

Non-classical structures of organic compounds: unusual stereochemistry and hypercoordination

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Abstract. Non-classical structures of organic compounds are defined as molecules containing non-tetrahedral tetracoordinate and/or hypercoordinate carbon atoms. The evolution of the views on this subject is considered and the accumulated theoretical and experimental data on the structures and dynamic transformations of non-classical organic compounds are systematised. It is shown that computational analysis using the methods and the software potential of modern quantum chemistry has now acquired high predictive capacity and is the most important source of data on the structures of non-classical compounds. The bibliography includes 227 references.

I. Introduction

Molecular structure is a key concept of theoretical organic chemistry. The description of molecular structures of organic compounds is underlain by the fundamental concept of two-centre two-electron covalent bonds, the tetravalence of carbon, and the tetrahedral geometry of the four single bonds it forms. Using only these concepts, which can be easily extended to other Main Group elements of the Periodic Table, it is possible to describe and predict all the key types of organic structures and kinds of isomerism. By means of a molecular meccano, these views can assume a material form as simple stereochemical models; these models appear to be an invention of Jacobus Henricus van't Hoff.[†] The fundamental nature of the principles that underlie these models can be compared only with the simplicity of their practical implementation, which can be understood by looking at the cardboard models

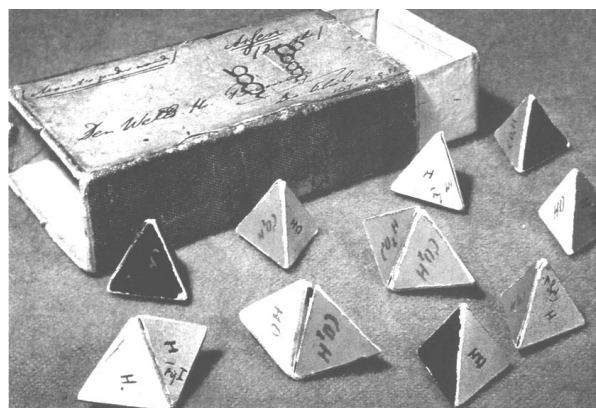


Figure 1. Three-dimensional stereochemical models hand-made personally by van't Hoff (courtesy Leyden Museum of Natural History).

made personally by van't Hoff (Fig. 1). By the same procedure, one can easily assemble molecular models of millions of organic and organoelement compounds. Actually, the prediction of the double-helix DNA structure (which is, perhaps, the most important discovery of the last century) required only one further structural concept — the notion of the hydrogen bond.

The development and extensive use of new methods for the investigation of molecular structure and dynamics as well as the development of organometallic chemistry, which linked organic chemistry to images and theoretical views of coordination chemistry, have extended the scope of the classical structural theory. Thus, it has become impossible to describe the whole diversity of the new types of structures and their dynamic transformations using only the ideas and the language of the classical structural theory. This triggered the development of two interrelated concepts, namely, the concepts of stereochemically non-rigid (fluxional) compounds and multicentre bonds. The development of the

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Received 15 May 2002

Uspekhi Khimii 71 (11) 989–1014 (2002); translated by Z P Bobkova

[†] The Russian version of van't Hoff's article 'Sur les formules de structure dans l'espace'¹ and his original drawings illustrating the construction of spatial structures of molecules can be found in the monograph by Bykov.²

multicentre bond concept, in turn, has entailed the notions of hypervalence and hypercoordination. Thus, the description of molecular structures in terms of the notion of multicentre bonds can be likened to a complication in the standard molecular meccano by adding a set of new units, *i.e.*, multicentre bonds ($mc-ne$, where $n = 1, 2$ and $m > n$), for example, three-centre two-electron bonds ($3c-2e$). Examples of consistent application of this approach to the analysis of chemical structures of compounds containing hypercoordinate carbon atoms and derivatives of polyhedral boranes can be found in monograph.³

The orbital approach to the analysis of molecular structures and their transformations, developed in the second half of the XX century and based on semiquantitative orbital interaction theory, is more general and has a much more extensive predictive capacity.⁴⁻⁶ This theory focuses on the closure of the electron shells of valence molecular orbitals and on the presence of a rather large energy gap between the frontier MO as the key factors that influence the thermodynamic stability of a molecular structure. Kinetic stability of a molecular structure with respect to rearrangements or fragmentation may be due to the possibility that these processes are thermally forbidden by the orbital symmetry rules. An important advantage of the orbital approach as a qualitative theory of modern theoretical chemistry is that its views and notions can be directly transferred to and used in organometallic chemistry, in the coordination chemistry of transition metals and even in solid-state chemistry.^{7,8} Detailed analysis of the data accumulated by the early 1990s on the structures and properties of non-classical organic compounds carried out using the orbital interaction theory has been reported in our monographs^{9,10} and reviews.^{11,12}

The reliability of any qualitative views needs to be validated by strict theoretical calculations. By the early 1990s, the capacity for performing such calculations for compounds with more than 6–7 non-hydrogen atoms was quite limited; therefore, calculations for molecular systems were mainly carried out in the valence approximation by semiempirical quantum chemistry methods. The semiempirical methods have played and still play an important role in the theoretical simulation of structural chemistry problems. However, these methods are hardly applicable to non-classical structures, as they are parametric techniques in which parameters are selected by adjusting the calculated data to well-known experimental results obtained for classical molecular structures (references).

The situation has markedly improved during the last decade. Enormous progress in the manufacture of a new generation of high-performance computers and in the development of concomitant software made possible (and almost routine now) calculations of rather complicated molecules by means of high-level *ab initio* quantum chemistry techniques.¹³ The accuracy of calculations of this type is quite comparable with that attained in the experiment. This opens up new routes both for additional analysis of the previously developed qualitative structural theory of non-classical organic compounds made at a higher quantitative level and for the computational design of new molecular systems and new structural patterns with unusual geometry and unusual coordination types.

The purpose of this review is to consider the main results of the above-mentioned evolution of the views on non-classical organic structures. Whereas in the early stages of development, considerations of non-classical structures were focused on discussion of the structures of carbonium cations with a hypercoordinate carbon atom,^{3,14} in recent years, they have been markedly extended due to the appearance of new data on unusual stereochemistry of organic compounds. Currently, non-classical organic structures constitute a rather diverse field of theoretical and structural chemistry, which cannot be covered within the framework of a single review. Therefore, we restricted ourselves mainly to the analysis of recent data concerning non-classical types of carbon coordination.

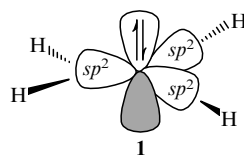
Defining of the problem is as important for each investigation as the results obtained during its solution. Therefore, to preserve the general outlook, we have composed the first sections of this review in such a way as to allow the evolution of each problem to be followed starting from its background up to the most recent results. This strategy is employed to consider the structures of compounds containing a non-tetrahedral tetracoordinate carbon atom[‡] (so-called anti-van't Hoff–LeBel chemistry) and structures of compounds with penta- and hexacoordinate carbon atoms.

The final sections of the review are devoted to the theoretical design of compounds in which hypercoordinate (with coordination numbers from five to eight) carbon atoms, and atoms and ions isoelectronic with them, are encapsulated into planar organic and organoelement cages.

II. Tetracoordinate carbon atom with a planar configuration of bonds in the molecules and ions of organic and organoelement compounds: stereoelectronic strategies of stabilisation

The idea of the existence of a tetracoordinate carbon atom with a planar bond configuration[§] in organic molecules was rejected long ago by van't Hoff and LeBel² because it fails to explain the numbers of isomers of methane derivatives. Subsequently, this idea did not attract the attention of researchers for almost a century until Hoffmann, Alder, and Wilcox,^{15,16} relying on the orbital interaction method, defined the problem of stabilisation of such a centre and proposed ways in which its structure could exist. Seemingly paradoxical at first glance, this problem immediately became (and still remains) one of the most intriguing challenges to the imagination and the capabilities of theoreticians and experimentalists. The initial and later stages of development of this problem have been the subject of detailed reviews.^{9,17-23} Our goal is to consider the most recent results and to distinguish the key strategies directed at solving the problem of stabilising a planar tetracoordinate carbon atom. In this context, the data of earlier studies are resorted to for discussion.

The reasons for the instability of the planar bond configuration at a tetracoordinate carbon atom become clear on examining the Walsh diagram for the methane molecule (Fig. 2). It can be seen that one of the triply degenerate bonding t_{1u} MO of the tetrahedral (T_d) structure is transformed in the planar D_{4h} form (**1**) into a nonbonding a_{2u} MO, which is the p_z AO of the carbon atom and is occupied by two electrons.



Thus, only six electrons are used in the formation of four C–H bonds in the planar structure. According to the most precise calculations, the planar D_{4h} form of the methane molecule is unstable with respect to dissociation giving a hydrogen atom and a methyl radical. This structure is 138.4 [QCISD(T)(fc)/6-311+G(3df,2p)//CISD(fc)/6-311G**]²⁴ or 136.2 kcal mol⁻¹ [CCD(full)/6-311++G**]²⁵ energetically less favourable than the tetrahedral T_d form.[¶] Moreover, the D_{4h} configuration does

[‡] Here and below, we mean the topological tetrahedral type rather than the exact tetrahedral geometry with angles of 109°28'.

[§] Below, carbon atoms with this bond configuration are referred to as planar tetracoordinate carbon atoms.

[¶] Expansion of the abbreviations and description of calculation techniques and the orbital basis sets can be found in the book by J B Foresman, A Frish *Exploring Chemistry with Electronic Structure Methods* (Pittsburg: Gaussian Inc., 1996).

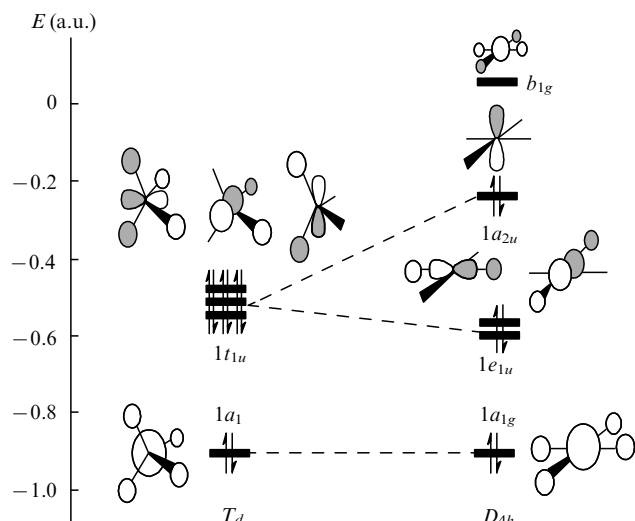
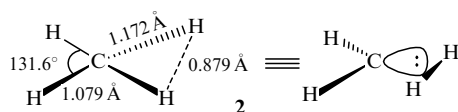


Figure 2. Correlation diagram of the molecular orbitals for tetrahedral and square-planar configurations of the methane molecule.

not even correspond to any local minimum in the potential energy surface (PES) of methane. As predicted by both earlier (MINDO/3) and later (RHF/4-31G) calculations,^{9,26} the vibrational spectrum of the planar structure contains four imaginary frequencies, which imply the occurrence of four types of deformations resulting in barrier-free rearrangements of the molecule.

A different planar form of methane with C_{2v} symmetry, structure **2**, is preferred from the energy standpoint.



This form is not matched by any local minimum in the PES either, but it presents interest as illustrating the adaptation of a planar structure to the electron deficiency experienced by its C–H bonds. This structure and the energetically more favourable structure **3g** (C_s symmetry), which is shown in Fig. 3, can be considered as complexes formed by singlet methylene (1A_1) and a hydrogen molecule. Both structures (**2** and **3g**) are stable with respect to dissociation into CH_2 and H_2 . Figure 3 shows the geometric structures of methane corresponding to all the stationary points in the PES found in calculations.²⁵

The electronic and steric structures of the model methane molecule with D_{4h} symmetry provide a key to the quest for stabilisation routes for compounds with a planar tetracoordinate carbon atom. Now we consider these routes.

1. π -Acceptor and σ -donor substituents

The replacement of hydrogen atoms in planar methane by π -acceptor groups results in delocalisation of the lone electron pair in the $1a_{2u}$ orbital (see Fig. 2), while σ -donor substituents partially make up for the electron deficiency of the σ -bonds in the D_{4h} and C_s structures of methane. The concept of electronic stabilisation first put forward by Hoffmann *et al.*^{15,16} and soon supported by extensive *ab initio* calculations²⁷ is the key and the most successful strategy used in computational and experimental quests for compounds with a planar tetracoordinate carbon atom. A recent review²¹ contains a rather comprehensive collection of data on the structures of a broad range of so-called polar organometallic compounds — derivatives of methane, ethene, and cyclopropane in which the hydrogen atoms have been replaced by lithium or sodium atoms or BeH, MgH, BH₂ or AlH₂ groups. This review considers both the results of early theoretical studies and the recent results obtained by Schleyer's group²⁸ using the density functional theory with an extended orbital basis set (B3LYP/6-

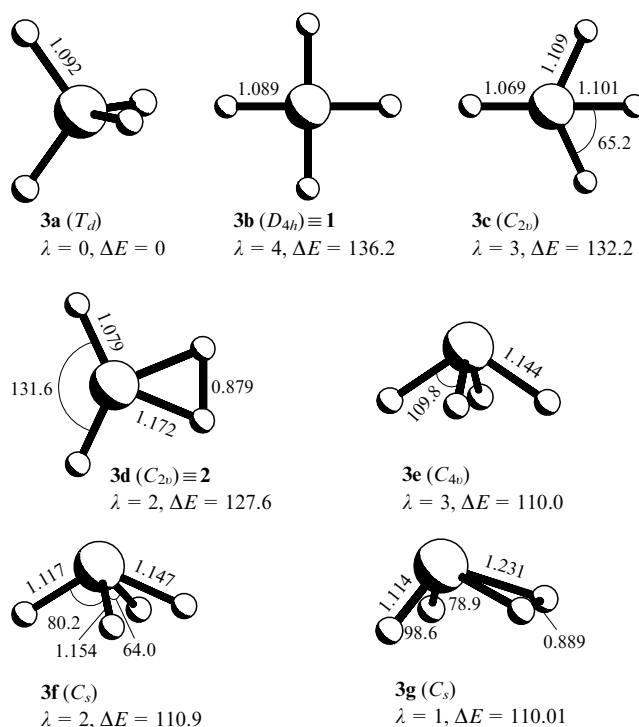
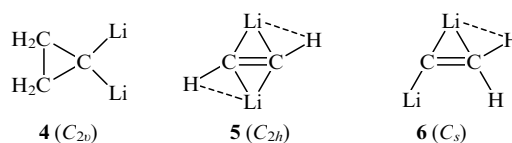


Figure 3. Geometric parameters of the structures corresponding to stationary points in the PES of the methane molecule found²⁵ by CCD(full)/6-311++G** calculations.

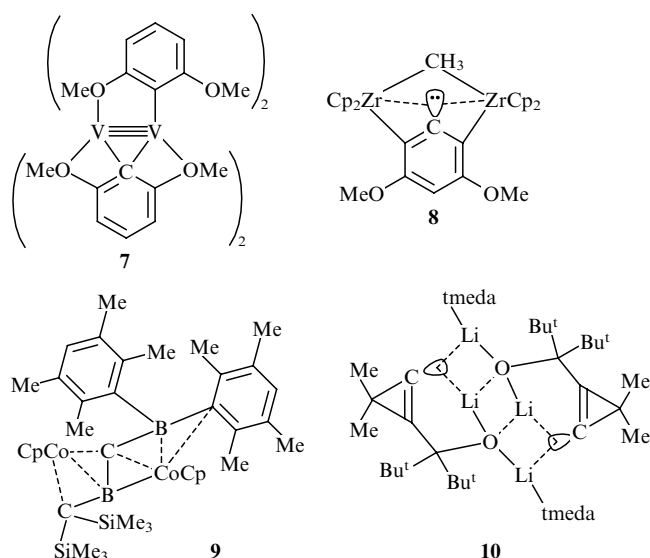
Here and below, λ is the number of negative eigenvalues of the Hess matrix in the given stationary points: for a minimum, $\lambda = 0$; for a transition state (first-order saddle point), $\lambda = 1$; for a second-order saddle point (the top of a two-dimensional hill), $\lambda = 2$. The relative energies (ΔE /kcal mol⁻¹) of configurations are corrected for the zero-point energy (ZPE) of harmonic vibrations. Here and below, the bond lengths are given in Ångströms and the bond angles are in degrees.

311++G**). The results fully confirm the expected effect, namely, a substantial decrease in the energy gap between the planar and tetrahedral structures (here and below, the tetrahedral topology is meant). For compounds such as 1,1-dilithiocyclopropane or 1,2- and 1,1-dilithioethenes, structures with planar tetracoordinate carbon centres (structures **4–6**, respectively) are energetically the most favourable.



Divanadium complex **7** was, apparently, the first compound with a planar tetracoordinate carbon atom to be studied experimentally. Its structure was established by X-ray diffraction analysis.²⁹ In this compound and in the structurally related dizirconocene complex **8**, the planar configuration exists due to the multicentre bond formed by the carbon sp^2 orbital of the phenyl anion, similar to binding in the C_{2v} form of methane (structure **2**). Complex **9** belongs to the extensive class of bimetallic complexes in which planar tetracoordinate carbon atoms are linked to transition (or nontransition) metal atoms.³⁰ A virtually planar geometry of the carbon centre was found in compound **10**, which is related to substituted 2-lithiocyclopropene,³¹ and in a number of carbides, for example, in $Ca_4Ni_3C_5$, which was studied in detail both experimentally³² and theoretically.³³ Numerous examples of bimetallic complexes with structures similar to **7–10** and a description of the methods for their synthesis can be found in reviews.^{22,23} All these data can serve as a good illustration for

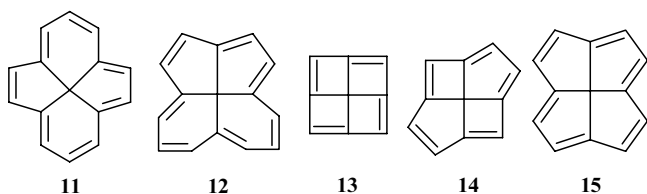
the effectiveness of R Hoffmann's concept of electronic stabilisation of a planar tetracoordinate carbon centre.



Cp is cyclopentadienyl, tmeda is tetramethylethylenediamine.

2. Carbon atom in the centre of the annulene ring

Yet another idea of stabilising a planar configuration of carbon, also proposed by R Hoffmann and coworkers,¹⁶ implies incorporation of this carbon atom into an annulene ring having an aromatic $(4n + 2)$ electron shell. This gives rise to structures such as, for example, compounds **11** and **12**. Indeed, extended Hückel calculations showed that these structures actually have a closed electron shell characterised by a rather wide energy gap between the highest occupied and lowest unoccupied molecular orbitals. Meanwhile, structures **13**–**15** with antiaromatic annulene rings proved to be unstable.



The MINDO/3³⁴ and MNDO³⁵ semiempirical calculations with geometry optimisation confirmed the instability of planar structures **13**–**15**. However, according to these calculation techniques, the planar configuration is not realised for compounds **11** or **12** either. Figure 4 shows the stable conformations of fenestranes molecules **11**, **12** and **15** which we determined by B3LYP/6-311 + G** calculations. It can be seen that the central carbon atom in these structures retains the tetrahedral configuration of bonds, although the angular distortions may reach 30°. It is of interest that in compounds **11** and **12**, the charges on the central carbon atom are +3.6 and +3.7, respectively,[†] *i.e.*, all the valence electrons of carbon are displaced to the periphery of the molecule. The aromaticity of the 14-membered rings ($\sim 18 \pi$ electrons) is retained and the effective radius of the central atom decreases, which results in a lower steric strain. However, in compound **15**, the charge on the central carbon atom is 2e lower (+1.9) and, as a consequence, the conjugated 12-membered ring contains 14 π electrons, which complies with the aromaticity condition.

[†] From here on, Mulliken charges are considered.

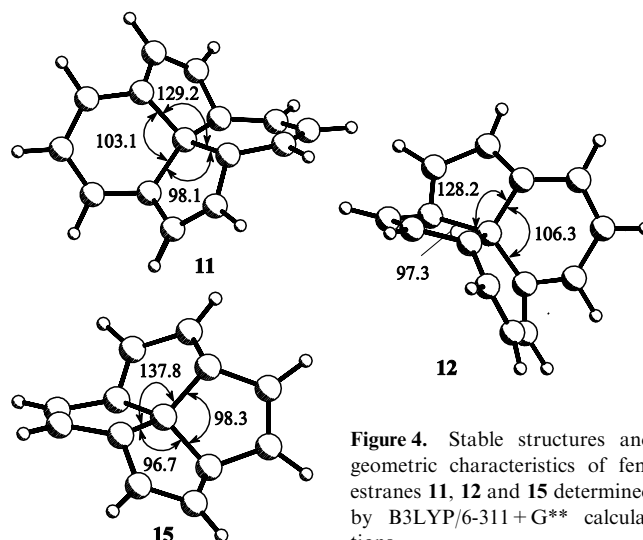


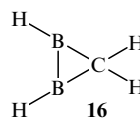
Figure 4. Stable structures and geometric characteristics of fenestranes **11**, **12** and **15** determined by B3LYP/6-311 + G** calculations.

3. Carbon atom in a small ring

One conclusion drawn by Schleyer and coworkers²⁷ on the basis of extensive calculations states that stabilisation of a planar tetracoordinate carbon atom could be attained by incorporating it into a small ring. This was explained by the fact that the angular strain in three- and four-membered rings (the HCH angle in planar structure **1** is 90°) would be lower than in the case of the tetrahedral configuration (the HCH angle is 109.5°). This conclusion is also supported by the fact²⁶ that the HCH angle in molecule **2** (C_{2v} symmetry) is close to the bond angles in small rings. The role of this factor shows itself, for example, in comparison of the relative stabilities of the acyclic dilithiomethane and 1,1-dilithiocyclopropane. In the latter case, structure **4** with a planar carbon atom is more stable, whereas for the former case, the tetrahedral configuration is 2.5 kcal mol⁻¹ energy preferred (B3LYP/6-311 + G** calculation).²¹

4. Planar tetracoordinate carbon atoms in organoboron cages. The stabilising role of ligand–ligand interactions

This approach to stabilisation of structures with a planar tetracoordinate carbon atom is focused on the combined realisation of the electronic and steric effects considered above. Even early *ab initio* calculations by the Hartree–Fock procedure³⁵ showed that incorporation of a tetracoordinate carbon atom into a three-membered 1,2-diboracyclopropane ring creates favourable conditions for ring flattening: the boron atoms have vacant p_z orbitals involved in the delocalisation of the lone electron pair of carbon and, hence, they exhibit σ -donor properties. However, allowance for electron correlation in terms of the MP2/6-31G* (see Refs 36, 37) or B3LYP/6-311 + G* (see Ref. 21) approximations showed that neither structure **16**



nor planar 2,3-diboraspriopentane **17c**, incorporating a diboracyclopropane ring, is a true minimum on the PES. According to the most precise MP2(full)/6-311 + G** calculations,³⁸ compound **17c** is a transition state of an almost barrier-free (the activation energy $\Delta E = 0.23$ kcal mol⁻¹) enantiotopomerisation of the tetrahedral conformation.

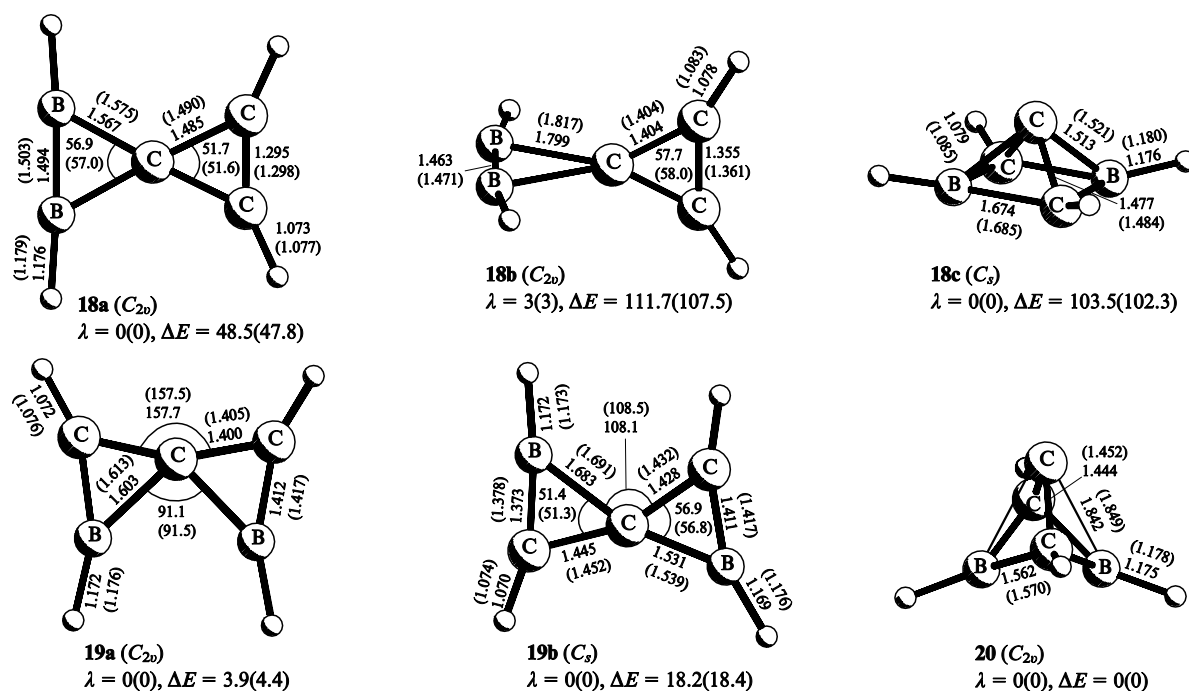
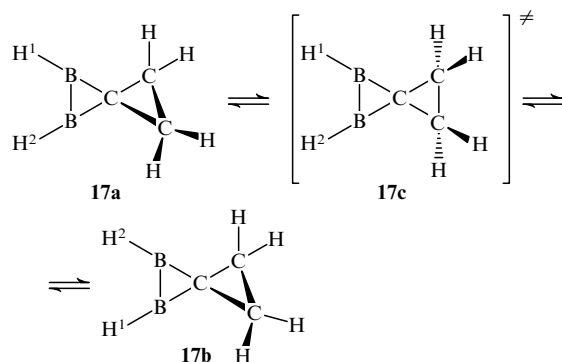


Figure 5. Geometric characteristics, relative energies (ΔE , kcal mol⁻¹), and λ values for boron-containing heterocyclic compounds **18a–c**, **19a,b** and **20** determined by MP2(full)/6-31G** and MP2(full)/6-311++G** calculations (the values in parentheses).³⁸



On passing to 2,3-diboraspicyclopentene, the energy levels of the tetrahedral (**18b**) and planar (**18a**) structures (Fig. 5) are reversed. In the planar structure **18a**, each three-membered ring contains two π electrons, *i.e.*, possesses a certain degree of aromaticity; this provides additional stabilisation to this structure. It can be seen from Fig. 6 that two bonding π MOs of structure **18a** fully correspond to the bonding π MO of the cyclopropenium ion. As a consequence, structure **18a** is indeed a true minimum on the PES. According to MP2(full)/6-311++G**+ZPE calculations, the structure with the planar carbon atom is 58.2 kcal mol⁻¹ energetically more favourable than structure **18b** with the tetrahedral spiro carbon atom. The latter corresponds to the top of a hill in the PES ($\lambda = 3$).

Figure 5 presents the data on the geometry of structures **18a** and **18b** and the type of PES stationary points corresponding to these structures. The same Figure also shows data for the isomeric stable species **19a** and **19b**, containing a planar tetracoordinate carbon atom. The structure **19a** is only 3.9 kcal mol⁻¹ energetically less favourable than the singlet carbene structure **20**, corresponding to the global minimum in the PES of C₃B₂H₄.

The stabilisation of the planar carbon centre in compounds **18a** and **19a,b** is due to a combination of all factors including the σ -donor and π -acceptor effects of the neighbouring boron atoms, the incorporation of this carbon in the small ring, and the presence

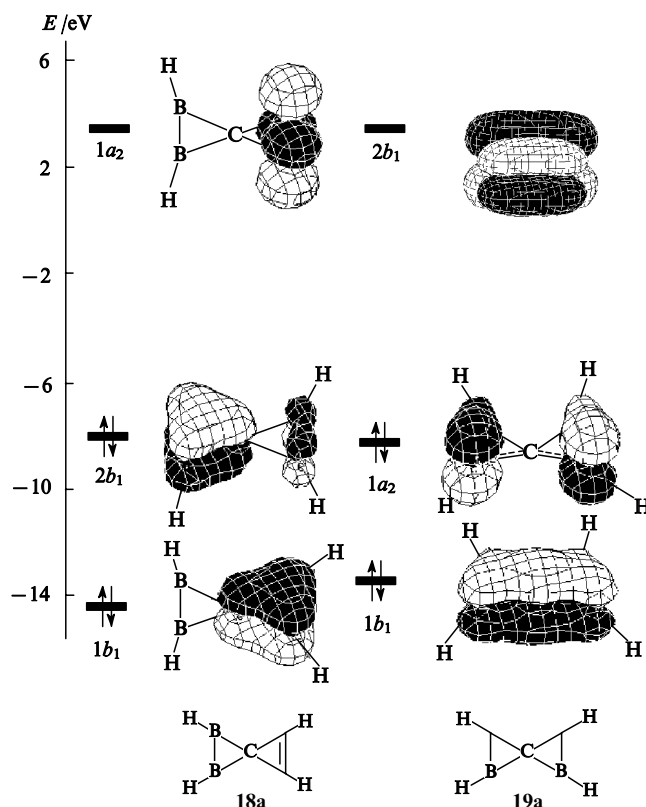
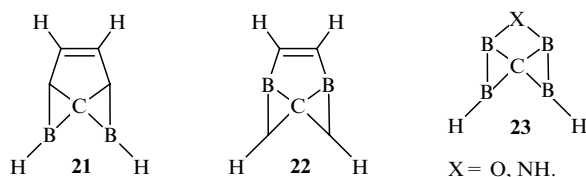


Figure 6. Shapes of the π -molecular orbitals of planar structures **18a** and **19a**.³⁸

of the stable π -conjugated system. The last-mentioned factor is nothing but creation of the conditions for stabilising ligand–ligand interactions, which are weaker or totally missing in the structures with tetrahedral carbon atoms. The enhancement of

this interaction following an extension of the π -system of the ligand environment provides additional stabilisation to structures with a planar carbon atom, for example, in compounds **21**–**23**.³⁸



5. The Jahn–Teller instability of tetrahedral structures

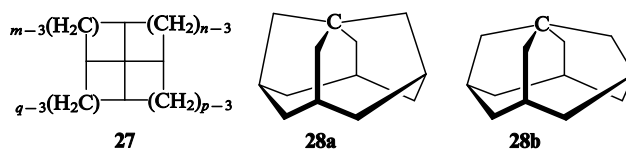
The ligand–ligand bonding interactions play an especially important role in the pentaatomic structures CX_2Y_2 , CX_3Y^{n-} and CX_4^{n-} ($X = Al, Ga; Y = Si, Ge; n = 0, 1$) which incorporate a planar tetracoordinate carbon atom.^{39–42} For example, the planar Al_4 cage in CAI_4^- behaves as an aromatic 2π -electron system.⁴³ According to calculations,⁴³ the stability of the planar structures for these compounds is directly related to the formation of bonding four-centre σ - and π -type orbitals in the ligand. In addition, the higher stability of the planar structures with respect to the tetrahedral isomers can be attributed to the fact that the 17- or 18-electron valence shells in the tetrahedral compounds CX_4 ($1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^1$ and $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^2$) correspond to degenerate electronic states and, hence, they are subject to Jahn–Teller deformations.⁴⁰ Meanwhile, 16-electron compounds with the closed $1a_1^2 1t_2^6 2a_1^2 2t_2^6$ electron shell, for example, CAI_4 , retain the tetrahedral structure. It can be seen from the data shown in Fig. 7 that the structures of the CSi_2Ga_2 (**24c**) and CGe_2Al_2 (**25c**) 18-electron compounds with tetrahedral carbon atoms are energetically less favourable than the planar *cis*- (**24a** and **25a**) and *trans*-isomers (**24b** and **25b**). They do not correspond to local minima on the PES, being transition states. It is of interest that in the case of CSi_2Al_2 (**26a**), the four-membered ring formed by the

ligands is not sufficiently large for the carbon atom to occupy its centre. As a consequence, the carbon atom is expelled from the ring plane to form a somewhat more stable pyramidal form **26c**. However, the energy gap and the vibration frequency with a negative force constant are so small that the fluctuating structure CSi_2Al_2 should be considered as having C_{2v} effective symmetry.

The photoelectron spectra of the CAI_4^- , CAI_3Si^- and CAI_3Ge^- anions generated by laser vaporisation of the corresponding carbide clusters and detected using time-of-flight photoelectron spectroscopy^{40–42} are consistent with a planar structure of these anions. Theoretical and experimental facts supporting the planar structure for the 17-electron $SiAl_4^-$ and $GeAl_4^-$ anions were obtained in a similar way. Planar and nearly planar C_s forms were found for the 16-electron species, $SiAl_4$ and $GeAl_4$.⁴⁴ The simple planar clusters such as **24**–**26** represent, in principle, new types of structural patterns that can exist in solid-state compounds with properties useful for high-technology materials.^{43–45}

6. Flattening of the tetrahedral configuration of the carbon atom in sterically strained saturated systems

The strategy for steric stabilisation of the planar angular deformation of bonds at a tetrahedral carbon atom by placing the atom at the centre of a saturated polycyclic system is similar to that considered above in Section I.2. Numerous theoretical and experimental studies have been devoted to the development of this approach (see the reviews^{17–20, 46} and references therein). Particular attention was drawn to $[m.n.p.q]$ fenestranes **27** and, subsequently, to bowlanes **28**. The most important result of these studies, as in the case of compounds of the type **11** and **12**, was the conclusion that complete flattening of the tetrahedral structure cannot be attained.



Both semiempirical (MINDO/3^{12, 47} and MNDO⁴⁸) and *ab initio*^{49, 50} calculations showed that the [4.4.4]fenestrane molecule (**29**), which is the best candidate to form a planar structure, exists preferentially as a flattened tetrahedral D_{2d} form (**29a** and **29b**). Contrary to suggestions,⁵¹ the isomeric pyramidal C_{4v} conformation proved to be energetically less favourable [by 28.5

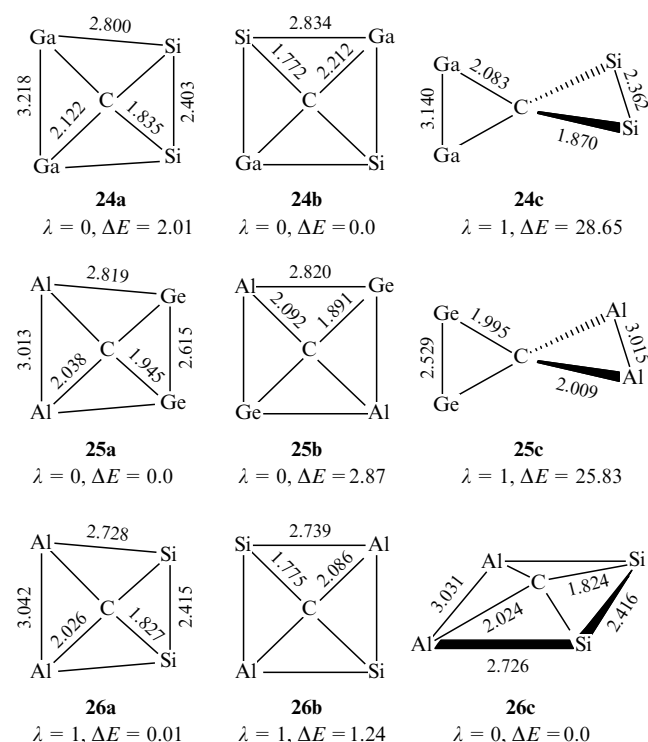
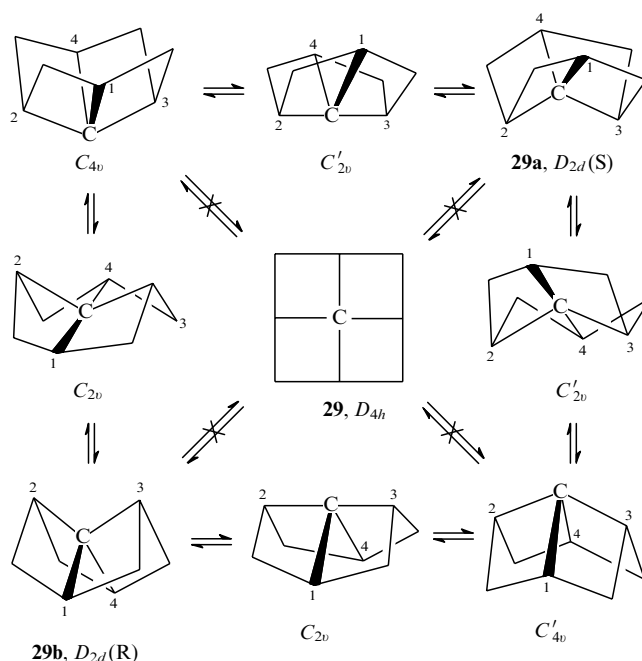


Figure 7. Geometric parameters, relative energies (ΔE /kcal mol⁻¹) and λ values for the CGa_2Si_2 (**24a**–**c**), CAI_2Ge_2 (**25a**–**c**) and CSi_2Al_2 (**26a**–**c**) clusters calculated by the MP2(fc)/6-31G** (for CGa_2Si_2 and CAI_2Ge_2) and MP2(full)/6-311++G** (for CSi_2Al_2) techniques.⁴⁰

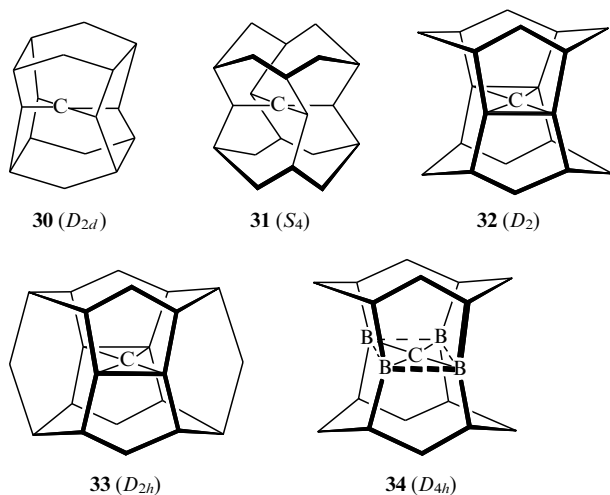


or 48.3 kcal mol⁻¹ according to MINDO/3⁴⁷ and MP2(fc)/4-31G⁵⁰ calculations, respectively]. Interconversion of the *D*_{2d} and *C*_{4v} forms proceeds *via* a transition state with *C*_{2v} symmetry, which is 17 kcal mol⁻¹ higher in energy than the *C*_{4v} form. The planar *D*_{4h} form **29** is unstable; it corresponds to the top of a hill on the PES. The pattern of conformational transitions given below reflects the general topology of the PES of [4.4.4]fenestrane.⁴⁷

Analogous structural transformations take place in the case of bowlane **28**. According to RHF/6-31G* calculations,⁵² the energy minimum corresponds to the flattened tetrahedral structure **28a**, while the structure **28b** with a pyramidalised quaternary carbon atom is a transition state in the interconversion of the mirror topomers **28a**.

7. Planar tetracoordinate carbon atom inside a rigid three-dimensional cage of bonds

A successful (in theory) route of development of the steric (mechanic) strategy for planarisation of bonds around a tetracoordinate carbon atom has been provided by computational design of alkaplans and spiroalkaplans. These polycyclic structures can be constructed from planar neopentane and spiro-pentane units by incorporating peripheral carbon atoms into rigidly connected cycloalkane fragments.^{53–56} Complete flattening of bonds around the central carbon atom is not attained in alkaplans; according to RHF/6-31G* calculations, the C–C–C angles in the hexaplane **30** and octaplane **31** molecules are 168.6° and 168.8°,^{53,54} In the case of spirooctaplane **32**, the deviation from the ideally planar configuration is only 3.1°. The complete planarisation of bonds around the central carbon is found in dimethanospiro[2.2]octaplane **33**; note that this result has been obtained by a rather high-level calculation (MP2/6-311+G**).⁵⁵ The higher occupied MO of each of the compounds **30–33** is a *p*_z orbital localised on the planar carbon atom. This accounts for the exceptionally low ionisation potentials of these hydrocarbons (4.5–5.0 eV), which are comparable with the ionisation potentials of alkali metals.



An interesting route of development of the alkaplans design can be found in a study by Wang and Schleyer.⁵⁷ In this case, flattening of a tetracoordinate carbon atom was attained using not only steric (mechanical) factors but also electronic factors which are favourable for this type of deformation. The calculations (B3LYP/6-311+G**) carried out by the researchers cited showed that boraplane **34**, formed from octaplane **31** *via* replacement of four carbon atoms adjacent to the central atom by boron atoms, has *D*_{4h} symmetry and, hence, contains a planar carbon atom. A peculiar feature of structure **34** is the perpendicular orientation of two B–C bonds with respect to the bonds of the central carbon atom. Unlike octaplane **31**, in the case of boraplane **34**, the highest occupied MO is not localised at the central atom but is distributed over the perimeter of the borocarbon skeleton. This involvement

of the lone electron pair in multicentre bonding is responsible for the additional stabilisation of the planar form, realised in neither octaplane **31** nor the C(BH₂)₄ fragment simulating the structure of the boraplane mirror plane.

III. The mechanism of intramolecular inversion of the tetrahedral configuration of bonds at the carbon atom

The results of theoretical and experimental studies of molecules and ions in the ground electronic state considered in the previous Section attest to the possibility of stabilisation of a planar tetracoordinate carbon atom. This brings up the question — whether it is possible to stabilise the structures of transition states of these compounds in such a way as to decrease substantially the energy barrier to the inversion of tetrahedral forms and to identify the classes of organic and organoelement compounds stereochemically non-rigid with respect to this inversion.[‡]

Even early semiempirical and *ab initio* (RHF/DZ) calculations^{58,59} of the PES for enantiotopomerisation of the methane molecule carried out assuming that the four C–H bonds remain equivalent along the whole reaction path showed that the square-planar structure **1** does not correspond to a first-order saddle point and does not represent a transition state of stereoisomerisation. When this constraint was eliminated,^{9,60} MINDO/3 calculations showed that inversion of the tetrahedral configuration of the methane molecule proceeds as an asymmetrical digonal twist deformation, the transition state being a *C*_s structure the geometry of which is quite similar to the geometry of the transition *C*_s structure **3g** and to other structures of this type determined using rigorous *ab initio* calculation techniques.^{24,61,62} The data presented in Table 1 show that the relative energy of the *C*_s transition state is approximately 25–30 kcal mol⁻¹ lower than the energy of the planar methane structure with *D*_{4h} symmetry. However, this structure is still unstable with respect to the CH₄ → CH₃⁺ + H⁺ decomposition, which requires 104 kcal mol⁻¹. This means that the non-dissociation route of methane inversion is impracticable under usual conditions.

Table 1. Inversion barriers of the methane molecule obtained in the most precise *ab initio* calculations.

Method	ΔE ^a /kcal mol ⁻¹	Ref.
MCSCF/TZV + + G(<i>d, p</i>)	125.6	61
SOCI/TZV + + G(<i>d, p</i>)	117.9	61
MP2(full)/6-311 + G**	109.2	24
CISD(fc)/6-311G**	117.9	24
QCISD(T)(fc)/6-311 + G(3 <i>df, 2p</i>)// CISD(fc)/6-311G**	110.2	24
QCISD(T)(fc)/6-311 + G(3 <i>df, 2p</i>)// CISD(fc)/6-311G** + ZPE	105.1	24
B3LYP/6-311G** + ZPE	109.4	62
CCD/6-311 + G**	115.4	25
CCD/6-311 + G** + ZPE	110.1	25

^a Energy difference between structures **3g** (transition state with *C*_s symmetry) and **3a** (ground state with *T*_d symmetry).

The inversion of the tetrahedral structure is one of the most important structural types of polytopal rearrangements. The reaction trajectories corresponding to digonal twist

‡ Stereochemically non-rigid molecules have low barriers to an intramolecular rearrangement (too low to be detected on the NMR time scale); therefore, they undergo fast (on the NMR time scale) reversible rearrangements.

($T_d - D_2 - \bar{T}_d$) or tetrahedral compression ($T_d - D_{2d} - \bar{T}_d$) deformations are symmetry allowed.^{15, 63, 64} The latter mechanism is also referred to as edge inversion^{65, 66} (as opposed to vertex inversion, characteristic of the stereoisomerisation of tricoordinated pyramidal structures). Detailed investigations^{61, 62} of the reaction pathway of methane stereoisomerisation using the method of intrinsic reaction coordinate (*i.e.*, the trajectory obtained by moving down from the point on the PES corresponding to the transition state along the transition vector⁶⁷) showed that these trajectories are actually more intricate (Fig. 8). As follows from Fig. 8, the change in the geometry can be described by the digonal twist pattern only at early stages of inversion, while after the initial rotation of the plane of one CH₂ fragment relative to the other, the central atom undergoes pyramidalisation, which is not taken into account in the above schemes.

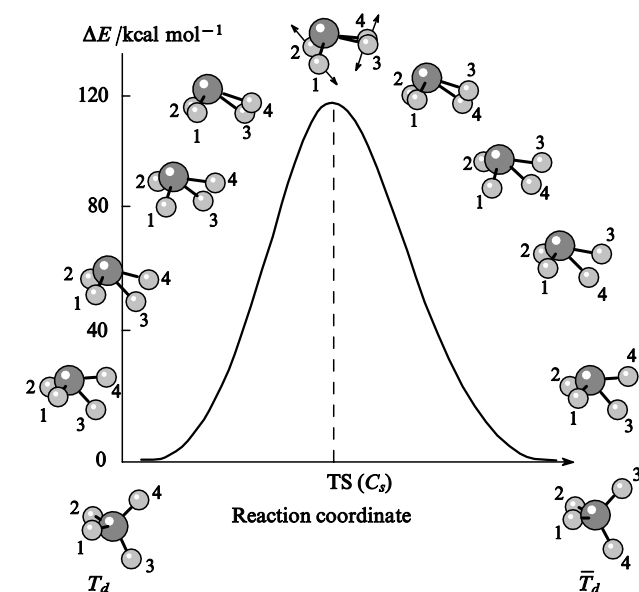
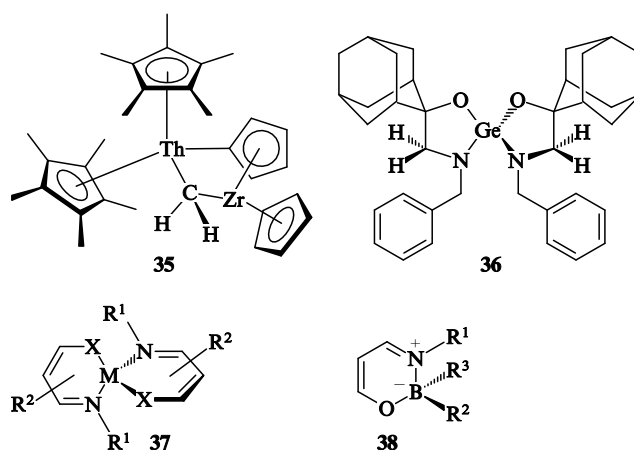


Figure 8. Geometry evolution of the methane molecule along the energy profile of the tetrahedral configuration $T_d - C_s - \bar{T}_d$ according to *ab initio* calculations.^{25, 62}

It would be of interest to find out how the decrease in symmetry caused by partial replacement of the hydrogen atoms in the methane molecule by other atoms or groups would influence the type of reaction trajectory in the inversion process. Such calculations based on the intrinsic reaction coordinate technique have so far been performed only for the difluoromethane molecule (the Hartree–Fock method in a small STO-3G basis set).⁶⁸ Two transition states (planar *cis*- and *trans*-structures) were identified; they correspond to the reaction pathways typical of the digonal twist and tetrahedral compression mechanisms, respectively.

The question of what structural factors could stabilise the C_s form of the transition state of the inversion of type **3g** tetrahedral configuration has not been discussed in the literature. In principle, it is clear that a solution of this problem is the same as the solution of the problem of stabilisation of a planar tetracoordinate carbon atom. Thus in complex **35**, due to the presence of two electropositive metal atoms at the carbon center, the barrier to inversion decreases to a level that can be determined by dynamic ¹H NMR from coalescence of the signals for the methylene group protons. According to EHMO calculations, stereoisomerisation of complex **35** proceeds *via* a non-dissociative mechanism and the transition state contains a planar tetracoordinate carbon atom.⁶⁹

The energy gap between the tetrahedral and planar structures formed by Main Group elements is known to narrow with a decrease in the electronegativity of the central atom.^{9, 70} On passing from carbon atom to isoelectronic Be^{2-} , B^- , Al^- , Si ,



$M = \text{Be, Zn, Cd, Hg}; X = \text{O, S, Se}; R^1, R^2, R^3 = \text{Alk, Ar, Hal, NO}_2.$
 $R^1, R^2 = \text{Alk, Ar, Hal, NO}_2.$

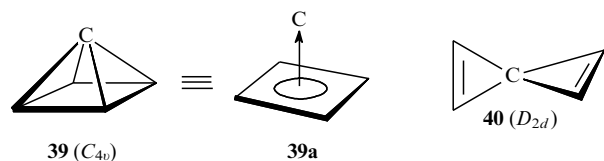
and Ge atoms and to d^{10} atoms (Zn, Cd, Hg), the ordering in energy of the frontier orbitals is reversed; as a consequence, stabilisation of the planar configuration can be attained by introducing electronegative substituents containing lone electron pairs. There are quite a few examples of stereochemically non-rigid compounds of this type, in particular, one can mention bis(ethanolamino)germanium derivative **36** (see Ref. 71) and the extensive group of bis-chelate complexes **37** (see Refs 72, 73). It should be noted, however, that in the general case, the non-dissociative intramolecular inversion of configuration is not the only mechanism responsible for the exchange processes observed by NMR.^{72–74} Among compounds **35–37**, quite reliable proof for the non-dissociative mechanism of inversion has been obtained only for complexes **37** with d^{10} metals,^{72, 75} whereas for complexes **35** and **36**, a mechanism involving cleavage–recombination of one bond at the central atom also cannot be ruled out. This mechanism is realised for beryllium complexes **37** and 1,3,2-oxazaboroles **38**.^{72, 76, 77}

IV. Structures with a pyramidal configuration of bonds at a tetracoordinate carbon atom

Analysis of the stereochemical configurations and chirality of compounds containing tetracoordinate atoms, in particular, tetracoordinate carbon atoms, is based on consideration of topological characteristics of three possible simplexes (configurations whose symmetry ensures equivalence of all four bonds).⁷⁸ Apart from the tetrahedral T_d and planar D_{4h} structures, this condition is satisfied only by the square-pyramidal C_{4v} form. Early EHMO and *ab initio* (RHF/DZ)^{58, 59} calculations predicted that the C_{4v} structure **3e** of methane (see Fig 3) is energetically more favourable than the D_{4h} form; it is this structure that is formed as the transition state in the inversion of the tetrahedral configuration. This sets the task of stabilising a pyramidal tetracoordinate carbon atom in the molecules of organic compounds. High-level *ab initio* calculations carried out in recent years^{24, 25} fully confirmed the first conclusion: the total energy of the C_{4v} configuration of the methane molecule (calculated with allowance for the zero-point energy) is lower than the total energy of the C_s structure **3g**. However, it was found that the stationary point corresponding to the methane molecule with C_{4v} symmetry on the PES of methane is a third-order saddle-point, and, hence, this structure is not a transition state.

The search for routes for stabilisation of compounds containing tetracoordinate carbon atoms with a pyramidal configuration of bonds (below, pyramidal carbon) is mainly carried out in two ways: (1) electronic stabilisation and (2) steric stabilisation. The most important results obtained along the former route include the theoretical prediction of stability of the parent compound of

this class, namely, tetracyclo[2.1.0.0.1³:0^{2,5}]pentane (**39**), which was called pyramidane, interpretation of the nature of the stability of structure **39** and a description of the possible methods for pyramidane synthesis.^{59, 79, 80}



The fact that structure **39** is a rather deep minimum on the PES of C_5H_4 was first established in a theoretical (EHMO, MINDO/3, HF/4-31G) study^{12, 59} of isomerisation routes of spiropentadiene **40**, the simplest spiroalkene, which was successfully synthesised only relatively recently.^{81, 82}

It can be seen from Fig. 9 that deformation of structure **40** with variation of the angle coordinates α and β gives rise to four topomers (degenerate isomers) of pyramidane **39**, having lower energies. However, structures **39** and **40** are separated from each other by a high energy barrier, which prevents the exothermic rearrangement $40 \rightarrow 39$. This is the reason for the kinetic stability of spiropentadiene and the possibility of its synthesis. The pyramidane structure does not correspond to the global energy minimum in the PES of C_5H_4 ; however, as in the case of spiropentadiene, it is characterised by high kinetic stability with respect to the possible decomposition and rearrangement reactions.

Pyramidane **39** is computed to be the simplest organic system with a pyramidal carbon atom. As [3.3.3]fenestrane, this compound is the first member of the $[m.n.p.q]$ fenestrane **27** family. Therefore, it comes as no surprise that study of the structure and

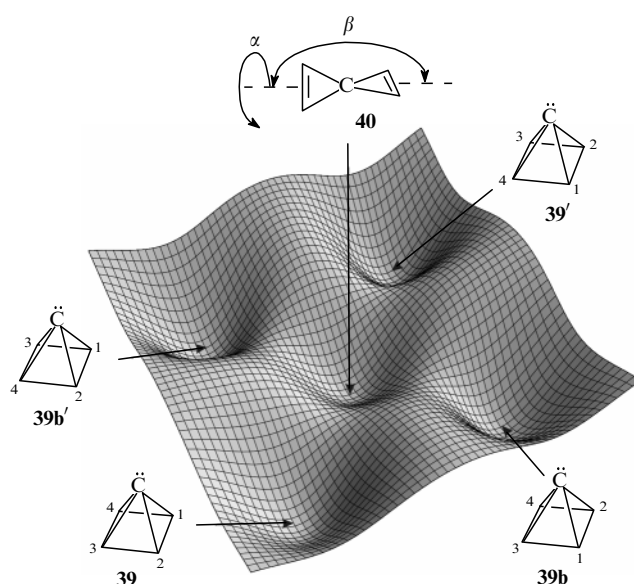


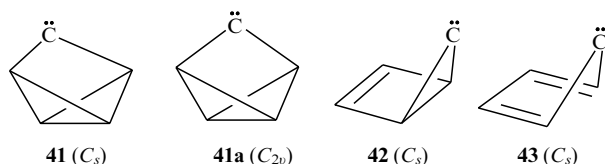
Figure 9. Topography of the PES of C_5H_4 for structures **39** and **40** during deformation of the latter along the angular coordinates α and β .⁵⁹

properties of this compound was the object of a large number of studies,^{83–88} in which *ab initio* calculations were carried out at different approximation levels. The results of calculations of the total and relative energies of the pyramidane **39** molecule and its most stable isomers **40–43** and some other parameters of these molecules are summarised in Table 2.

Table 2. Total ($-E_{\text{tot}}$ /a.u.) and relative (ΔE /kcal mol⁻¹) energies of the pyramidane molecule **39** and its isomers **40–43** in the ground singlet electronic state, charges on the quaternary carbon atoms and dipole moments calculated by *ab initio* quantum-chemistry methods.

Calculation method	$-E_{\text{tot}}$	ΔE	q_C	μ /D	Ref.	Calculation method	$-E_{\text{tot}}$	ΔE	q_C	μ /D	Ref.
Pyramidane 39 (C_{4v})						Isomer 41a^a (C_{2v})					
RHF/3G	189.08749	0	-0.102	1.43	84	RHF/3G	189.06525	13.7	-0.24	3.2	84
RHF/6-31G*	191.45834	0	-0.43	1.79	86	RHF/6-31G*	191.41790	24.4	—	—	86
MP2(fc)/6-31G*	192.09980	0	—	—	86	MP2(fc)/6-31G*	192.03046	42.8	—	—	86
OCISD(T)//MP2/6-31G*	192.15317	0	—	—	86	OCISD(T)//MP2/6-31G*	192.0954	35.4	—	—	86
B3LYP/6-311+G**	(192.78107)	0	-0.46	1.83	88	B3LYP/6-311+G**	(192.72932)	32.5	-0.34	3.65	88
MP2(full)/6-311+G**	192.30990	0	-0.42	1.77	88	MP2(full)/6-311+G**	192.22987	50.2	-0.29	3.67	88
CCSD/6-311+G**	192.31312	0	-0.46	1.84	88	CCSD/6-311+G**	192.26066	32.9	-0.22	3.41	88
Isomer 40 (D_{2d})						Isomer 42 (C_s)					
RHF/3G	189.07558	27.3	-0.123	0	84	RHF/3G	—	—	—	—	84
RHF/6-31G*	191.44637	6.2	+0.25	0	86	RHF/6-31G*	191.44109	10.3	-0.84	—	86
MP2(fc)/6-31G*	192.07803	12.1	—	0	86	MP2(fc)/6-31G*	192.06529	21.3	—	—	86
OCISD(T)//MP2/6-31G*	192.13976	6.8	—	0	86	OCISD(T)//MP2/6-31G*	191.13154	13.2	—	—	86
B3LYP/6-311+G**	(192.71311)	5.0	+0.40	0	88	B3LYP/6-311+G**	(192.76380)	10.8	-0.40	3.97	88
MP2(full)/6-311+G**	192.26986	25.1	+0.59	0	88	MP2(full)/6-311+G**	192.26111	30.6 ^b	-0.36	3.86	88
CCSD/6-311+G**	192.29504	11.3	+0.48	0	88	CCSD/6-311+G**	192.28738	16.1 ^b	-0.55	3.90	88
Isomer 41 (C_s)						Isomer 43 (C_s)					
RHF/3G	—	—	—	—	84	RHF/3G	189.11556	-17.8	—	1.1	84
RHF/6-31G*	191.43272	15.8	-0.77	—	86	RHF/6-31G*	191.48997	-19.9	-0.34	—	86
MP2(fc)/6-31G*	192.06434	22.3	—	—	86	MP2(fc)/6-31G*	192.10866	-6.2 ^c	—	—	86
OCISD(T)//MP2/6-31G*	192.12006	20.8	—	—	86	OCISD(T)//MP2/6-31G*	192.17408	-13.7	—	—	86
B3LYP/6-311+G**	(192.74965)	19.7	-0.46	4.26	88	B3LYP/6-311+G**	(192.81089)	-18.7	+0.15	1.02	88
MP2(full)/6-311+G**	192.26209	30.0	-0.24	4.53	88	MP2(full)/6-311+G**	192.30280	4.4	+0.28	0.68	88
CCSD/6-311+G**	192.28218	19.4	-0.36	4.31	88	CCSD/6-311+G**	192.32741	-9.0	-0.155	1.46	88

^a The C_{2v} structure **41a** is a transition state for the conformational isomerisation of **41** proceeding according to the pattern of wagging vibrations of the carbene centre with respect to the plane of the other four carbon atoms.^{85, 87, 88} ^b At this level of approximation, the C_s structure **42** has one imaginary frequency in the vibrational spectrum. ^c At this approximation level, the C_s structure **43** is a flattened region in the C_5H_4 PES (a first-order saddle point). The adjacent minimum corresponds to a C_2 cumulene form whose total energy is 0.6 kcal mol⁻¹ lower than the energy of the C_s structure.



It follows from the above data that the structure of pyramidane **39** is only 9 kcal mol⁻¹ energetically less favourable than the structure of its carbene isomer **43** which is most stable in the singlet electronic state. The singlet–triplet splitting calculated for structure **39** is rather large (46.8 kcal mol⁻¹) and the strain energy per C–C bond (19 kcal mol⁻¹) is lower than the strain energy in the tetrahedrane molecule (~25 kcal mol⁻¹).^{9,84} However, it can be expected that pyramidane **39** has a relatively high kinetic stability. The lowest vibration frequencies calculated for the C_{4v} structure of pyramidane^{85,88} are rather high: 453.6 and 478.9 cm⁻¹ (CCD/6-311+G**). The PES of C_5H_4 contains no reaction valley to connect the two minima corresponding to isomers **39** and **43**.^{12,85} The pyramidane structure is energetically more favourable than the structures of other classical carbenes, **41** and **42**. As shown by semiempirical^{79,83} and *ab initio*^{85,87,88} calculations, both carbenes can serve as precursors of pyramidane and appropriate precursors can be found for each of these carbenes.^{89,90} It has been reported⁸⁷ that the potential barrier to thermal isomerisation of bicyclo[2.1.0]pent-2-en-5-ylidene (**42**) into pyramidane **39** is equal to 16.3 kcal mol⁻¹, while a similar transformation of tricyclo[2.1.0.0^{2,5}]pent-3-ylidene (**41**) requires overcoming a potential barrier of only 3.5 kcal mol⁻¹. This implies that the generation of these precursors would be accompanied by immediate isomerisation in pyramidane. Simultaneously, structure **39** is separated from more stable isomers, for example 3-ethynylcyclopropene, by relatively high barriers corresponding to a half-life of more than 4–5 h at room temperature. Thus, synthesis of pyramidane should be possible.

The nature of the stability of the pyramidane molecule and features of its geometric structure (Fig. 10) are adequately interpreted using the scheme of orbital interactions (Fig. 11) between the fragments forming this molecule — the basal cyclobutadiene fragment and the apical carbon atom (structure **39a**). Stabilisation is mainly due to the formation of the bonding $1e$ MO of the pyramidane molecule upon overlap of the p_x, p_y AO of the apical carbon atom with the degenerate e_g MO of the cyclobutane fragment. The sp_z AO pair of the carbon atom and the cyclobutadiene a_{2u} MO form a bonding ($1a_1$), a nonbonding ($2a_1$), and a high-lying antibonding MO of molecule **39**; only the first two of these orbitals are occupied with electrons.

This type of electronic structure is typical of all the pyramidal molecules formed by a π -conjugated cyclic fragment and an apical atom or group. Pyramidal structures of this type have only four bonding (or three bonding and one nonbonding) MOs, which can be populated by π -electrons of the basal fragment and by all valence electrons of the apical atom (or group). The eight-electron

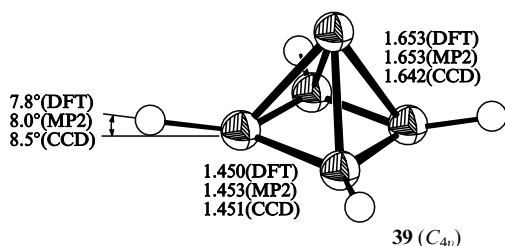


Figure 10. Geometric characteristics of the pyramidane molecule (**39**) calculated by the B3LYP/6-311+G** (DFT), MP2(full)/6-311+G** (MP2) and CCD(full)/6-311+G** (CCD) techniques.⁸⁸

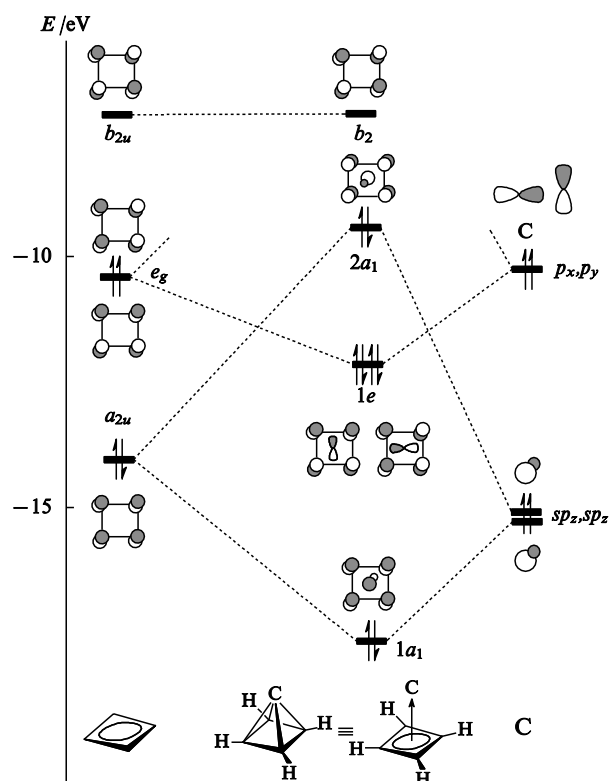
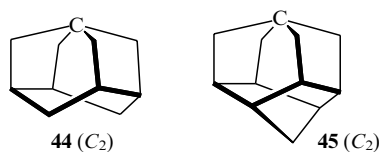


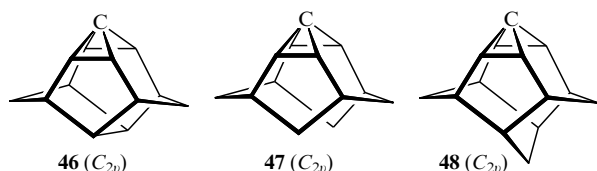
Figure 11. Diagram of the orbital interactions of the fragments of pyramidane molecule **39** ↔ **39a** according to Refs 9 and 12.

The π -MO energy levels of the cyclobutadiene molecule with D_{4h} symmetry were calculated using the EHMO method, the energy levels of the hybrid orbitals of carbon correspond to those given in Ref. 91.

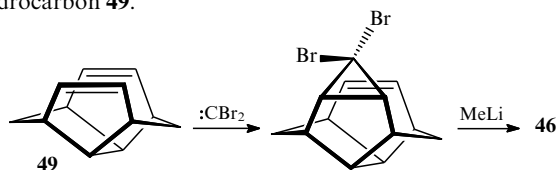
rule determining the stability of pyramidal structures follows from the foregoing.^{9,11,12} This rule, attributed to three-dimensional aromaticity conditions,^{92,93} holds for both heteroatomic systems and transition metal π -complexes (provided that isolobal relations are taken into account).⁷ Numerous examples of pyramidal structures can be found in reviews^{9,12,94–97} and recent works.^{25,98}

The stability of non-classical pyramidal structure **39** is completely dictated by electronic factors. The efficiency of steric (mechanical) stabilisation of organic compounds with a tetra-coordinate pyramidal carbon atom was demonstrated by Rasmussen and Radom.⁸⁶ As in alkylplanes and spiroalkylplanes (see Section II.7), in compounds with a pyramidal carbon atom, the rigid cage of bonds is based on neopentane and spironeopentane structures with an additional cycloalkane fragment attached. The B3LYP/6-31G* and MP2(fc)/6-31G* calculations showed that the stable hemialkylplane (**44**, **45**) and hemispiroalkylplane (**46–48**) hydrocarbon structures obtained in this way contain a pyramidal quaternary carbon atom. The degree of pyramidalisation of bonds at the carbon atom in hemialkylplanes is low but in spirohemialkylplanes, this value approaches that in pyramidane **39** and the calculated lengths of the C–C bonds involving the apical carbon atom (1.632–1.650 Å) are similar to the corresponding bond lengths in pyramidane.



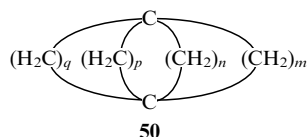


The strain energies of structures **44–48** are comparable with the strain energies of well-studied strained structures such as cubane and prismane. Thus, there are reasons for assuming that these compounds could be synthesised. Relying on an efficient method for the preparation of bridged spirooctaplanes,^{99–101} Rasmussen and Radom⁸⁶ proposed the following method for the synthesis of hemispirooctaplane **46** from the available hydrocarbon **49**.



It follows from the data of Table 2 that the apical carbon atom in structure **39** bears a considerable negative charge, while the highest occupied MO is localised almost entirely on this atom and can actually be regarded to be a lone electron pair orbital (see Fig. 10). Similar results have also been obtained for hydrocarbons **44–48**. This fact is responsible for fairly low (4.5–5.0 eV) ionisation energies calculated for pyramidane, hemialkylalkanes, and hemispiroalkylalkanes, commensurate in magnitude with the ionisation potentials of light alkali metals, as well as the exceptionally high basicity of these compounds. The proton affinities of compounds with a pyramidal tetracoordinate carbon atom calculated using various methods (they are given in Table 3) are record-breaking values for organic compounds including superbases such as proton sponges.

Formerly, it has been considered that $[m.n.p.q]$ paddlanes **50**, like $[m.n.p.q]$ fenestranes **27**, can also contain pyramidal carbon atoms in the molecule.^{51, 104}

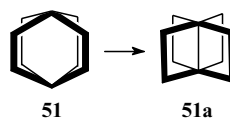


However, all paddlanes known to date contain at least one large ring ($m > 8$), which leads to flattening of the tetrahedral configuration of the quaternary carbon atoms. The structures of lower [1.1.1.1]- and [2.2.2.2]paddlanes (structure **51**) do not

Table 3. Proton affinity PA (kcal mol⁻¹) in the gas phase (298 K) for structures with a tetracoordinate pyramidal carbon atom.

Compound	Calculation method	PA	Ref.
39	CCD/6-311 + G**	236.8	88
	HF/3-21G	253.3	82
	MP2/6-311 + G**//MP2/6-31G*	230.6	86
28b	MP2/6-311 + G**//MP2/6-31G*	269.3	86
46	MP2/6-311 + G**//MP2/6-31G*	280.1	86
47	MP2/6-311 + G**//MP2/6-31G*	280.8	86
48	MP2/6-311 + G**//MP2/6-31G*	281.8	86
Tetramethyl-substituted hemispirooctaplane 47	MP2/6-311 + G**//MP2/6-31G*	285.1	86
1,8-Bis(dimethylamino)naphthalene (proton sponge)	MP2/6-311 + G**//HF/6-31G*	245.5	102
	Experimental data	245.7	103

correspond to minima in the PES;^{48, 52, 105} according to the results of MINDO/3 and MNDO semiempirical calculations,⁴⁸ structure **51** relaxes towards unusual structure **51a** in which the distance between two planar carbon atoms is only 1.56 Å.



Essentially pyramidalised tetracoordinate carbon atoms are found in yet another group of sterically strained compounds, tricyclo[$n.1.0.0^{1,3}$]alkanes.^{99–101, 106–109} The first member of this series of bridged spirooctaplanes, compound **52**, has a sufficient lifetime along the pyramidane-to-spiropentane rearrangement pathway to be detected at -55 °C.^{107, 110} Tricyclo[2.1.0.0^{1,3}]alkane (**53**) is still unknown but the next members of this series — compounds **54**, **55** and some of their derivatives — have been prepared and isolated.^{99–101}

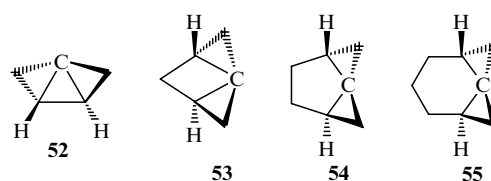
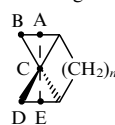


Table 4 summarises the data characterising the spatial structures and strain energies of molecules **52–55**. As the ring size increases, *i.e.*, on passing from compound **52** to compound **55**, the CH_2-C-CH_2 angle rapidly decreases, together with the strain energy of the molecule. For compound **55**, the strain energy almost does not differ from that of spirooctaplane (63 kcal mol⁻¹).

Table 4. Angular parameters characterising the configuration of the quaternary carbon atom in molecules **52–55** and strain energies of these structures found by MP2/6-31G** *ab initio* calculations.¹⁰¹

Compound	n	Folding angle ^a /deg	Twisting angle ^b /deg	Strain energy /kcal mol ⁻¹
52	0	71.5	21.3	137.2
53	1	47.8	6.1	115.5
54	2	26.1	6.3	79.2
55	3	15.0	1.5	66.0

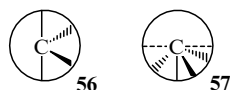
^a The folding angle is $180^\circ - \angle ACE$; ^b the twisting angle is $90^\circ - \gamma$ (γ is the dihedral angle between the ABC and CDE planes).



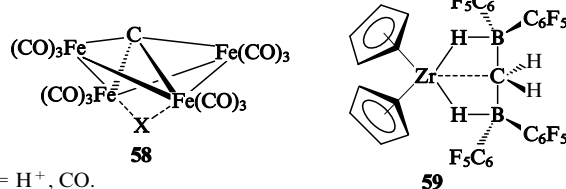
V. Tetracoordinate carbon atom with a bisphenoidal configuration of bonds and inverted tetracoordinate carbon atom

The size of the CH_2-C-CH_2 angle in tricyclo[2.1.0.0^{1,3}]alkane **53** approaches 180° , and the bond configuration at a quaternary carbon atom is fairly close to that found in bisphenoid **56** ('butterfly' conformation). It has been proposed to call tetracoordinate carbon centres of this type 'half planar'.⁶⁴ In terms of the topological definition,⁹ according to which structures with tetracoordinate carbon atoms are divided into classical and non-classical (anti-van't Hoff–LeBel) ones, depending on the arrangement of the four bonds around carbon — either in both or in only one hemisphere, respectively, — structures of type **56** should be considered non-classical. For compounds containing tetracoordi-

nate carbon atoms, the only other non-classical topological form is represented by structure **57** with an inverted configuration of bonds at the carbon atom.



The half planar tetracoordinate carbon atom occurs in the structures of carbide clusters **58**^{111–113} and in zirconium complex **59**.¹¹⁴



X = H⁺, CO.

The electronic factors promoting stabilisation of the half planar carbon atom in these structures are similar to those effective in structures with planar or pyramidal centres (Fig. 12). In this case, as in the case of planar (D_{4h}) or pyramidal (C_{4v}) structures, the highest occupied MO of the methane molecule having C_{2v} symmetry is formed by the $2a_1$ AO of the lone electron pair of carbon (this AO is delocalised to a very low extent over equatorial C–H bonds). The electrons of this orbital are not involved in bonding, which results in weakening of the σ bonds formed by a half planar carbon atom. Therefore, σ -donor (for example, BHAr₂⁻ groups in compound **59**) and π -acceptor groups are expected to stabilise the tetracoordinate half planar carbon atom. These views have been confirmed by calculations⁶⁴ for model compounds **60**. The results of these calculations are given in Table 5.

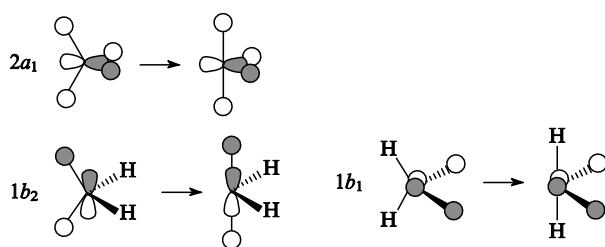
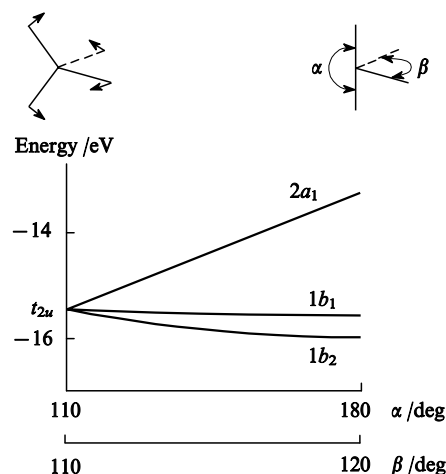
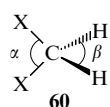


Figure 12. Walsh diagram illustrating the transformation of the t_{2u} orbitals of tetrahedral methane (see Fig. 2) during its deformation into the structure with a half planar carbon atom.⁶⁴

Table 5. Deformation energies (eV) of tetrahedral structures (the α and β angles correspond to structures with the minimum energy) and charges on the carbon atom in compounds **60** determined by EHMO calculations.⁶⁴

X	α^a /deg	β^a /deg	ΔE^b /eV	$\Delta E'^c$ /eV	q_C
H	109.5	109.5	3.06	0.98	-0.44
Me	117	105	3.76	1.15	-0.39
OH	112	117	6.46	2.65	+0.82
CN	114	107	2.70	0.93	-0.01
BH ₃ ⁻	120	102	2.06	0.54	-0.96

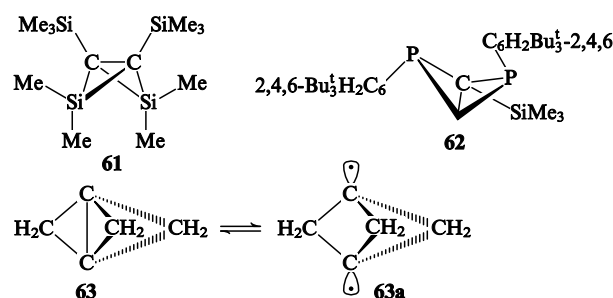
^a The α and β values are given for the tetrahedral configuration corresponding to the global minimum in the PES of disubstituted methane **60**.

^b The deformation energy of the tetrahedral structure into a structure with a half planar carbon atom ($\alpha = 180^\circ$, $\beta = 140^\circ$). ^c The deformation energy of the tetrahedral structure into a structure with a carbon atom geometry identical to that in complex **59** ($\alpha = 180^\circ$, $\beta = 140^\circ$).

In derivative **60** with σ -donor substituents (X = BH₃⁻) in the axial positions, the energy gap between the tetrahedral and bisphenoidal conformations decreases by 1.0 eV, mainly, due to substantial charge transfer to the central carbon atom (*cf.* the charges q_C on half planar carbon atoms).

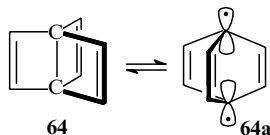
It should be noted that the conformation **56** is destabilised by the strong effect of the π -donor and σ -acceptor hydroxy group, pulling the electron density off the half planar carbon. As a result, the carbon atom acquires a positive charge. Stabilisation of configuration **56** in complex **59** and the rare earth metal complexes (Me₃SiCH₂)Y[(μ -CH₂)₂SiMe₂][(μ -OBu^t)Li(THF)₂]₂ (see Ref. 115) and (Me₃SiCH₂)Sm[(μ -OPh)(μ -CH₂SiMe₃)Li(THF)][(μ -OPh)₂.Li(THF)] (see Ref. 116) is also promoted by the additional coordination of a half planar carbon atom to a metallic centre formed due to electron donation from the carbon $2a_1$ AO to the metal AO.

An inverted (umbrella) configuration of bonds at the carbon atom (structure **57**) can be found in the molecules of some bicyclobutane derivatives, for example, in structures **61**¹¹⁷ and **62**,¹¹⁸ and undoubtedly, in the molecule of highly strained [1.1.1]propellane (**63**), which was synthesised by Wiberg and Walker¹¹⁹ in 1982.



The structures, methods of synthesis and the chemistry of [1.1.1]propellane and its derivatives and higher homologues have been considered in numerous reviews^{120–122} and theoretical studies.^{85, 123–126} As noted by Wiberg,¹²² [1.1.1]propellane appears to be the first multiatomic molecule whose stability, structure, vibrational and photoelectron spectra, and the enthalpy of formation were predicted before its synthesis and all the theoretical predictions were successfully confirmed by subsequent experimental research. Theoretical investigations of compound **63** were mainly focused on elucidating the nature of the central C–C bond and the possibility of its dissociation to give the isomeric biradical **63a**. The results of *ab initio* calculations^{122, 125, 126} convincingly confirm the conclusion, drawn on the basis of orbital interaction analysis,¹²³ stating that the non-dissociated form **63** is preferred. According to HF/6-31G* calculations, the energy benefit is equal to 65 kcal mol⁻¹. The energy gap between structures **63** and **63a**, interrelated by 'bond-stretch isomer-

ism',^{127, 128} is rather narrow (the difference between the heats of formation of these compounds is only ~ 5 kcal mol⁻¹). The situation is reversed on passing to [2.2.2]propellatriene (**64**). Although the structure **64** with an inverted carbon atom is an energy minimum, the singlet biradical **64a** is energetically more favourable (by 5.1 kcal mol⁻¹), as shown by CASSCF/6-31G* calculations.¹²⁹



The inverted configuration of carbon atoms has been predicted by MP2/6-31G** and B3LYP/6-31G** calculations (see Ref. 130) for a series of polycyclic structures with a bicyclooctane skeleton.

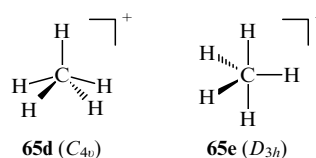
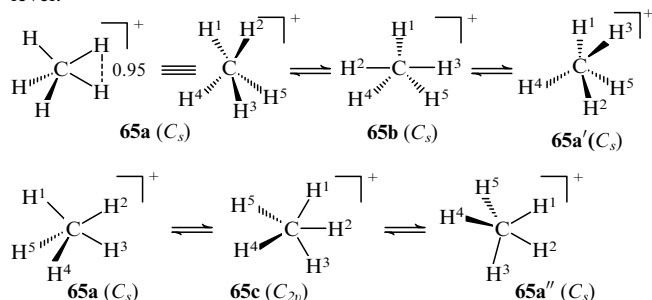
VI. Carbonium ions with penta-, hexa- and heptacoordinate carbon atoms

The preceding Sections of the review were devoted to unusual (*i.e.*, other than tetrahedral) types of carbon coordination. In this and subsequent Sections, we consider compounds of hypercoordinate carbon in which a carbon atom is linked by covalent bonds to five and more atoms. Since a carbon atom has only four valence electrons, it can form only four two-electron (classical) bonds; hence hypercoordination of carbon implies delocalisation of σ -electrons.¹³¹ This effect does not fit into the scope of classical octet theory.^{3, 132} It is noteworthy that the notion of non-classical structure was first introduced to describe the structures of hypercoordinate carbon.^{131, 133}

1. Methonium ion

The methonium ion is the parent compound for pentacoordinate carbon derivatives. Protonated methane (**65**) was first detected in the gas phase by mass spectroscopy by Talrose and Lubimova^{134, 135} and in superacid liquid media by Olah and co-workers.^{136–138} The methonium ion is important for astrophysics, as its microwave spectrum serves as an indicator of methane content in molecular galactic clouds. The methonium ion is the prototype of intermediate structures formed upon ion–molecular interactions¹³⁹ and, what is more important, in the reactions of saturated hydrocarbons with electrophiles;^{3, 140–143} therefore, it comes as no surprise that the study of its structure and properties has received particular attention from theoreticians. The results of calculations (up to the MP4SDQ/6-311G**//MP2/6-31G* level) carried out before 1984 are summarised in a monograph.¹⁴⁴

The possible structures of the CH₅⁺ cation are described by conformations **65a–e**. The global minimum in the PES of CH₅⁺ corresponds to structure **65a** with C_s symmetry, which can be regarded as a complex of the CH₃⁺ (C_{3v}) cation with an H₂ molecule. The stability of this complex is ensured by the formation of the 3c–2e bond (according to theoretical and experimental data, the energy of dissociation into fragments is 42–44 kcal mol⁻¹). This conclusion was confirmed by recent calculations at the most advanced (of those attainable to date) theoretical level.^{145–149}



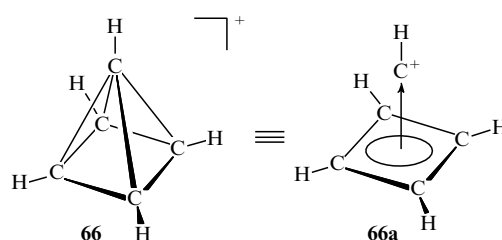
Structure **65b** (C_s) corresponds to a first-order saddle point in the PES and serves as the transition state for rotation of the H₂ fragment; the potential barrier to this process found using various calculation methods is exceptionally low (less than 0.1 kcal mol⁻¹). Structure **65c** (C_{2v}) is also a transition state but of another process, namely, the exchange by hydrogen atoms between the CH₃ and H₂ fragments. A number of experimental studies have been devoted to isotope exchange reactions of this type proceeding at high rates.^{3, 137, 140} The energy of structure **65c** is only 0.9 kcal mol⁻¹ higher than the energy level of structure **65a**; with allowance for the zero-point vibrations, structures **65a–c** are nearly equivalent in energy. This means that proton 'exchange' in the methonium ion is almost barrier-free even at 0 K. Thus it has been hypothesised that the CH₅⁺ cation does not have any definite structure at all. It was proposed that the methonium cation should be considered as an intramolecular liquid and its structure described by statistical functions rather than atomic coordinates (see the publication¹⁵⁰ concerning the structure of the methonium cation entitled 'Cheshire cat smiles'). Powerful experimental proof pointing to an extremely high degree of stereochemical non-rigidity (fluxionality) of methonium cation was obtained when a high-resolution IR spectrum of this cation was finally recorded (after many years of unfruitful efforts) in a matrix of a small number ($n = 1–6$) of hydrogen molecules whose presence is needed for retarding the exchange processes. This spectrum proved to be much more complicated than would be expected for a structure having any definite type of symmetry. Indeed, in the 2770–3150 cm⁻¹ range alone, ~ 900 spectral lines were found.

The question of whether the methonium cation with its unusual fluxional behaviour can be described by a particular molecular structure is still debatable.^{148, 150–152} However, such a question does not arise for its derivatives. There exist a fairly broad spectrum of compounds in which structures like **65a,c**^{3, 138, 139, 149} or **65b** are realised. The latter is found, in particular, in the structures of σ -complexes formed by metal ions (from Sc⁺ to Cu⁺) with the methane molecule. The structure and stereodynamics of these complexes have been studied theoretically (using density functional theory techniques) in relation to simulation of the problem of decreasing the barrier to the stereomutation of the methane molecule.⁶² It was shown that, when this transformation is catalysed by metal ions, the potential barrier to enantiotopomerisation decreases to 43–50 kcal mol⁻¹. In addition to the stationary points corresponding to structures **65a–c**, the PES of CH₅⁺ was found to contain higher-order stationary points corresponding to highly symmetrical forms **65d,e**.

Stabilisation of such bond configurations at a pentacoordinate carbon atom can be achieved only in more complicated structures.

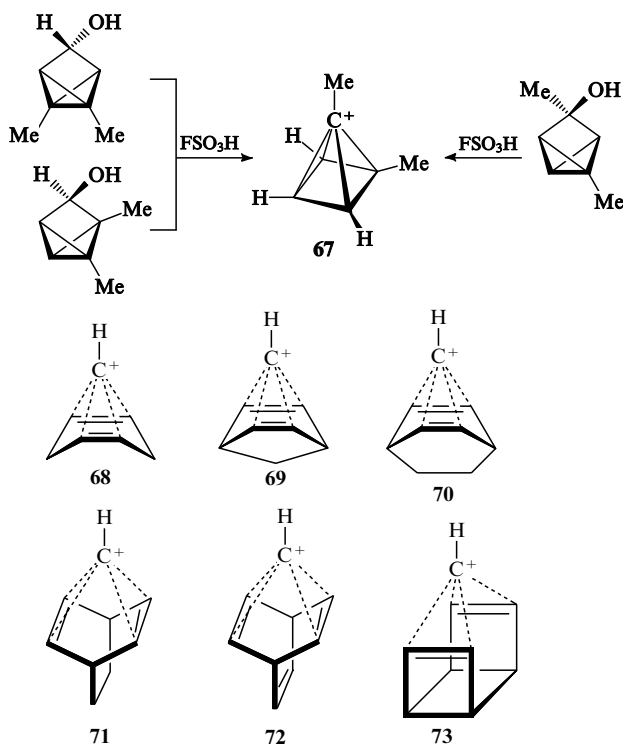
2. The pyramidal cation (CH)₅⁺

The (CH)₅⁺ cation (**66**) is a classical example of a structure with a square-pyramidal configuration of bonds about a pentacoordinate carbon atom.^{153–155}

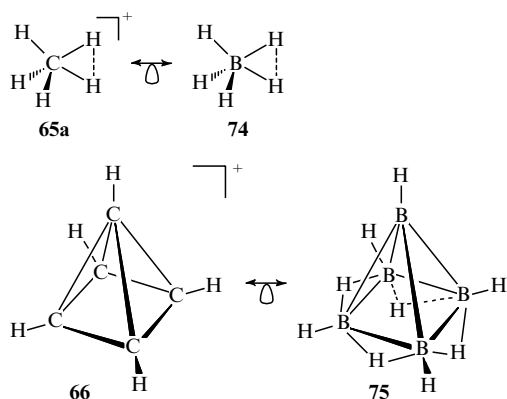


The possibility of the existence of a stable cation of this type was pointed out by Williams.¹⁵⁶ This prediction soon received theoretical substantiation based on the analysis of orbital interactions and EMHO calculations.¹²⁷

Almost simultaneously, Masamune *et al.*¹⁵⁷ synthesised the first derivative of the pyramidal $(\text{CH})_5^+$ cation, compound **67**, its bishomo-derivatives and other analogues (**68–73**).^{158–160}



Just as the CH_5^+ cation (**65a**) resembles the structure of the stable^{153–155} isoelectronic and isolobal pentahydridoborane **74** with a hypercoordinate boron atom, the $(\text{CH})_5^+$ cation (**66**) has the structure of the isolobal *nido*-pentaborane **75**.



The geometry of the pyramidal cation **66** is shown in Fig. 13. In the $(\text{CH})_5^+$ cation, unlike pyramidane **39**, which is its conjugate base, the C–C bonds involving the apical carbon atom are only slightly elongated compared with usual single C–C bonds. The lengths of the C–C bonds in the four-membered ring are intermediate between the lengths of standard single and double bonds. The C–H bonds in this ring are deflected toward the apical centre, as in pyramidane **39**, which is due to favourable overlap of the p_x and p_y orbitals of the apical carbon with the σ^* -orbitals of the C–H bonds.

The pyramidal cation **66** has an unusual electronic structure: its electron density is concentrated on the apical carbon atom. Thus according to CCD/6-311+G** calculations, the negative charge on this carbon equals -0.18 and the whole positive charge

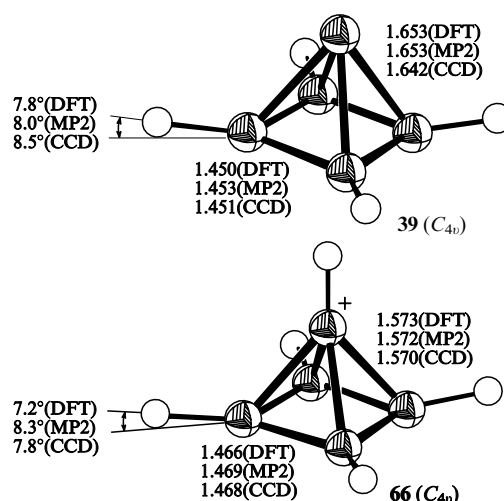
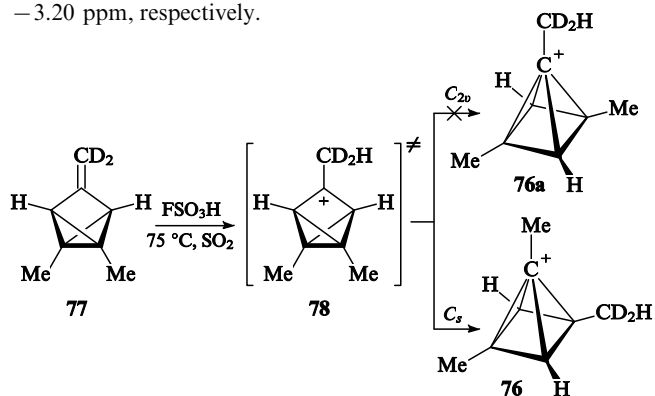


Figure 13. Geometric characteristics of the pyramidane molecule **39** and the $(\text{CH})_5^+$ (**66**) cation determined by the B3LYP/6-311+G** (DFT), MP2(full)/6-311+G** (MP2) and CCD(full)/6-311+G** (CCD) calculations.⁸⁸

is dispersed in the basal plane.⁸⁸ This type of charge distribution accounts for the typical pattern of the ^1H and ^{13}C NMR spectra of pyramidal cations **66**, **68–73**, namely, the carbon signals of the apical groups are shifted to exceptionally high fields [the $\delta^{13}\text{C}$ chemical shifts are from $+2.4$ (for structure **69**) to -33.6 (for structure **72**)] and the signals for the basal carbon atoms are shifted downfield. This provides the possibility of easy detection of the formation of non-classical pyramidal cations in the course of reactions.

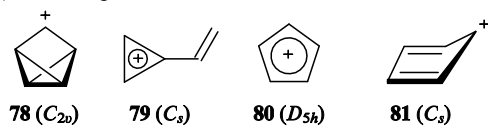
The synthesis of the 1,3,5-trimethyl derivative **76** from 1,5-dimethyl-3-methylenetricyclo[2.1.0.0^{2,5}]pentane (**77**) serves as a good illustration for the mechanism of transformation of the tricyclo[2.1.0.0^{2,5}]pentane skeleton in the pyramidal structure precursors **78**.¹⁶¹ It was found that the CD_2H group formed upon protonation of the deuterated compound **77** occupies only the basal position in cation **76**, *i.e.*, during the transformation of compound **77** into cation **76**, the deuterium label is not transferred from the basal carbon to the apical one. Thus, the formation of cation **76** does not proceed along the C_{2v} -symmetry pathway but follows the C_s pathway, allowed by the principle of orbital symmetry conservation.⁴ The chemical shifts ($\delta^{13}\text{C}$) of the apical quaternary carbon atom and the methyl-group carbon atom attached to it in compound **76** are about -20.89 and -3.20 ppm, respectively.



The eight-electron rule, like more general electron count rules for polyhedral structures,^{92, 162, 163} explains adequately the kinetic stability of the $(\text{CH})_5^+$ cation and its derivatives. The only difference in the orbital interaction diagram of cation **66** from the orbital interaction diagram of the pyramidane molecule presented in Fig. 11 is the fact that the nonbonding $2a_1$ MO localised on the

apical carbon atom in pyramidane **39** is transformed into the orbital of the C–H σ -bond in cation **66**.⁹

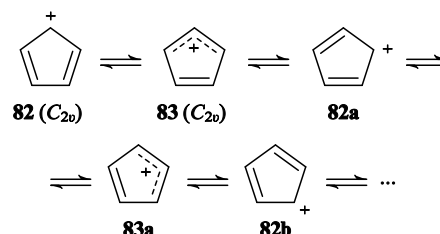
The square-pyramidal structure **66** is not the most stable form of $(\text{CH})_5^+$. According to the data of *ab initio* calculations^{164–166} (Table 6), the global minimum in the PES of $(\text{CH})_5^+$ is the vinylcyclopropenyl cation (**79**), which is only 2–3 kcal mol⁻¹ more favourable than the D_{5h} structure of the cyclopentadienyl cation (**80**) in the triplet electronic state.



However, the rearrangements **66** → **79** and **66** → **80** do not take place, the former — due to the absence of a reaction valley connecting the cations **66** and **79** in the PES of the singlet electronic state of $(\text{CH})_5^+$ and the latter rearrangement is spin forbidden. Therefore, it is important to know to what extent the pyramidal structure **66** is energetically less favorable than the other possible structures of the $(\text{CH})_5^+$ cation which are stationary points in the PES of the singlet electronic state.

Early MINDO/3 semiempirical calculations^{167–169} provided the conclusion that the nonplanar C_s structure of the cyclopentadienyl cation **81** is preferred from the energy standpoint. However, more recent *ab initio* calculations^{88, 164, 165} showed that the C_s structure (**81**) does not correspond to a minimum on the PES and relaxes to the planar C_{2v} form (**82**), which is only 3–4 kcal mol⁻¹ energetically more favourable than the pyramidal structure **66** and is separated from it by a rather high potential barrier. In the case of the cyclopentadienyl cation, one more C_{2v}

form (**83**) is possible; it is almost equivalent in energy to the C_{2v} structure **82**. According to the most advanced calculations,^{88, 165} structure **82** is a local minimum on the PES, while structure **83** is a first-order saddle point. Structure **83** corresponds to the transition state between the degenerate isomers (topomers) of structure **82**. The potential barrier to interconversion of the topomers of the singlet cyclopentadienyl cation **82** is only 0.1–0.2 kcal mol⁻¹, i.e., the reaction proceeds almost without a barrier (*cf.* the topomerisation of CH_5^+).^{88, 165} The most important results of calculations^{88, 92, 164–166} are summarised in Table 6.



The C_{4v} configuration of bonds at the pentacoordinate carbon atom can be realised in electrically neutral structures formed upon replacement of the CH^+ group by the isolobal BH group. This can give rise to a series of stable square-pyramidal *nido*-carboranes whose electronic structure would satisfy the eight-electron rule. Carboranes **84b,c**, which are isomers of borole **84a**, shown in Fig. 14 are examples of such structures. As shown by calculations,⁹⁸ structure **84c** containing a pentacoordinate pyramidal

Table 6. Total and relative energies of the pyramidal $(\text{CH})_5^+$ cation **66** and isomeric structures **78**, **82** and **83** in the ground singlet electronic state calculated by *ab initio* quantum chemistry methods.

Calculation method	$-E_{\text{tot}}$ /a.u.	ΔE /kcal mol ⁻¹	λ	Ref.
Isomer 66 (C_{4v})				
HF/6-31G*	191.86520	0 (42.7) ^a	0	165
MP2/6-31G**//6-31G*	192.5263	0 (12.9) ^a	0	164
MP4SDTQ/6-31G**//MP2/6-31G*	192.58611	—	0	165
B3LYP/6-311+G**	(193.1679)	—	0	88
MP2(full)/6-311+G**	192.68932	—	0	88
CCSD/6-311+G**	192.70330 ^b	—	0	88
Isomer 78 (C_{2v})				
B3LYP/6-311+G**	(193.0098)	—	1 ^c	88
MP2(full)/6-311+G**	192.64397	—	1 ^c	88
CCSD/6-311+G**	192.66056	—	1 ^c	88
Isomer 82 (C_{2v})				
HF/6-31G*	191.90215	-23.2	0	165
MP2/6-31G**//6-31G*	191.9105	-3.7	1 ^c	164
MP4SDTQ/6-31G**//MP2/6-31G*	192.52005	-3.5	0	165
Isomer 83 (C_{2v})				
HF/6-31G*	191.90235	-23.3	0	165
MP4SDTQ/6-31G**//MP2/6-31G*	192.51986	-3.4	1 ^c	165

^a The values in parentheses are the energies of the relatively most stable cyclic D_{5h} structure **80** of the cyclopentadienyl cation in the triplet state.

^b Calculation by the G2 method [approximately equivalent to QCISD(T)/6-311+G(3df,2dp) in the approximation level with allowance for the zero-point vibration energies] gives the values $-E_{\text{tot}} = 192.68503$ a.u. and $\Delta E = 13.1$ kcal mol⁻¹ for structure **66** (relative to the energy of **80**) (see Ref. 166). ^c First-order saddle point (transition state).

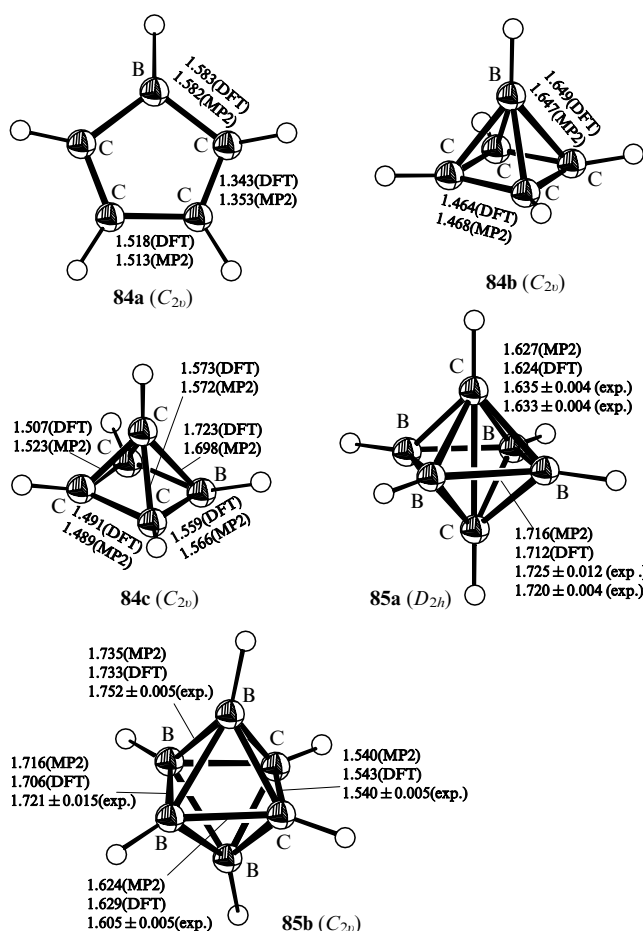


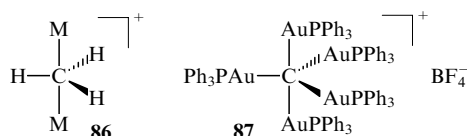
Figure 14. Geometric characteristics and relative energies of the structures of borole (**84a**), its non-classical pyramidal isomers **84b** and **84c**, and 1,6- (**85a**) and 1,2-closo-carboranes $\text{C}_2\text{B}_4\text{H}_6$ (**85b**) calculated using the MP2(full)/6-311+G** and B3LYP/6-311+G** methods.^{98, 172} (Experimental data for closo-carboranes $\text{C}_2\text{B}_4\text{H}_6$ were taken from Ref. 172.)

carbon atom, being thermodynamically less stable than structures **84a,b**, is likely, nevertheless, to have rather high kinetic stability. A similar configuration is found for the carbon atoms in square-bipyramidal *closo*-carboranes whose structures have been studied in detail both experimentally³ and theoretically.^{170–172}

The stability of the bipyramidal systems produced by adding apical groups to a π -conjugated ring is controlled by the ten-electron rule.⁹ Irrespective of the size of the central ring, these structures have only five bonding MO, and the total number of electrons (the number of ring π -electrons + the number of valence electrons in the apical group) in a stable bipyramidal molecule or ion should not exceed 10. The simplest hydrocarbon system which meets this condition is the octahedral $C_6H_6^{4+}$ ion. However, this compound is unstable for electrostatic reasons. The replacement of four CH^+ groups by BH groups results in two stable electrically neutral bipyramidal 1,6- (**85a**) and 1,2-carboranes (**85b**), which contain pyramidal pentacoordinate carbon centres (see Fig. 14).

3. Trigonal-bipyramidal configuration of bonds at a pentacoordinate carbon atom

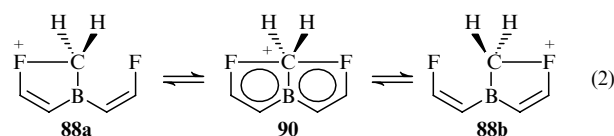
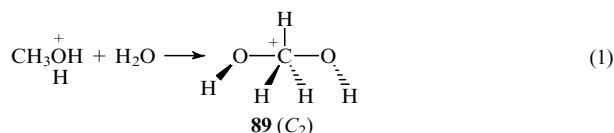
A trigonal-bipyramidal configuration of bonds is not realised in the methonium ion CH_3^+ , but can be stabilised by replacing the hydrogen atoms by electropositive atoms or groups. According to HF/4-31G calculations,¹⁷³ the D_{3h} conformation is preferred for disubstituted cations **86**. As shown by X-ray diffraction analysis, this configuration occurs in penta-aurated methonium ion **87**^{174,175} (the ligand AuL is isolobal to single-electron H and CH_3 groups).



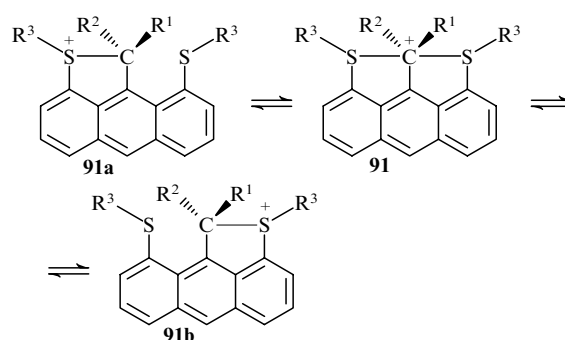
M = Li, BeH.

The electronic structure of compounds with the D_{3h} configuration of bonds at the central atom, which is a Main Group element, can be represented by a combination of three equatorial $2c-2e$ bonds formed by the sp^2 orbitals of the central atom and one hypervalent $3c-2e$ bond of the central atom with two apical ligands. The greater the difference between the electronegativities of the atoms forming this bond, the lower its electron deficiency and the greater the contribution of the electrostatic component which stabilises the structure (for discussion of factors determining the structure of hypervalent compounds, see Refs 5, 176–182). Higher stability of such polarised structures is attained when ligands with like charges are separated in space, *i.e.*, placed in the apical positions of the D_{3h} structure.

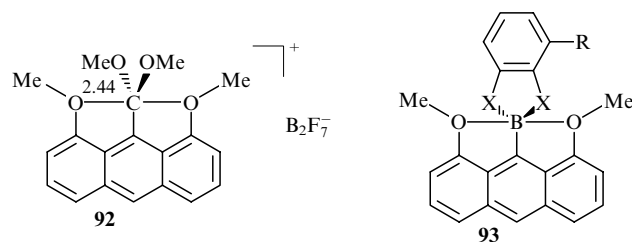
By following this scheme, one can also propose another way of stabilising the trigonal-bipyramidal configuration of bonds at pentacoordinate carbon atoms in carbonium ions. In this case, a considerable difference between the electronegativities of the central atom and the apical ligands is attained by using atoms or groups with high electronegativity as the ligands. This type of stabilisation of trigonal-bipyramidal structures of transition states is peculiar to S_N2 reactions at tetrahedral carbon atoms involving compounds with highly nucleofugal (including positively charged) groups. Examples are¹⁸³ two model reactions, namely, degenerate gas-phase hydrolysis of protonated methanol [reaction (1)] and intramolecular rearrangement of hypothetical cation **88** [reaction (2)].



The results of MP2(full)/6-31G** and MP2(full)/6-311++G** calculations showed that putative intermediates **89** and **90** containing pentacoordinate carbon atoms with the trigonal-bipyramidal configuration of bonds, which are formed presumably in these reactions, are considerably stabilised: the differences between the energies of the intermediates and the initial structures amount to 12.8 and 3.8 kcal mol⁻¹. However, neither these nor other similar structures correspond to minima in the PES and, hence, they are not intermediates but are transition states. A similar result has been obtained in an attempt to 'freeze' (this term was proposed by Martin¹⁸⁴) the pentacoordinate structure of transition state **91** formed during the rearrangement of 1,8-bis(arylthio)anthracene-9-carbonium ion.¹⁸⁵ In this cation, the heteropentadiene fragment is incorporated in a rigid cage, which fixes both the attacking and leaving groups in the orientation required by the S_N2 reaction conditions.^{10,186–188} The structure **91** corresponds to a transition state (rather than an intermediate) of a reaction with a low potential barrier whose height is 10–20 kcal mol⁻¹ (depending on the solvent and the substituents).



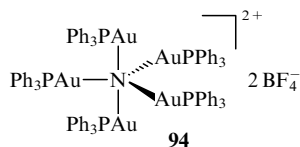
Stabilisation of a structure with a trigonal-bipyramidal configuration of bonds at the pentacoordinate carbon atom was achieved by Akiba *et al.*¹⁸⁹ They modified the dynamic system **91** by replacing the sulfur atoms by more electronegative oxygen atoms and thus ensured better conditions for collinearity of the axial bonds. They isolated and characterised the salt **92**, the cation of which contains a pentacoordinate carbon atom with a trigonal-bipyramidal configuration of bonds. The complete structural analogy between compound **92** and compounds with a pentacoordinate boron atom was confirmed by X-ray diffraction analysis of neutral pentacoordinate compounds of boron **93** (10-B-5) prepared recently by the same researchers.¹⁹⁰



X = O, S; R = H, OMe.

Thus, by varying the structure, one can embody all the theoretically possible types of coordination of a pentacoordinate carbon atom. Incidentally we would like to mention interesting results of theoretical^{155,191,192} and experimental^{175,192,193} studies of the structures of dicationic systems containing pentacoordinate nitrogen atoms, which are isoelectronic to carbonium cations. In these studies, relying on high-level (QCISD/6-311G** and CCSD(T)/

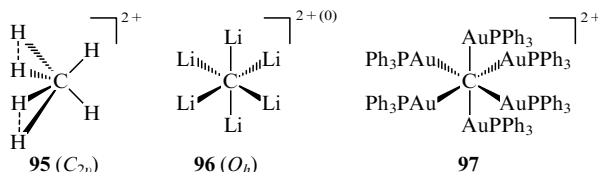
aug-cc-pVTZ) calculations, a structure with C_{4v} symmetry was attributed to the NH_5^{2+} dication (according to X-ray diffraction analysis,¹⁹³ its penta-aurated analogue **94** has a perfect D_{3h} configuration).



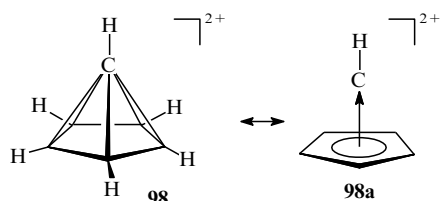
4. Hexa- and heptacoordinate carbonium ions

In the most symmetrical octahedral O_h configuration, structures of type AH_6 , where A is a Group IV element, have four bonding molecular orbitals, which can be occupied by eight electrons ($1a_{1g}^2 t_{1u}^6 e_g 2a_{1g}$).^{5,6,9} One might expect that this type of octahedral structure would exist for the diprotonated methane CH_6^{2+} . Nonempirical calculations^{194–197} confirm the expected stability of the CH_6^{2+} dication. Besides, they indicate that the C_{2v} form in which the eight valence electrons are distributed over two $2c-2e$ and two $3c-2e$ C–H bonds, rather than the O_h form, is preferred for dication **95** for energy reasons.

As for the methonium ion **65**, dication **95** is a stereochemically non-rigid structure. According to MP3/6-31G**//6-31G** calculations,¹⁹⁵ redistribution of hydrogen atoms between the C–H bonds in the structure **95** in the gas phase requires overcoming a small potential barrier (only 4.3 kcal mol⁻¹). The octahedral bond configuration, which is unfavourable for the diprotonated methane, can be stabilised for its derivatives. Examples of this type are the CLi_6^{2+} (**96**)^{198,199} and $\text{C}(\text{AuPPh}_3)_6^{2+}$ (**97**) dications.¹⁷⁴ The latter has been isolated preparatively as the tetrafluoroborate salt.¹⁷⁴

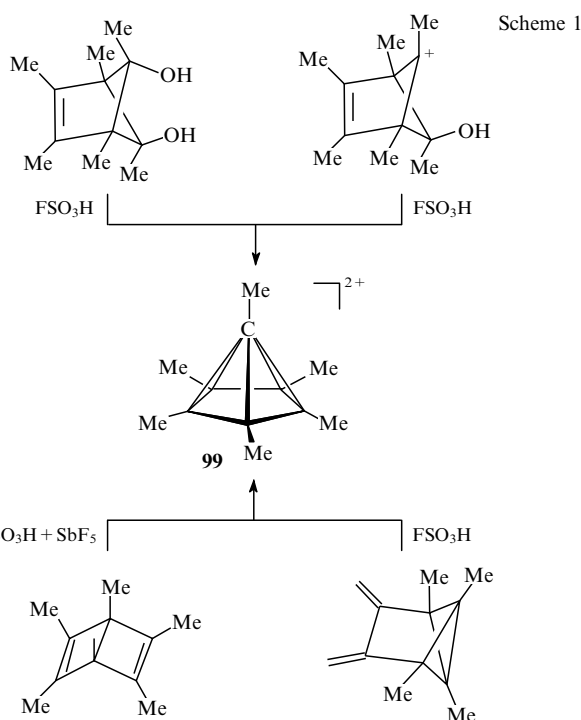


The pyramidal dication **98** is the prototype of polyhedral organic structures containing a hexacoordinate carbon atom.

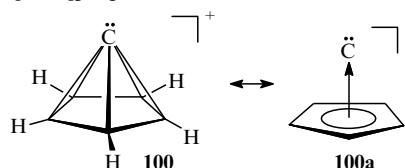


The hexamethyl derivative **99** of this dication has been prepared by Hogeveen and Kwant^{200,201} in superacid media using various precursors (Scheme 1).

The ¹H and ¹³C NMR signals of the apical centres in **99** occur at a high field (δ ¹³C –2.0 ppm).^{200,201} As in the case of the $(\text{CH})_5^+$ (**66**) cation, the pyramidal structure of $(\text{CH})_6^{2+}$ (**98**) does not correspond to the deepest minimum in the PES. The transition of this structure to the energetically favourable isomer (according to HF/3-21G calculations), the fulvene dication, is associated with overcoming a high potential barrier.²⁰² The kinetic stability of the dication **98** is interpreted by the eight-electron rule.⁹ This rule also predicts the existence of another pentagonal-pyramidal non-classical structure **100**, which is the conjugate base of the dication **98** (in the same way as pyramidane **39** is the conjugate base for the pyramidal cation **66**). Nonempirical calculations⁸⁸ carried out at different approximation levels indicate that structure **100** actually corresponds to a minimum on the C_6H_5^+ PES. As can be seen from the data presented in Fig. 15, the bonds connecting the apical and the basal carbon atoms in the dication **98** are substantially



elongated with respect to similar bonds in the square-pyramidal ion **66**. In the cationic carbene **100**, the lengths of these bonds approach the greatest values known for C–C bonds.^{203,204} The longest single C–C bond known to date (1.80 Å) has been found in a [1.1.1]propellane derivative.⁴⁶



A hexacoordinate carbon atom can exist not only in ions but also in electrically neutral species. The octahedral CLi_6 (**96**) molecule can serve as an example.^{144,198,205} This molecule contains two valence electrons more than could be accommodated in the four bonding MO of the octahedral structure. These electrons

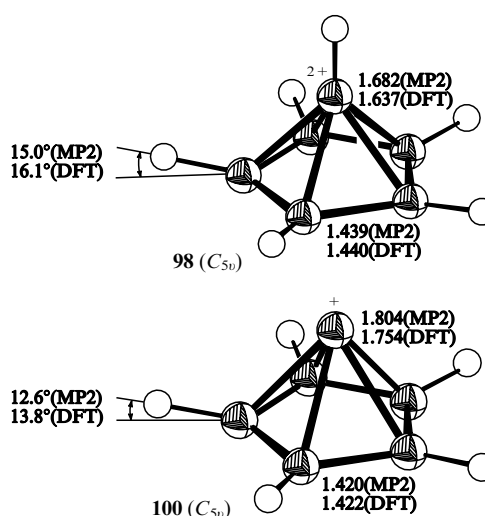
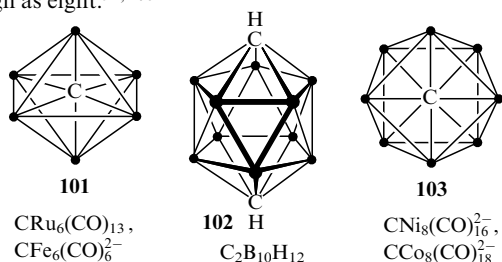
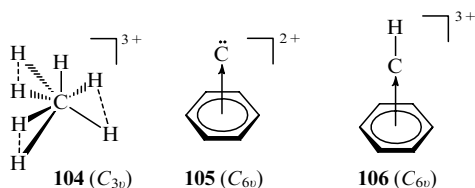


Figure 15. Geometric characteristics of the C_6H_5^+ cation (**100**) and $\text{C}_6\text{H}_6^{2+}$ (**98**) dication calculated by the B3LYP/6-311+G** and MP2(full)/6-311+G** methods.⁸⁸

are localised in the C–Li bonds. An additional bonding a_{1g} MO having a spherical symmetry is formed by delocalisation of orbitals of the lithium atoms surrounding the central carbon atom. In relation to the C–Li bonds, this MO is antibonding; nevertheless, it makes a substantial contribution to the molecular stabilisation due to ligand–ligand interactions [cf. stabilisation of the tetracoordinate planar carbon atom in structures **24**–**26** (see Fig. 7)]. Multicentre bonds also determine the stability of a series of carbide clusters **101** and carboranes **102** in which the formal coordination number of carbon is six. In nickel and cobalt clusters **103** with an antiprism structure, the coordination number is as high as eight.^{94,206}



The simplest stable structure containing a heptacoordinate carbon atom is triprotonated methane **104**. In this compound, eight valence electrons are distributed over three $3c-2e$ C–H₂ bonds and one $2c-2e$ C–H bond.¹⁹⁷ The results of MP2/6-31G** and QCISD(T)/6-311G** calculations indicate that the whole positive charge in structure **104** is concentrated on the hydrogen atoms (each carries a charge of $\sim +0.6$), whereas the carbon atom is negatively charged ($q_{\text{C}} = -1.27$). Thus, the stability of this three-charged ion is mainly due to electrostatic forces.



Electrostatic interactions are also important for stabilisation of pyramidal cations with a six-membered basal ring. According to MP2/6-311 + G** and B3LYP/6-311 + G** calculations,⁸⁸ the di- and trication structures **105** and **106** in which the apical carbon atoms are coordinated to six and seven centres, respectively, exist, as predicted by the octet rule, as fairly deep minima in the PES.

The geometry calculated for structures **105** and **106** is shown in Fig. 16. In both cases, the $\text{C}_{\text{ap}}-\text{C}_{\text{bas}}$ distances exceed the critical values for the single C–C bond lengths and the electron populations of the $\text{C}_{\text{ap}}-\text{C}_{\text{bas}}$ bonds are rather low.

The presence of one $2c-2e$ C–H bond in the structure of triprotonated methane **104** provides an opportunity to replace this bond by a three-centre $3c-2e$ C–H₂ bond and thus to approach the CH_8^{4+} tetracation. However with a charge of +4, the Coulomb repulsion of the hydrogen atoms, which carry the entire positive charge, becomes the predominant destabilising factor. The results of MP2/6-31G** calculations showed that the CH_8^{4+} ion is unstable. The corresponding PES contains no minima for any of the possible CH_8^{4+} structures.^{143,197} Meanwhile, the isolobal trinuclear boronium ion BH_8^{3+} is kinetically stable, although the calculation indicates that various pathways of its dissociation are highly exothermic. The structure of BH_8^{3+} (**107**) found by MP2/6-31G** and QCISD(T)/6-311G** calculations has four tetrahedrally oriented $3c-2e$ B–H₂ bonds.²⁰⁷

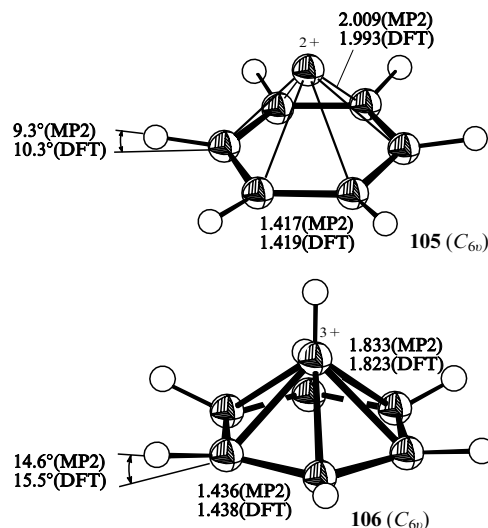
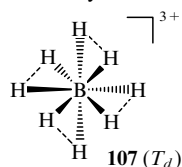
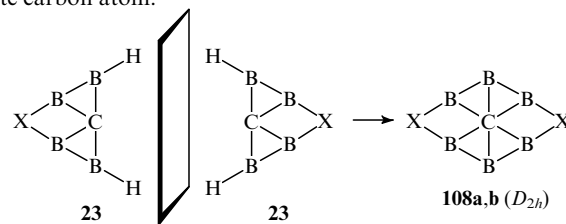


Figure 16. Geometric characteristics of the $\text{C}_7\text{H}_6^{2+}$ dication (**105**) and $\text{C}_7\text{H}_7^{3+}$ trication (**106**) calculated by the B3LYP/6-311 + G** and MP2(full)/6-311 + G** methods.⁸⁸

VII. Planar hexacoordinate carbon atom inside a cyclic borocarbon cage

A new line in the study of compounds with hypercoordinate carbon atoms is the quest for structures with a planar hexacoordinate carbon atom. The problem of stabilisation of these structures has been attacked simultaneously by two research groups, which have arrived at similar solutions.

One approach^{25,208,209} is based on expansion of the rigid cage of bonds formed by a planar tetracoordinate carbon atom in cyclic structures like **21**–**23**. This expansion results in a higher coordination number of the carbon atom. For example, 'doubling' of molecule **23** (by reflecting it in a mirror accommodating the central carbon atom and two boron atoms in the plane of the mirror) furnishes structure **108** containing a planar hexacoordinate carbon atom.

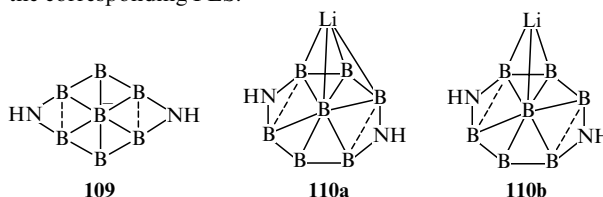


X = O (a), NH (b).

According to MP2(full)/6-311 + G** calculations, the resulting structure **108** has D_{2h} symmetry and corresponds to a minimum on the PES.

The calculated geometry of molecule **108a,b** is shown in Fig. 17. The C–B bond lengths are only ~ 0.1 Å longer than the length of the typical single C–B bond.²¹⁰ The replacement of the central carbon atom in structure **108** by the B[−] isolobal centre, as expected, does not weaken the stability of the structure.

The anion **109** and molecules **110a,b** (Fig. 18) are minima on the corresponding PES.²⁰⁹



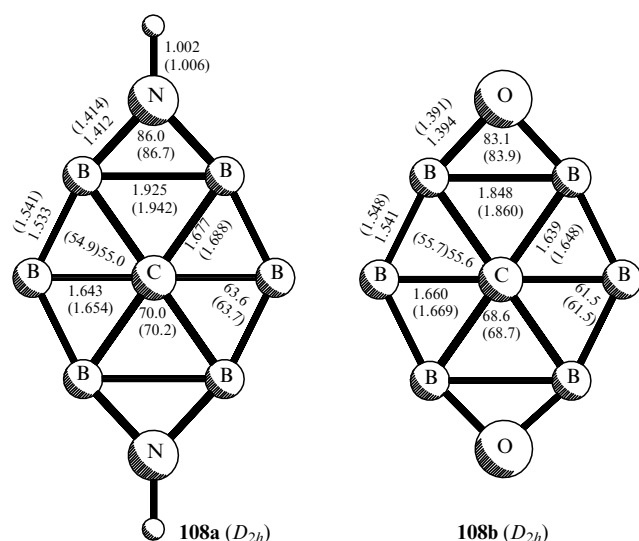
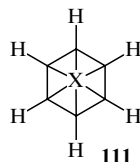


Figure 17. Geometric characteristics of molecules **108a,b** ($X = \text{NH}, \text{O}$) containing hexacoordinate carbon atoms calculated by the MP2(full)/6-31G** and MP2(full)/6-311 + G** methods (values in parentheses).²⁵

The lengths of the B–B bonds formed by the central boron atom ($\sim 1.7 \text{ \AA}$) are within the limits of values typical of these bonds.²¹¹ Analysis of the electronic structure of compounds **108–110** shows that they are 6π -electron aromatic systems. The two electrons lent by the central carbon atom or by the B^- anion are delocalised in the π -system of the ligands. As a consequence, the carbon atom in the structure **108** bears a positive charge ($+0.8$ to $+0.9$), which decreases its effective radius and reduces the steric strain in the planar system. The aromatic nature of molecule **110** is emphasised by the presence of shortened peripheral B–B bonds, which are $0.06\text{--}0.08 \text{ \AA}$ shorter than the double $\text{B}=\text{B}$ bond ($\sim 1.63 \text{ \AA}$).²¹²

The second approach to solving the problem of stabilisation of a hexacoordinate carbon centre²¹³ is also underlain by the idea of surrounding this centre by a rigid cage composed of boron atoms. At the first stage of the investigation,²¹³ carried out by B3LYP/6-311 + G** calculations using the density functional theory, a model planar structure **111** was considered with various atoms or ions X being placed at the midpoint of the benzene ring.

For none of the structures designed in this way (even for the structure with $X = \text{He}$ or C^{4+}), were the researchers able to locate an energy minimum on the PES. Since the geometry of structure **111** ($X = \text{C}^{4+}$) was quite realistic (the $\text{C}_{\text{centre}}\text{--C}$ bond lengths were normal, 1.516 \AA) and the instability of the structure was mainly due to excess charge, subsequent modification of the structure **111** with $X = \text{C}^{4+}$ was carried out in the usual way.



The total charge of the molecule was neutralised by successive replacement of the carbon centres in the ring by boron atoms. Along this route, a number of stable structures **112–116**, containing a planar hexacoordinate carbon atom, have been identified. Two factors contribute to the stability of these structures: first, expansion of the inner cavity containing the carbon centre caused by the fact that C–B bonds are longer than C–C bonds; and second, aromaticity of these structures. It was noted²¹³ that, although structures **112–116** are not the most stable isomers,

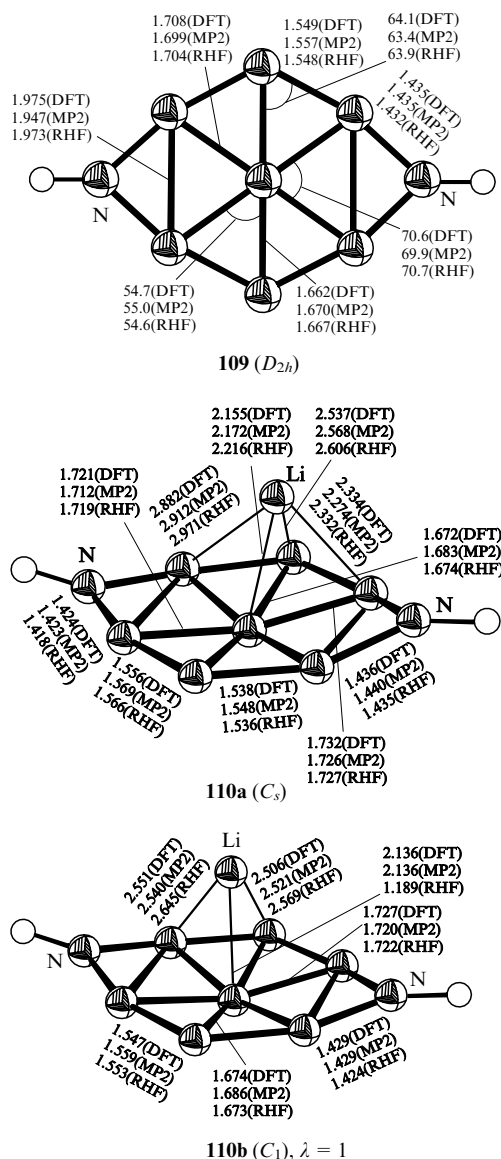
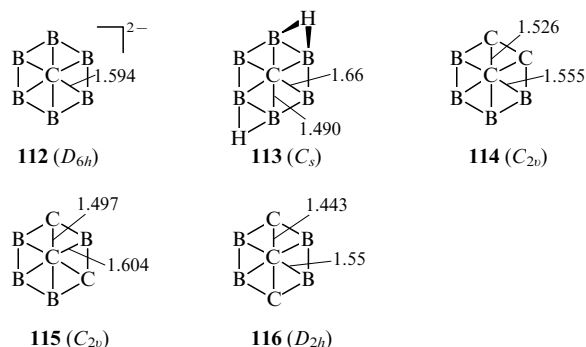


Figure 18. Geometric characteristics of anion **109** and molecules **110a,b** containing hexacoordinate boron atoms calculated by the RHF/6-31G** (RHF), MP2(full)/6-31G** (MP2) and B3LYP/6-311 + G** (DFT) methods.^{208, 209}

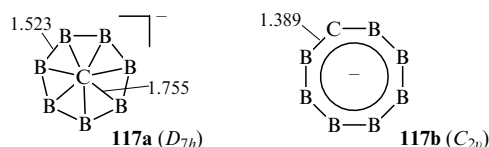
The molecular configuration of **110b** is the transition state structure for rotation of the lithium atom above the ring (topomerisation) with a potential barrier of 0.20 (RHF), 0.63 (MP2) or $0.03 \text{ kcal mol}^{-1}$ (DFT).

they are separated from the latter by rather high potential barriers and, therefore, the synthesis of these species may be practical.

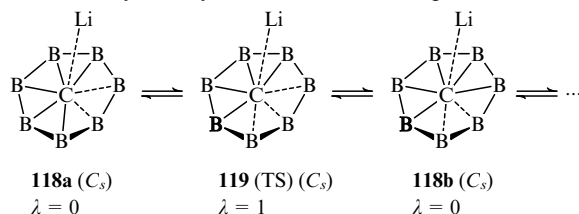


VIII. Molecules and ions containing planar penta-, hepta- and octacoordinate carbon atoms or atoms of other non-transition elements

The possibility of the existence of stable compounds incorporating a planar heptacoordinate carbon atom is pointed out by the results of B3LYP/6-311+G** calculations for the cyclic CB₇ anion.²¹⁴ In this approximation, the *D*_{7h}-symmetric structure **117a** is a local minimum in the PES, which is separated from another local minimum corresponding to a more stable (by 9 kcal mol⁻¹) isomer **117b** by a fairly high potential barrier. The ion pairs formed by anions **117a** and **117b** with the Li⁺ counterions have the same energy. Like the cyclic structures with a hexacoordinate carbon atom considered above, the seven-membered analogue **117a** is also aromatic. Figure 19 shows the shapes of the four π MO of anion **117a**, three occupied orbitals and the lowest unoccupied one. The B–B (1.523 Å) and C–B (1.389 Å) bond lengths in the seven- and eight-membered rings in anions **117a** and **117b** are close to the C–B bond length in the H₂C=BH molecule (1.376 Å) and B–B bond length in the HB=BH molecule (1.523 Å), calculated by the same technique;²¹³ this indicates that these are conjugated double bonds.



The ring in compound **117a** is larger than the B₆ and C₂B₄ rings in compounds **108**–**116**; this entails an increase in the C_{centre}–B bond lengths in anion **117a** by approximately 0.2 Å. Due to this elongation, the bond becomes markedly weaker than the usual bonds in carboranes.²¹⁵ Therefore, even minor symmetry distortions can lead to substantial changes in the type of structure. The symmetry of the structure of ion pair **118** is reduced



to *C*_s. These structures should be fluxional, following a bond switching isomerisation pattern (see Refs 216, 217), the calculated potential barrier being not higher than 0.1 kcal mol⁻¹.

A similar structure and the same type of structural rigidity are typical of neutral C₂B₆ (**120**) and NB₇ (**121a,b**) rings. The cyclic structure **120** is formed from cyclic structure **117a** through replacement of the B⁻ anion by an isoelectronic carbon atom, while **121** is produced when the central carbon is replaced by nitrogen. Calculations of the geometry of these molecules (Fig. 20) demonstrate that the central carbon atom in structure **120** forms only five (of the seven possible) rather short (within the range of usual lengths of C–B bonds) C–B bonds, and the nitrogen atoms in structures **121a** and **121b** form four and five short N–B bonds. However, the calculated potential barriers to migration of the central atoms inside the seven-membered rings do not exceed 0.8 kcal mol⁻¹, which permits these atoms to be regarded as effectively heptacoordinate planar atoms.²¹⁴

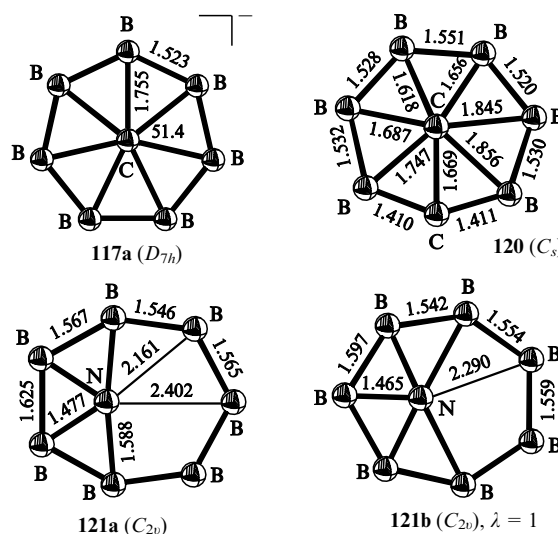


Figure 20. Geometric characteristics of anion **117a** and molecules **120** and **121a,b** calculated by the B3LYP/6-311 + G(2*df*) methods.²¹⁴

The symmetrical *D*_{8h} structure **122** resulting from insertion of a carbon atom inside an eight-membered ring composed of boron atoms is unstable, according to the results of B3LYP/6-311G** calculations.²¹⁸ On the PES of the CB₈ molecule, this structure is matched by a flattened top of a hill (two imaginary vibration frequencies). Although the B–B bonds in the rings are double, the size of the eight-membered ring is so large that the B–C distances in structure **122** exceed the longest known value for B–C bond length. If the carbon atom in structure **122** is replaced by an isoelectronic atom or cation (Si or P⁺) with a greater atomic radius, structures **123** and **124** obtained in this way will be stable (matched by potential energy minima). The calculated B–Si (2.038 Å) and B–P (2.041 Å) bond lengths exceed only slightly the corresponding sums of the covalent radii (1.98 and 1.91 Å). Structures **123** and **124**, like structures **112**–**117**, contain aromatic sextets of π -electrons.

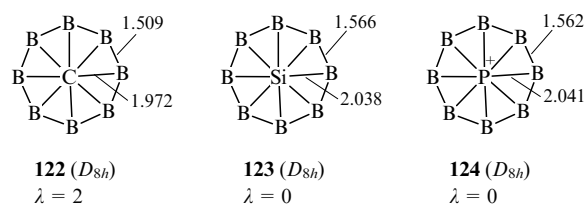
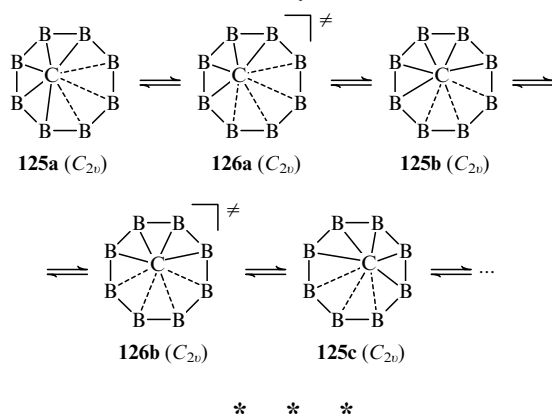


Figure 19. Shapes and energy levels of the π -orbitals of anion **117a** calculated by the B3LYP/6-311G** method (see Ref. 214).

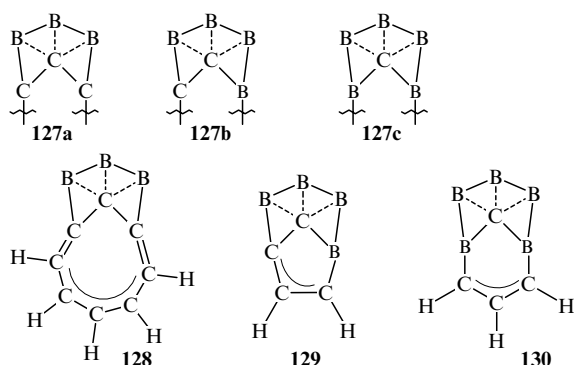
For the cyclic CB₈ molecule, the stable form is structure **125** (*C*_{2v} symmetry) in which the C–B bond lengths are 1.627 and

1.753 Å, and the other C...B distances (non-bonding contacts) occur within the limits of 2.5–2.9 Å. This structure, like analogous seven-membered structures **118**, **120** and **121**, tend to undergo low-barrier rearrangements [the potential barrier calculated in the CCD(fc)/6-311G**//B3LYP/6-311G** approximation is 2.05 kcal mol⁻¹] resulting in fast exchange of ligand positions in the environment of the central atom. Thus, the carbon atom in structure **125** is effectively octacoordinated.

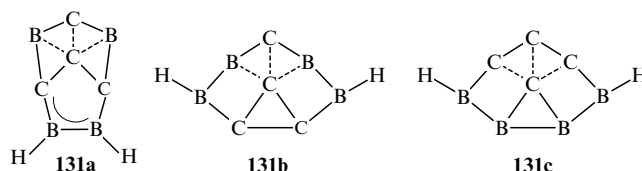


As this review was being prepared for publication, new important studies devoted to derivatives of planar tetracoordinate and hypercoordinate carbon were published.

Wang and Schleyer²¹⁹ further developed the strategy described in their preliminary communication⁵⁷ involving delocalisation of the non-bonding higher occupied MO of alkylanes over the molecular cage by replacing the carbon centers in various positions of the cage by boron atoms and carried out B3LYP/6-31G* calculations for a series of new boralkanes with a planar tetracoordinate carbon atom. The same researchers also proposed a general approach to the design of stable organoboron structures incorporating planar pentacoordinate carbon centres.²²⁰ It was found that the replacement of two-electron π -donor groups (O, NH, HC=CH) in structures **21**–**23** containing a planar tetracoordinate carbon atom by single-electron π -donor B or C atoms provides the possibility of increasing the coordination number of the planar carbon center. The insertion of non-classical substituents **127a**–**c** thus obtained into the skeletons of various aromatic hydrocarbons in place of the three-carbon (CH)₃ chains gives rise to structures with pentacoordinate planar carbon atoms (for example, structures **128**–**130**), whose stability was confirmed by B3LYP/6-311 + G** calculations.

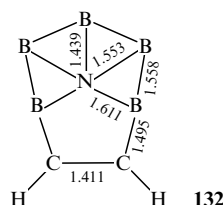


This result is also confirmed by our MP2/6-311 + G** *ab initio* calculations for a number of other structures (for example, isomers **131**) with a pentacoordinate carbon atom.²²¹ We showed that by observing the above conditions of aromatic stabilisation of non-classical structures (see Sections II.3 and VII), stable structures with a pentacoordinate carbon atom can also be produced by other permutations of atoms in units **127** and in structures of type **128**–**130**.

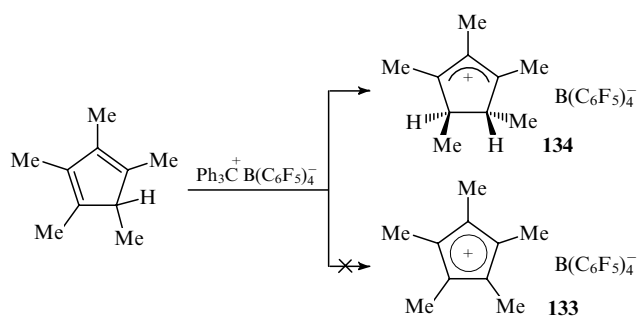


Compound	$\Delta E/\text{kcal mol}^{-1}$	
	B3LYP/6-311 + G**	MP2/6-311 + G**
131a	0	0
131b	11.6	7.1
131c	32.4	21.9

The requirement of aromatic stabilisation and the selection of appropriate fragments of type **21**–**23**, **127a**–**c** and others allow one to predict rather reliably the existence of stable molecules and ions with hypercoordinate planar centres of any other element. The B3LYP/6-311 + G** calculations for stable structure **132** with a planar pentacoordinate nitrogen atom serves as an example.²²¹



In relation to the discussion of the pyramidal (CH)₅⁺ cation and its isomers (see Section VI.2), of interest is the debate initiated by the recent publication²²² reporting the synthesis of the unexpectedly stable pentamethyl derivative of the singlet cyclopentadienyl cation (CMe)₅⁺ (**133**). According to X-ray diffraction analysis data, the cation structure corresponds to structural type **83**. However, the subsequent high-level quantum-chemical calculations²²³ suggested that in reality, the researchers were dealing with the dihydro derivative **134** rather than with the cation **133**; this was recognised as proven after additional analysis.^{224, 225}



The outcome of this debate is an illustrative example of the increasing role of precise quantum-mechanical calculations in the study of structures with non-standard geometric and electronic characteristics.

IX. Conclusion

The results of the theoretical and experimental studies considered demonstrate the diversity of structural types of molecules containing atoms with a non-standard spatial orientation of bonds and coordination numbers other than those dictated by the valence rules. Not that these compounds are necessarily thermodynamically or kinetically stable — they often are metastable local minima. But one can think of generating them, and studying them. The advances in theoretical simulation methods and the stupendous progress in the development of the computing power of modern quantum chemistry enabled quite substantiated state-

ment of the problem of looking for new structures which might have been rejected only a few years ago by researchers with a classical way of thinking on the basis that 'that can't be so because it can never be so' (see, for example, the caustic remark²²⁶ concerning the studies searching for compounds with a planar tetracoordinate carbon atom). Meanwhile, these studies initiated by theoretical analysis have received some experimental validation. Many compounds of this type have already been synthesised.

Currently, theoretical investigations of new non-classical organic compounds are directed at elucidating the factors influencing stability and investigating the unusual dynamics and properties of such molecules and ions. Elucidation of unusual structural patterns presents substantial interest in the design of new high-tech materials with specific properties, while technological developments, especially ultralow-temperature laser vaporisation,²²⁷ allow one to expect that more theoretical predictions will be confirmed by experimental proof. The situation in this field seems to resemble the history of the development of fullerene chemistry.

As has already been noted, high-level *ab initio* calculations with obligatory allowance for the electron correlation energy are the most accurate and reliable methods for theoretical identification and evaluation of the possible existence of non-classical structures. The question thus arises of how one might choose particular structures on which calculations are to be performed. It is clear that exhaustive screening of atomic compositions cannot be a suitable strategy. There is good reason to believe that analysis of orbital interactions of molecular fragments based on the perturbation theory still remains conceptually the most comprehensive and the most fruitful way of designing stable non-classical structures. This conclusion is based on the fact that orbital interactions make, as a rule, the major contribution to stabilisation or, conversely, destabilisation of molecular structures.

Yet another, more utilitarian line is to simulate a non-classical organic structure that would resemble one or another inorganic or organometallic complex or cluster. The stability of molecules and ions of such compounds is ensured by the formation of multi-centre bonds, of a type which is dictated by the structure of the complex or cluster and can be reproduced in the organic analogue on the basis of the isolobal analogy.

It is evident that the principles of stabilisation of non-classical organic structures, *i.e.*, carbon compounds, can be directly extrapolated to the compounds of other non-transition elements. Some examples of unusual geometric configurations and types of coordination of boron, nitrogen, silicon, and phosphorus atoms have been included in this review.

The notion of 'non-classical compounds' appeared 50 years ago when the first examples of these structures became known, the term itself being introduced mainly to designate exceptions to customary rules. Nowadays, the exceptions appear to become indistinguishable from the rules. George Olah, who has been awarded the Nobel Prize for his contribution to the development of this field of chemistry, believes¹⁴³ that classification of structures into classical and non-classical ones will gradually vanish from chemists' language and chemists' practice, as the understanding of the general principles of the chemical bond becomes more profound.

The review was written with financial support from the Russian Foundation for Basic Research (Project Nos 00-15-97320, 01-03-32546, 02-03-33227) and the Civilian Research and Development Foundation (Grant RCI-2323-RO-02).

References

1. J H van't Hoff *Arch. Neerl. Sci. Exactes Nat.* **9** 445 (1874)
2. G V Bykov *Istoriya Stereokhimiĭ Organicheskikh Soedinenii* (History of Stereochemistry of Organic Compounds) Ch. 3 (Moscow: Nauka, 1966)
3. G A Olah, G K S Prakash, R E Williams, L D Field, K Wade *Hypercarbon Chemistry* (New York: Wiley, 1987)
4. R B Woodward, R Hoffmann *The Conservation of Orbital Symmetry* (Weinheim: Verlag Chemie, 1971)
5. T A Albright, J K Burdett, M-H Whangbo *Orbital Interactions in Chemistry* (New York: Wiley, 1985)
6. B M Gimarc *Molecular Structure and Bonding* (New York: Academic Press, 1979)
7. R Hoffmann *Angew. Chem., Int. Ed. Engl.* **21** 711 (1982)
8. R Hoffmann *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (Weinheim: VCH, 1988)
9. V I Minkin, R M Minyaev, Yu A Zhdanov *Nonclassical Structures of Organic Compounds* (Moscow: Mir, 1987)
10. V I Minkin, B Ya Simkin, R M Minyaev *Quantum Chemistry of Organic Compounds. Mechanisms of Reactions* (Berlin: Springer, 1990)
11. V I Minkin, R M Minyaev *Usp. Khim.* **51** 586 (1982) [*Russ. Chem. Rev.* **51** 332 (1982)]
12. V I Minkin, R M Minyaev, in *Progress in Theoretical Chemistry* Vol. 3 (Ed. I G Csizmadia) (Amsterdam: Elsevier, 1982) p. 121
13. J A Pople *Angew. Chem., Int. Ed. Engl.* **38** 1894 (1999)
14. H C Brown *The Nonclassical Ions Problem* (With Comments P v R Schleyer) (New York: Plenum, 1977)
15. R Hoffmann, R W Alder, C F Wilcox Jr *J. Am. Chem. Soc.* **92** 4992 (1970)
16. R Hoffmann *Pure Appl. Chem.* **28** 181 (1971)
17. V I Minkin, R M Minyaev, in *Fizicheskaya Khimiya. Sovremennyye Problemy* (Physical Chemistry. Topical Problems) (Ed. Ya M Kolotyrkin) (Moscow: Khimiya, 1983) p. 180
18. B R Venepalli, W C Agosta *Chem. Rev.* **87** 399 (1987)
19. W C Agosta, in *The Chemistry of the Alkanes and Cycloalkanes.* (Eds S Patai, Z Rappoport) (Chichester: Wiley-Interscience, 1992) p. 927
20. W Luef, R Keese *Adv. Strain Org. Compd.* **3** 229 (1993)
21. K Sorger, P v R Schleyer *J. Mol. Struct. (THEOCHEM)* **338** 317 (1995)
22. D Röttger, G Erker *Angew. Chem., Int. Ed. Engl.* **36** 812 (1997)
23. W Siebert, A Gunale *Chem. Soc. Rev.* **28** 367 (1999)
24. M J M Pepper, I Shavitt, P v R Schleyer, M N Glukhovtsev, R Janoschek, M Quack *J. Comput. Chem.* **16** 207 (1995)
25. R M Minyaev, T N Gribanova *Izv. Acad. Nauk, Ser. Khim.* **786** (2000)^a
26. M N Glukhovtsev, B Ya Simkin, V I Minkin *Zh. Org. Khim.* **26** 2241 (1990)^b
27. J B Collins, J D Dill, E D Jemmis, Y Apeloig, P v R Schleyer, R Seeger, J A Pople *J. Am. Chem. Soc.* **98** 5419 (1976)
28. K Sorger, P v R Schleyer, R Fleischer, D Stalke *J. Am. Chem. Soc.* **118** 6924 (1996)
29. F A Cotton, M Millar *J. Am. Chem. Soc.* **99** 7886 (1977)
30. I Hyla-Kryspin, R Gleiter, M-M Rohmer, J Devemy, A Gunale, H Pritzko, A Siebert *Chemistry* **2** 294 (1997)
31. H Dietrich, W Mahdi, W Storck *J. Organomet. Chem.* **349** 1 (1988)
32. U E Musanke, W Jeitschko *Z. Naturforsch., B: Chem. Sci.* **46** 1177 (1991)
33. E F Merschrod, S H Tang, R Hoffmann *Z. Naturforsch., B: Chem. Sci.* **53** 322 (1998)
34. M C Böhm, R Gleiter, P Schang *Tetrahedron Lett.* **2575** (1979)
35. J Chandrasekhar, E-U Würthwein, P v R Schleyer *Tetrahedron* **37** 921 (1981)
36. K Krogh-Jespersen, D Cremer, D Poppinger, J A Pople, P v R Schleyer, J Chandrasekhar *J. Am. Chem. Soc.* **101** 4843 (1979)
37. E D Jemmis, G Subramanian, G N Srinivas *J. Am. Chem. Soc.* **114** 7939 (1992)
38. T N Gribanova, R M Minyaev, V I Minkin *Collect. Czech. Chem. Commun.* **64** 1780 (1999)
39. P v R Schleyer, A I Boldyrev *J. Chem. Soc., Chem. Commun.* 1536 (1991)
40. A I Boldyrev, J Simmons *J. Am. Chem. Soc.* **120** 7967 (1998)
41. X Li, L-S Wang, A I Boldyrev, J Simmons *J. Am. Chem. Soc.* **121** 6033 (1999)
42. L-S Wang, A I Boldyrev, X Li, J Simmons *J. Am. Chem. Soc.* **122** 7681 (2000)
43. A E Kuznetsov, A I Boldyrev, X Li, L-S Wang *J. Am. Chem. Soc.* **123** 8825 (2001)

- doi> 44. A I Boldyrev, X Li, L-S Wang *Angew. Chem., Int. Ed.* **39** 3307 (2000)
- doi> 45. X Li, A E Kuznetsov, H-F Zhang, A I Boldyrev, L-S Wang *Science* **291** 859 (2001)
- doi> 46. I V Komarov *Usp. Khim.* **70** 1123 (2001) [*Russ. Chem. Rev.* **70** 991 (2001)]
47. V I Minkin, R M Minyaev, V I Natanzon *Zh. Org. Khim.* **16** 673 (1980)^b
- doi> 48. E-U Würthwein, J Chandrasekhar, E D Jemmis, P v R Schleyer *Tetrahedron Lett.* **22** 843 (1981)
49. K B Wiberg, J J Wendoloski *J. Am. Chem. Soc.* **104** 5679 (1982)
50. J M Schulman, M L Sabio, R L Disch *J. Am. Chem. Soc.* **105** 743 (1983)
51. A Greenberg, J F Liebman *Strained Organic Molecules* Ch. 6 (New York: Academic Press, 1978)
52. M P McGrath, L Radom, H F Schaefer III *J. Org. Chem.* **57** 4847 (1992)
53. M P McGrath, L Radom *J. Am. Chem. Soc.* **115** 3320 (1993)
54. J E Lyons, D R Rasmussen, M P McGrath, R H Nobes, L Radom *Angew. Chem.* **106** 1722 (1994)
- doi> 55. D R Rasmussen, L Radom *Angew. Chem.* **111** 3052 (1999)
56. L Radom, D R Rasmussen *Pure Appl. Chem.* **70** 1977 (1998)
- doi> 57. Z-X Wang, P v R Schleyer *J. Am. Chem. Soc.* **123** 994 (2001)
58. V I Minkin, R M Minyaev, I I Zakharov *J. Chem. Soc., Chem. Commun.* 213 (1977)
59. V I Minkin, R M Minyaev, I I Zakharov, V I Avdeev *Zh. Org. Khim.* **14** 3 (1978)^b
60. R M Minyaev, G V Orlova, I A Yudilevich, L G Barlas, V I Minkin *Zh. Org. Khim.* **23** 2267 (1987)^b
61. M S Gordon, M W Schmidt *J. Am. Chem. Soc.* **115** 7486 (1993)
- doi> 62. K Yoshizawa, A Suzuki, T Yamabe *J. Am. Chem. Soc.* **121** 5266 (1999)
- doi> 63. E L Muetterties *Tetrahedron* **30** 1595 (1974)
- doi> 64. U Radius, S J Silverio, R Hoffmann, R Gleiter *Organometallics* **15** 3737 (1996)
65. D A Dixon, A J Arduengo III *Int. J. Quantum Chem., Quantum Chem. Symp.* **22** 85 (1988)
66. A J Arduengo III, C A Stewart *Chem. Rev.* **94** 1215 (1994)
67. K Fukui *Acc. Chem. Res.* **14** 363 (1981)
68. R M Minyaev, M E Kleetskii, G V Orlova, V I Minkin *Zh. Org. Khim.* **24** 1353 (1988)^b
69. G M Smith, M Sabat, T J Marks *J. Am. Chem. Soc.* **109** 1854 (1987)
70. M-B Krogh-Jespersen, J Chandrasekhar, E-U Würthwein, J B Collins, P v R Schleyer *J. Am. Chem. Soc.* **102** 2263 (1980)
71. A J Arduengo III, D A Dixon, D C Roe, M Kline *J. Am. Chem. Soc.* **110** 4437 (1988)
- doi> 72. V I Minkin, L E Nivorozhkin, M S Korobov *Usp. Khim.* **63** 303 (1994) [*Russ. Chem. Rev.* **63** 289 (1994)]
73. V I Minkin, L E Nivorozhkin *Russ. Khim. Zh.* **40** 12 (1996)^c
74. R Hoffmann, V I Minkin, B K Carpenter *Bull. Soc. Chim. Fr.* **133** 117 (1996)
- doi> 75. A L Nivorozhkin, E V Sukhonenko, L E Nivorozhkin, N I Borisenko, V I Minkin, Yu K Grishin, O A Diachenko, T G Takhir'ov, D B Tagiev *Polyhedron* **8** 569 (1989)
- doi> 76. M S Korobov, G S Borodkin, N I Borisenko, T A Ryskina, L E Nivorozhkin, V I Minkin *J. Mol. Struct. (THEOCHEM)* **200** 61 (1989)
77. A G Starikov, R M Minyaev, V I Minkin *Izv. Akad. Nauk, Ser. Khim.* 250 (1999)^a
78. V Prelog *Chem. Ber.* **4** 382 (1968)
79. V I Minkin, R M Minyaev *Zh. Org. Khim.* **15** 225 (1979)^b
80. W E Billups, M M Haley *J. Am. Chem. Soc.* **113** 5084 (1991)
81. I Shavitt, D W Ewing, J E Del Bene *J. Am. Chem. Soc.* **113** 9389 (1991)
82. E D Jemmis, P v R Schleyer *J. Am. Chem. Soc.* **104** 4781 (1982)
- doi> 83. V I Minkin, R M Minyaev, G V Orlova *J. Mol. Struct. (THEOCHEM)* **110** 241 (1984)
84. V Balaji, J Michl *Pure Appl. Chem.* **60** 189 (1988)
- doi> 85. E Lewars *J. Mol. Struct. (THEOCHEM)* **423** 173 (1998); **507** 165 (2000)
- doi> 86. D R Rasmussen, L Radom *Chem. Eur. J.* **6** 2470 (2000)
- doi> 87. J P Kenny, K M Krueger, J C Rienstra-Kiracofe, H F Schaefer III *J. Phys. Chem. A* **105** 7745 (2001)
88. V I Minkin, R M Minyaev *Dokl. Akad. Nauk* **385** 502 (2002)^d
89. P Dowd, H Irgartinger *Chem. Rev.* **89** 985 (1989)
90. O M Nefedov, A I Ioffe, L G Menchikov *Khimiya Karbenov (The Chemistry of Carbenes)* (Moscow: Khimiya, 1990)
91. J Hinze, H H Jaffe *J. Am. Chem. Soc.* **84** 540 (1962)
- doi> 92. R B King *Chem. Rev.* **101** 1119 (2001)
93. V I Minkin, M N Glukhovtsev, B Ya Simkin *Aromaticity and Antiaromaticity. Electronic and Structural Aspects* Ch. 9 (New York: Wiley-Interscience, 1994)
94. Yu L Slovokhotov, Yu T Struchkov *Usp. Khim.* **54** 556 (1985) [*Russ. Chem. Rev.* **54** 323 (1985)]
95. H Schmidbaur *Angew. Chem.* **97** 893 (1985)
96. P Jutzi *Adv. Organomet. Chem.* **26** 217 (1986)
- doi> 97. P Jutzi, N Burford *Chem. Rev.* **99** 969 (1999)
98. R M Minyaev, V I Minkin, A G Starikov, T N Gribanova *Izv. Akad. Nauk, Ser. Khim.* 2219 (2001)^a
99. L Skattebøl *J. Org. Chem.* **31** 2789 (1966)
100. R Boese, D Bläser, K Gomann, U H Brinker *J. Am. Chem. Soc.* **111** 1501 (1989)
- doi> 101. K B Wiberg, J R Snodgrass *J. Org. Chem.* **63** 1390; 1402 (1998)
102. B Kovačević, Z B Maksić, R Vianello *J. Chem. Soc., Perkin Trans. 2* 886 (2001)
103. E P Hunter, S G Lias *J. Phys. Chem., Ref. Data* **27** 413 (1998)
104. H Dodziuk *Top. Stereochem.* **21** 351 (1994)
105. M Thommen, R Keese *Synlett* 231 (1997)
106. K B Wiberg *J. Org. Chem.* **50** 5285 (1985)
107. K B Wiberg, N McMurdie, J V McClusky, C M Hadad *J. Am. Chem. Soc.* **115** 10653 (1993)
108. H Dodziuk, J Leszczynski, K S Nowinski *J. Org. Chem.* **60** 6860 (1995)
109. H Dodziuk, K S Nowinski *J. Mol. Struct. (THEOCHEM)* **311** 97 (1994)
- doi> 110. K B Wiberg, J V McClusky *Tetrahedron Lett.* **28** 5411 (1987)
111. J S Bradley, G B Ansell, M E Leonowicz, E W Hill *J. Am. Chem. Soc.* **103** 4968 (1981)
112. C J Adams, M I Bruce, B W Skelton, A H White *J. Chem. Soc., Chem. Commun.* 975 (1996)
- doi> 113. O Rossell, M Seco, G Segales, S Alvarez *Organometallics* **16** 236 (1997)
114. R E v H Spence, D J Parks, W E Piers, M-A McDonald, M J Zaworotko, S J Rettig *Angew. Chem., Int. Ed. Engl.* **34** 1230 (1995)
- doi> 115. W J Evans, T J Boyle, J W Ziller *J. Organomet. Chem.* **462** 141 (1993)
116. D L Clark, J C Gordon, J C Huffman, J G Watkin, B D Zwick *Organometallics* **13** 4266 (1994)
117. G Fritz, S Wartanessian, E Matern, W Honle, H G v Schnering *Z. Anorg. Allg. Chem.* **475** 87 (1981)
- doi> 118. E Niecke, A Fuchs, M Nieger *Angew. Chem.* **111** 3213 (1999)
119. K B Wiberg, F H Walker *J. Am. Chem. Soc.* **104** 5239 (1982)
120. D Ginsburg *Propellanes — Structure and Reactions* (Weinheim: VCH, 1975)
121. K B Wiberg *Acc. Chem. Res.* **17** 379 (1984)
122. K B Wiberg *Chem. Rev.* **89** 975 (1989)
123. W-D Stohrer, R Hoffmann *J. Am. Chem. Soc.* **94** 779 (1972)
124. S P Zil'berg, A I Ioffe, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.* 358 (1984)^a
125. D Feller, E R Davidson *J. Am. Chem. Soc.* **109** 4133 (1987)
126. K B Wiberg, R F W Bader, C D H Lau *J. Am. Chem. Soc.* **109** 985 (1987)
127. W-D Stohrer, R Hoffmann *J. Am. Chem. Soc.* **94** 1661 (1972)
128. G Parkin *Acc. Chem. Res.* **25** 455 (1992)
- doi> 129. E R Davidson *J. Am. Chem. Soc.* **119** 1449 (1997)
- doi> 130. H Dodziuk, J Leszczynski, K Jackowski *J. Org. Chem.* **64** 6177 (1999)
131. P D Bartlett *Nonclassical Ions* (New York: Benjamin, 1965)
132. G A Olah, K Wade, R E Williams (Eds) *Electron Deficient Boron and Carbon Chemistry* (New York: Wiley-Interscience, 1991)
133. J D Roberts, R H Mazur *J. Am. Chem. Soc.* **73** 3542 (1951)
134. V L Tal'roze, A K Lyubimova *Dokl. Akad. Nauk SSSR* **86** 909 (1952)^d
- doi> 135. V L Talrose, A K Lyubimova *J. Mass Spectrom.* **33** 502 (1998)
136. G A Olah, R H Schlosberg *J. Am. Chem. Soc.* **90** 2726 (1968)
137. G A Olah, G K S Prakash, J Sommer *Superacids* (New York: Wiley, 1985)

138. G A Olah, K K Laali, Q Wang, G K S Prakash *Onium Ions* (New York: Wiley, 1998)
- doi> 139. M Alcamí, O Mu, M YaKhez *Mass Spectrosc. Rev.* **20** 195 (2001)
140. G A Olah, A Molnar *Hydrocarbon Chemistry* (New York: Wiley, 1995)
- doi> 141. G A Olah, G Rasul *Acc. Chem. Res.* **30** 245 (1997)
- doi> 142. G A Olah, G K S Prakash, T Mathew, E R Marínez *Angew. Chem., Int. Ed.* **39** 2547 (2000)
- doi> 143. G A Olah *J. Org. Chem.* **66** 5943 (2001)
144. W J Hehre, L Radom, P v R Schleyer, J A Pople *Ab Initio Molecular Orbital Theory* Ch. 7 (New York: Wiley-Interscience, 1985)
- doi> 145. P R Schreiner, S J Kim, H F Schaefer III, P v R Schleyer *J. Chem. Phys.* **99** 3716 (1993)
- doi> 146. H Müller, W Kutzelnigg, J Noga, W Klopper *J. Chem. Phys.* **105** 1863 (1997)
147. D Marx, A Savin *Angew. Chem., Int. Ed. Engl.* **36** 2077 (1997)
148. P R Schreiner *Angew. Chem., Int. Ed.* **39** 3239 (2000)
- doi> 149. P Ahlberg, A Karlsson, A Goepfert, S O N Lill, P Dinér, J Sommer *Chem. Eur. J.* 1936 (2001)
- doi> 150. D Marx, M Parrinello *Science* **284** 59 (1999)
- doi> 151. E T White, J Tang, T Oka *Science* **284** 135 (1999)
152. G M Kramer *Science* **286** 1051 (1999)
153. R E Mesmer, W L Jolly *Inorg. Chem.* **1** 608 (1962)
154. T J Tague, L Andrews *J. Am. Chem. Soc.* **116** 4970 (1994)
155. J D Watts, R J Bartlett *J. Am. Chem. Soc.* **117** 825 (1995)
156. R E Williams *Inorg. Chem.* **10** 210 (1971)
157. S Masamune, M Sakai, H Ona, A J Jones *J. Am. Chem. Soc.* **94** 8955; 8956 (1972)
158. S Masamune *Pure Appl. Chem.* **44** 861 (1975)
159. H Schwarz *Angew. Chem., Int. Ed. Engl.* **20** 991 (1981)
- doi> 160. M D Levin, P Kaszynski, J Michl *Chem. Rev.* **100** 169 (2000)
161. V I Minkin, N S Zefirov, M S Korobov, N V Averina, A M Boganov, L E Nivorozhkin *Zh. Org. Khim.* **17** 2616 (1981)^b
162. R Wade *Adv. Inorg. Chem. Radiochem.* **18** 1 (1976)
163. D M P Mingos *Acc. Chem. Res.* **17** 311 (1984)
164. J Feng, J Leszczynski, B Weiner, M C Zerner *J. Am. Chem. Soc.* **111** 4648 (1989)
- doi> 165. M N Glukhovtsev, B Reindl, P v R Schleyer *Mendeleev Commun.* 100 (1993)
- doi> 166. M N Glukhovtsev, R D Bach, S Laiter *J. Phys. Chem.* **100** 10952 (1996)
167. W J Hehre, P v R Schleyer *J. Am. Chem. Soc.* **95** 5837 (1973)
168. M J S Dewar, R C Haddon *J. Am. Chem. Soc.* **95** 5836 (1973)
169. M J S Dewar, R C Haddon *J. Am. Chem. Soc.* **96** 255 (1974)
170. M L McKee *J. Am. Chem. Soc.* **114** 879 (1992)
171. M Bühl, P v R Schleyer *J. Am. Chem. Soc.* **114** 477 (1992)
- doi> 172. R M Minyaev, V I Minkin, T N Gribanova, A G Starikov *Mendeleev Commun.* 132 (2001)
173. E D Jemmis, J Chandrasekhar, P v R Schleyer *J. Am. Chem. Soc.* **101** 527 (1979)
174. H Schmidbaur *Pure Appl. Chem.* **65** 691 (1993)
175. H Schmidbaur *Chem. Soc. Rev.* **24** 391 (1995)
176. J I Musher *Angew. Chem., Int. Ed. Engl.* **8** 54 (1969)
177. A E Reed, P v R Schleyer *J. Am. Chem. Soc.* **112** 1434 (1990)
178. W Kutzelnigg *Angew. Chem., Int. Ed. Engl.* **23** 272 (1984)
179. D G Gilheany *Chem. Rev.* **94** 1339 (1994)
- doi> 180. G M Landrum, N Goldberg, R Hoffmann, R M Minyaev *New J. Chem.* 883 (1998)
- doi> 181. H F Bettinger, P v R Schleyer, H F Schaefer III *J. Am. Chem. Soc.* **120** 11 439 (1998)
182. J J Curnow *J. Chem. Educ.* **75** 910 (1998)
183. R M Minyaev, V I Minkin *Izv. Akad. Nauk, Ser. Khim.* 1246 (1999)^a
184. J C Martin *Science* **221** 509 (1983)
185. J C Martin, R J Basalay *J. Am. Chem. Soc.* **95** 2572 (1973)
186. M V Bazilevskii, S G Koldobskii, V A Tikhomirov *Usp. Khim.* **55** 1667 (1986) [*Russ. Chem. Rev.* **55** 948 (1986)]
187. S S Shaik, H B Schlegel, S Wolfe *Theoretical Aspects of Physical Organic Chemistry. The SN2 Mechanism* (New York: Wiley-Interscience, 1992)
- doi> 188. S Wolfe, K Yang, N Weinberg, Z Shi, Y-H Hsieh, R D Sharma, S Ro, C-K Kim *Chem. Eur. J.* **4** 886 (1998)
189. K-y Akiba, M Yamashita, Y Yamamoto, S Nagase *J. Am. Chem. Soc.* **121** 10 644 (1999)
- doi> 190. M Yamashita, Y Yamamoto, K-y Akiba, S Nagase *Angew. Chem.* **112** 4221 (2000)
- doi> 191. J E Del Bene, J D Watts, R J Bartlett *Int. J. Quantum. Chem.* **70** 1003 (1998)
- doi> 192. G A Olah, A Burrichter, G Rasul, G K S Prakash *J. Am. Chem. Soc.* **119** 4594 (1997)
193. A Grohman, J Riede, H Schmidbaur *J. Chem. Soc., Dalton Trans.* 783 (1991)
194. K Lammertsma, G A Olah, M Barzaghi, M Simonetta *J. Am. Chem. Soc.* **104** 6851 (1982)
195. K Lammertsma, M Barzaghi, G A Olah, J A Pople, P v R Schleyer, M Simonetta *J. Am. Chem. Soc.* **105** 5258 (1983)
196. R M Minyaev, G V Orlova *Zh. Strukt. Khim.* **24** (6) 38 (1983)^c
- doi> 197. G A Olah, G A Rasul *J. Am. Chem. Soc.* **118** 8503 (1996)
198. P v R Schleyer, B Tidor, E D Jemmis, J Chandrasekhar, E-U Würthwein, A J Kos, B T Luke, J A Pople *J. Am. Chem. Soc.* **105** 484 (1983)
199. A E Reed, F Weinhold *J. Am. Chem. Soc.* **107** 1919 (1985)
- doi> 200. H Hogeveen, P W Kwant *Tetrahedron Lett.* 1665 (1973)
201. H Hogeveen, P W Kwant *Acc. Chem. Res.* **8** 413 (1975)
202. K Lammertsma, P v R Schleyer *J. Am. Chem. Soc.* **105** 1049 (1983)
203. G Kaupp, J Boy *Angew. Chem., Int. Ed. Engl.* **36** 48 (1997)
204. H-J Quadbeck-Seeger, R Faust, U Knaus, U Siemeling *World Records in Chemistry* (Weinheim: Wiley-VCH, 1999)
- doi> 205. P v R Schleyer, J Kapp *Chem. Phys. Lett.* **255** 363 (1996)
- doi> 206. P Chini *J. Organomet. Chem.* **200** 37 (1980)
- doi> 207. G Rasul, G A Olah *Inorg. Chem.* **36** 1278 (1997)
- doi> 208. T N Gribanova, R M Minyaev, V I Minkin *Mendeleev Commun.* 169 (2001)
209. T N Gribanova, R M Minyaev, V I Minkin *Zh. Neorg. Khim.* **46** 1340 (2001)^f
210. A F Wells *Structural Inorganic Chemistry* (London: Clarendon Press, 1986)
211. M Hildebrand, H Pritzkow, W Siebert *Angew. Chem., Int. Ed. Engl.* **24** 759 (1985)
- doi> 212. P Power *Inorg. Chim. Acta* **198–200** 443 (1992)
- doi> 213. K Exner, P v R Schleyer *Science* **290** 1937 (2000)
214. R M Minyaev, T N Gribanova, A G Starikov, V I Minkin *Dokl. Akad. Nauk* **382** 785 (2002)^d
215. J Casanova *The Borane, Carborane and Carbocation Continuum* (Chichester: Wiley-Interscience, 1998)
216. G Maier, H-O Kalinowski, K Euler *Angew. Chem., Int. Ed. Engl.* **21** 693 (1982)
217. K Hassenrück, H-D Martin, R Walsh *Chem. Rev.* **89** 1125 (1989)
- doi> 218. R M Minyaev, T N Gribanova, A G Starikov, V I Minkin *Mendeleev Commun.* 213 (2001)
- doi> 219. Z-X Wang, P v R Schleyer *J. Am. Chem. Soc.* **124** 11 979 (2002)
- doi> 220. Z-X Wang, P v R Schleyer *Science* **292** 2465 (2001)
221. T N Gribanova, R M Minyaev, I I Minkin, in *Tezisy VI Mezhdunarodnogo Seminara po Magnitnomu Rezonansu, Rostov-na-Donu, 2002* (Abstracts of Reports of the VIth International Seminar on Magnetic Resonance, Rostov-on-Don, 2002) p. 258
- doi> 222. J B Lambert, L Lin, V Rassolov *Angew. Chem.* **114** 1487 (2002)
- doi> 223. T Müller *Angew. Chem., Int. Ed.* **41** 2276 (2002)
- doi> 224. M Otto, D Scheschkewitz, T Kano, M M Midland, J B Lambert, G Bertrand *Angew. Chem., Int. Ed.* **41** 2275 (2002)
225. J B Lambert *Angew. Chem., Int. Ed.* **41** 2279 (2002)
226. A B D'Haye, E Heff, G Hashiji *J. Chem. Res. (S)* 1931; (*M*) 7777 (1977)
- doi> 227. V E Bondybey, A M Smith, J Agreiter *Chem. Rev.* **96** 2113 (1996)

^a — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*

^b — *Russ. J. Org. Chem. (Engl. Transl.)*

^c — *Mendeleev Chem. J. (Engl. Transl.)*

^d — *Dokl. Chem. (Engl. Transl.)*

^e — *Russ. J. Struct. Chem. (Engl. Transl.)*

^f — *Russ. J. Inorg. Chem. (Engl. Transl.)*