by such interaction is that the in-phase overlap of the identical antibonding π-MO of [*n*]annulenes leads to such a pronounced splitting of their levels that the lowest level becomes the bonding MO of [*n*]prismane (Fig.13).

This result is obtained only under the conditions of a close parallel approach of the [*n*]annulene rings. For distances of the order of magnitude of the van der Waals contacts, the $p_\sigma-p_\sigma$ overlap integral is small and the splitting of the π-levels is insufficient to overcome the repulsive interactions (Fig.13). This has been confirmed by direct calculations of the interaction energy of two benzene molecules[168,181] and also by structural data for benzene dimers obtained by the method of molecular beams[182], which show that the perpendicular orientation of the planes of the rings in the dimer is preferable.

The unfavourable nature of the [*n*]prismane structures for clusters of other elements can be understood from the correlation MO diagram in Fig.13. The $D_{2d}$ structure of the *closo*-dianion $(BH)_8^{2-}$ is more favourable by almost 400 kcal $mol^{-1}$ than the cubic structure of the $O_h$ type (LXXXIX)[183], since $(BH)_8^{2-}$ has only two electrons to fill all the bonding MO of the $O_h$ structure (Fig.13). On the other hand, the polychalcogenides $S_8$, $S_8^{2+}$, $S_4N_4$, and $Se_{10}^{2+}$ [161] would have several antibonding MO populated by electrons in the [*n*]-prismane form. At the same time cluster (VI), which is isoelectronic with cubane (LXXXIX), has a structure similar to the latter.

The conditions for the stabilisation of the structure as a consequence of the formation of bonding MO, obtained by the in-phase combination of the antibonding MO of the fragments, which has been considered in relation to [*n*]prismanes, is fairly general for skeletal organic compounds. It is readily

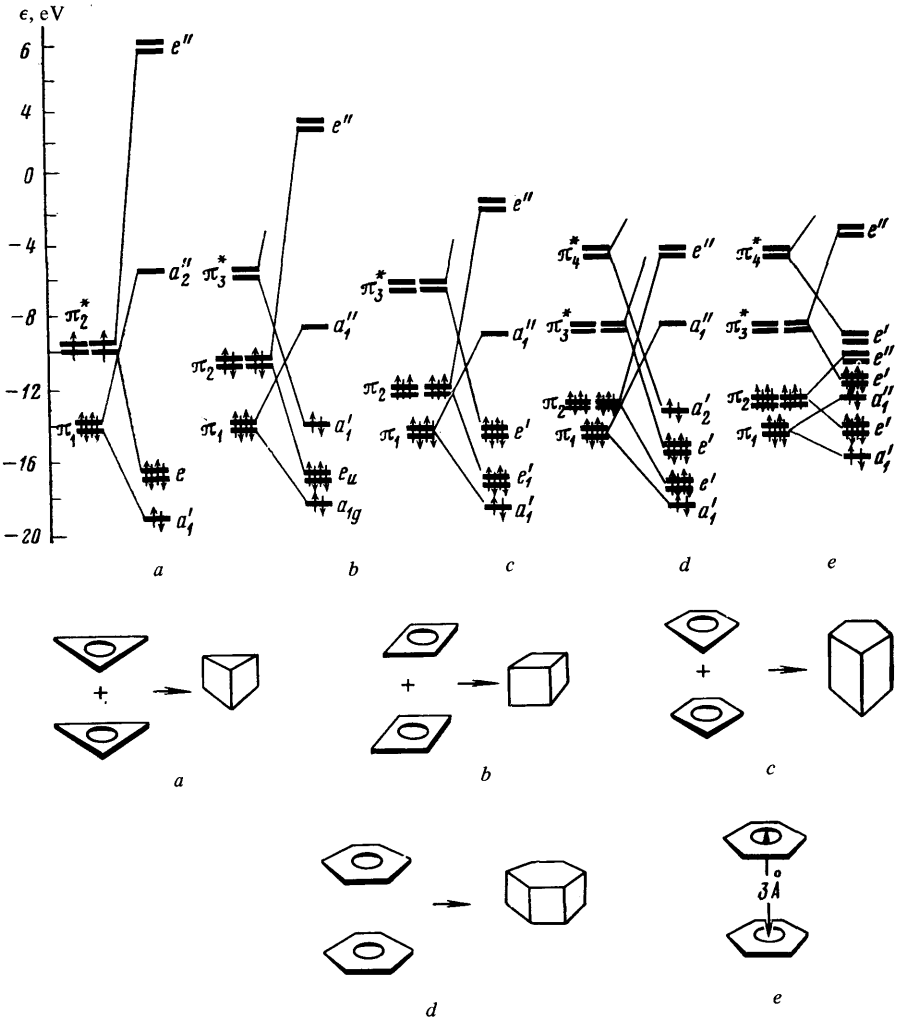
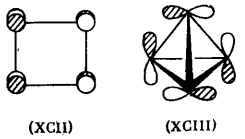


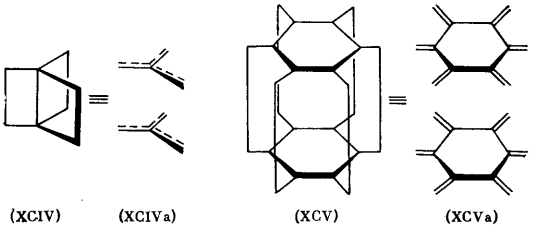

Figure 13. Schematic illustration of the formation of the MO of [*n*]prismanes as a result of the $\pi_\sigma-\pi_\sigma$ overlap of the π-MO of the [*n*]annulene fragments[177]. The energy levels of the annulenes and the overlap integrals of the π-MO for the equilibrium distances in [*n*]prismane have been obtained by calculations using the extended Hückel method (the $p_\sigma-p_\sigma$ overlap integral was assumed to be 0.3). The splitting of the levels following the approach of two benzene molecules to a distance exceeding the equilibrium distance in [6]prismane and equal to the sum of the van der Waals radii of the carbon atoms (the $p_\sigma-p_\sigma$ overlap integral is 0.1), for which the dimer is unstable, is shown on the right-hand side of the Figure. The correlation diagrams (*a*)–(*e*) correspond to structures (*a*)–(*e*).

seen that components of the highest occupied MO of cyclobutadiene (XCII) and tetrahedrane (XCIII) are made up of antibonding π*-MO of acetylenic fragments (cf. Fig.3):



(XCII) (XCIII)

The structures of the highest occupied MO of [2.2.2]propellane (XCIV)[44] and of the molecule of superphane (XCV) synthesised recently[184] also correspond to the case considered.



(XCIV) (XCIVa) (XCV) (XCVa)

On the other hand, the analogous parallel superposition of [5]- and [3]-annulenes does not lead, following their mutual approach in different relative orientations, to the appearance

of local minima of the biradical type on the PES of $(CH)_8$.[177] Analysis of the orbital interactions of the three-membered rings of $Fe_3(CO)_9$ and [5]annulene also leads to the conclusion that there is no stabilising effect. The structural consequences of the orbital interactions of the polyene chains and rings with the edges, faces, and individual vertices occupied by isolobal $CH^{n+}$ groups and organometallic fragments have been examined in a number of studies[22,23,146].

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The approach to the study of the nature of the stabilisation of molecules and ions with a strained or non-classical structure which has been considered here is applicable to the entire branched series of skeletal and polyhedral structures. The possibility of formulating electron count rules for inner, skeletal, or all valence electrons, which are valid for specific structural types regardless of whether the structure belongs to the series of organic, organometallic, or inorganic compounds, emphasises both the fact that the principles of electronic structure are common to these compounds and the decisive role of topological factors in their orbital organisation.

Like any broad generalisation, these rules have many exceptions. In the present review we did not concentrate attention on these, since the causes of the deviations from the predictions based on the electron count rules can be understood and foreseen on the basis of the same research techniques which have led to the formulation of the rules and also on the basis of more rigorous schemes for the fragmentation of structures.

The deviations from the rules formulated above are most frequently seen in the effect of substituents. Such are the sharp deviations from the classical structures of hydrocarbons where hydrogen atoms are replaced by lithium atoms or BH groups[98,185-187] and conversely the stabilisation of classical structures following the replacement of hydrogen atoms in carbaboranes by halogen atoms[188]. Direct allowance for the orbitals of the substituents within the framework of the scheme of reconstruction analysis explains the above effects.

The orbital approach to the analysis of complex structures has been recently extended as far as the field of the crystal chemistry of organic and inorganic compounds[189]. It has been shown that $\pi_\sigma - \pi_\sigma$ interactions of the orbitals of the $A_6$ and $A_3X_3$ hexagonal cells actually determine the structures of the crystal lattices of graphite, sphalerite, wurtzite, etc.

This approach has become a powerful instrument for the molecular design of new unusual organic structures and their organometallic analogues.

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