Physical Chemistry

Stabilization of nonclassical types of valence bond orientation at the carbon atom in organoboron compounds*

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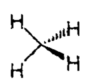
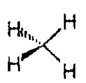
The complete topological structure of the potential energy surface (PES) of methane in the inversion region was studied by the *ab initio* CCD(full)/6-311++G** method. The necessity of taking into account nuclear motions was shown. Penta- and hexacoordination of carbon atoms in boron-containing organic compounds was investigated by the *ab initio* MP2(full)/6-31G** and MP2(full)/6-311++G** methods. The $CB_4H_4Li_2$, $CB_6N_2H_2$, and CB_6O_2 systems containing hexacoordinated carbon atoms correspond to rather deep minima on the relevant PES and can be the subject of synthetic studies. According to the *ab initio* calculations, pyramidal boron-containing systems with hypercoordinated carbon atoms, which fulfill the "8e rule," also correspond to rather deep PES minima and can be detected experimentally.

Key words: "planar" carbon atom, "pyramidal" carbon atom, hypercoordinated carbon atom, methane, topology of the potential energy surface, *ab initio* quantum-chemical calculations.

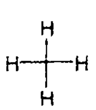
In 1874, van't Hoff[1] and Le Bel[2] independently recognized that a tetracoordinated tetravalent carbon atom prefers the tetrahedral arrangement of substituents in its compounds of the type **1**. Later, the hypothesis for profound stability of this type of carbon compounds has been experimentally and theoretically substantiated and has become a cornerstone of structural organic chemistry.



1a



1b



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Stereochemical "rigidity" of the carbon tetrahedron was explained by high thermal activation barrier to enantiomerization (inversion at the carbon center) of an organic compound. The first *ab initio* calculations[3] of the planar methane structure **2** as a feasible transition state of the methane inversion **1a** $\rightleftharpoons$ **1b** confirmed this explanation and revealed that the energy of planar form **2** is more than 150 kcal mol^{-1} higher than that of tetrahedral form **1**, which is much higher than the C—H bond dissociation energy in the CH_4 molecule. These calculations also indicated that planar configuration **2** is extremely unstable toward the tetrahedral distortion. Later,[4] it was established that the high thermodynamic instability of planar methane structure **2** compared with that of tetrahedral form **1** is due to strong destabilization of the p_{π}-orbital of carbon atom. It was also proposed

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* Dedicated to Academician V. I. Minkin on the occasion of his 65th birthday.

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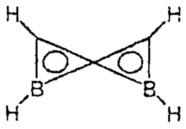
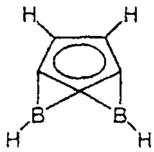
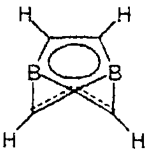
that the tetracoordinated carbon atom can stereoelectronically stabilize the planar structure due to involvement of the lone electron pair of the C atom in π-conjugation with peripheral ligands and the range of compounds was outlined in which such a stabilization can occur.[4] In fact, this study has laid the groundwork for "planar carbon chemistry."[5—9] Currently, after more than 25 years of search for this type of systems, numerous organometallic compounds with "planar" carbon atom are known.[6—10] Recently, novel stable types of organoboron compounds, 3—5, with "planar" tetracoordinated carbon atom were predicted. This has opened a new line of synthetic studies, namely, the search for the systems with "planar" carbon atom.[11]



3, C_{2v}



4, C_{2v}

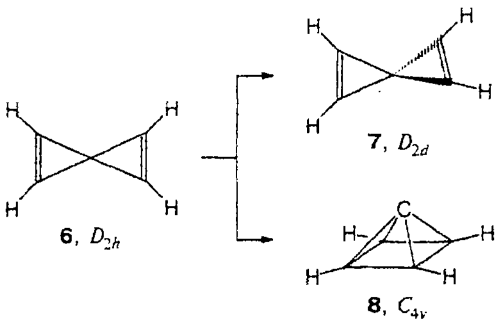


5, C_{2v}

In the planar methane structure **2**,[4] compounds **3—5**, as well as in other systems with "planar" carbon atom,[6—11] the central C atom forms multicenter orbitals with four neighboring atoms situated in basal plane. It can be assumed that the number of atoms in the basal plane involved in the same fashion in the formation of multicenter orbitals with participation of the central C atom can be larger (5 or more). In addition, the interaction between the lone electron pair and apical ligands, which results in hexacoordinated state of the central carbon atom, cannot also be ruled out. Despite the fact that the problem of penta- and hexacoordinated carbon atoms is discussed in the literature (see, *e.g.*, the monograph[5]), the possibility for such interactions to occur has not been studied in detail.

Analysis of possible distortions of a planar methane structure first performed in 1977 [12] revealed that it is unstable not only toward the tetrahedral distortion, but also toward other types of pyramidal distortion. In the light of the results obtained in that study pyramidal structures with tetracoordinated carbon atom appeared to be more preferable for stereoelectronic stabilization than planar forms.[5,12] For instance, the planar structure of spirocyclopentadiene **6** can be distorted to give not only the tetrahedral form **7**, but also a stable pyramidal form **8** (pyramidane),[13] which corresponds to a rather deep minimum on the potential energy surface (PES).

Based on the analysis of the electronic structure of pyramidane, a simple qualitative "8e rule" was suggested[13]: *a pyramidal form (of the type 8) is stable if the total number of valence electrons in the apical group and π-electrons in the basal ring does not exceed 8.* This made it possible not only to explain the stability of pyramidane, the Masamune[14] and Hogeveen[15] pyramidal cations, and other structures,[5] but also to predict the existence of novel types of pyramidal systems, *e.g.*, fenestrane,[16] hetero-derivatives of pyramidane, and related compounds.[17] In fact, the studies by Minkin[5] and Hoffmann[19,20] have laid the theoretical foundations of the chemistry of nonclassical tetracoordinated carbon structures, which has been intensively developing at present.[21,22] Stability of pyramidane **8** has been studied in detail (see Refs. 5, 23, and references cited therein); however, no *ab initio* quantum-chemical investigations of organoboron compounds with pyramidal structure have been performed as yet. The effect of counterions on the structural and energy characteristics of pyramidal systems predicted by the "8e rule" has also not been studied.[5]



6, D_{2h}

7, D_{2d}

8, C_{4v}

Analysis of possible distortions of planar methane structure provides a basis for the establishment of enantiomerization (inversion) pathways of the molecules of organic compounds and for the search for new nonclassical structures with tetracoordinated carbon atom. However, it is inadequate to gain a deep insight into the mechanisms of the inversion of tetrahedral structures. The solution of this problem requires an analysis of the complete topological structure of the methane PES in the corresponding region of the configuration space. To date, it has been possible to locate several stationary points on the PES of methane and to show that the inversion of methane proceeds with the formation of an intermediate structure with C_s symmetry and strongly different C—H bond lengths.[5,24,25] According to high-level *ab initio* calculations,[24,25] neither planar nor pyramidal structure of the CH_4 molecule are transition states of the methane inversion. However, no detailed analysis of the methane PES topology in the configuration space region between the two minima corresponding to tetrahedron **1a** and its mirror image **1b** has been carried out as yet, though such attempts have been undertaken on the basis of CNDO calculations.[26] It is impossible to gain a deep insight into the inversion process and preferential types of stabilization of nonclassical systems with tetracoordinated carbon atom without performing such an analysis.

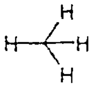
In this work, we established the complete topological structure of the methane PES in the region of the inversion of tetrahedral form and predicted new types of boron-containing compounds with planar and pyramidal structure containing a hypercoordinated carbon atom.

Calculation procedure

The *ab initio* calculations were carried out by the restricted Hartree—Fock (RHF) method with inclusion of correlation of all (valence and core) electrons at the second-order level of Møller—Plesset perturbation theory (MP2(full)) in the DZ (6-31G**) and TZ (6-311++G**) split-valence basis sets using the GAUSSIAN-94 [27] AND GAMESS [28] program packages on RISC-6000, DEC Alpha-station 500 and Duranga workstations. The structures corresponding to stationary points on the PES of methane were calculated by the coupled clusters (CCD) method[27] with the TZ basis set. Full optimization of the geometry of the molecular structures corresponding to the energy minima ($\lambda = 0$; hereafter λ is the stationary point index equal to the number of negative values of the Hesse matrix at this point[29]) and to the saddle points ($\lambda = 1$) on the PES were carried out up to the gradient magnitude of 10^{-5} au Bohr^{-1}. The structures corresponding to the energy minima on the PES were found by the method of steepest descent (movement along the gradient line) from the saddle point to the neighboring stationary point (a saddle point or a minimum).[29] The initial direction of the gradient line was specified by minor displacement (1/100 of the length of the normalized transition vector) along the transition vector. Graphic images of the molecular structures shown in the figures were obtained using the PC MODEL program[30] (the PLUTO mode) for which Cartesian atomic coordinates taken from the *ab initio* calculations served as input parameters.

Results and Discussion

Topology of the methane PES and the pathway of methane inversion (enantiomerization). According to calculations, there are seven stationary points on the PES of the singlet ground state of methane molecule (the energy of the triplet PES is higher than that of the singlet PES),[24,25] which correspond to nonequivalent structures. The minimum ($\lambda = 0$) corresponds to the tetrahedral form of methane molecule (**1a**,**b**), the next three stationary points correspond to planar structures **2**, **9**, and **10**, and the last three stationary points correspond to pyramidal structures **11**—**13**.



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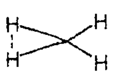

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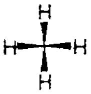

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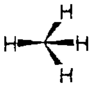


12

13

The calculated energy and geometric characteristics of these structures are shown in Fig. 1 and listed in Table 1. Except for form **12**, which was first found in this work, they are in good agreement with the results of previous calculations.[24,25] A true transition structure is form **13** corresponding to a rather high barrier to inversion (115.4 kcal mol^{-1}). The inclusion of zero-point harmonic vibrational energy (*ZPE*) correction due to nuclear motions decreases this value to 110.1 kcal mol^{-1}. From the data in Table 1 it can be seen that the inclusion of *ZPE* correction decreases the relative energy of pyramidal structure **11**. Hence if nuclear motions are taken into account, the inversion pathway will pass through structure **11** rather than through structure **13**. This indicates that consideration of nuclear motions is crucial for correct prediction of the reaction pathway in the case of flattened PES.

The gradient line connecting form **1a** and its mirror image **1b** and passing through the saddle point corresponding to the transition state of inversion is uniquely defined by the topological structure (the distribution of stationary points and their interrelations) of the methane PES in the region between the two minima **1a**, **1b** and the stationary point corresponding to planar structure **2**.[29] In this connection, it should be noted that, according to the Longuet-Higgins theorem,[31] the total number (m) of equivalent D_{4h}-structures on the entire methane PES is $m = |P_I|/|D_{4h}| = 3$, where $|P_I| = 4!\times 2 = 48$ is the order of the permutation-inversion group for the CH_4 molecule and $|D_{4h}| = 16$ is the order of the D_{4h} point symmetry group.[32] The equality $m = 3$ indicates that there are three topologically equivalent independent regions on the PES of methane; only one of them is discussed in this work. We will restrict ourselves to

Table 1. Results of *ab initio* calculations[a] of CH_4 structures with tetracoordinated carbon atom

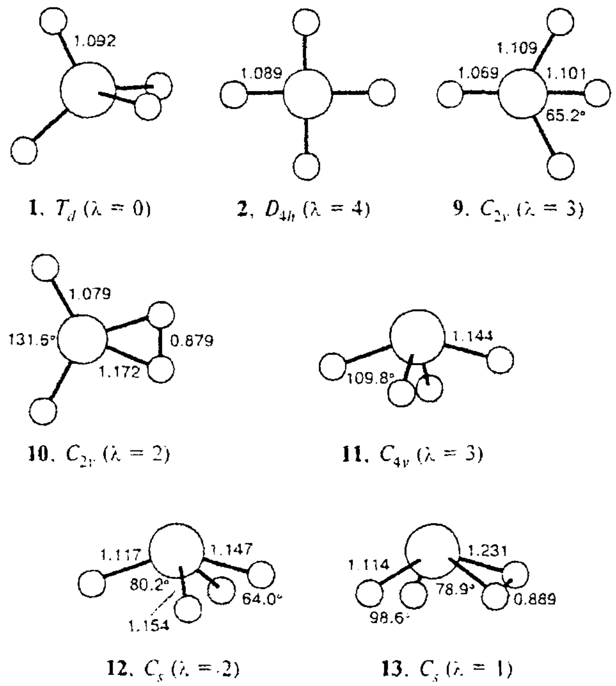
Structure	Symmetry	Electron state	E_{tot} (MCSCF[b])	λ	ΔE	E_{tot} (MP2[c])	λ	ΔE	E_{tot} (CCD[d])	λ	ΔE	ΔE_{ZPE}
1	T_d	$^1A_1$	40.29509	0	0	40.39837	0	0	−40.42061	0	0	0
2	D_{4h}	^1A_g	−40.03441	4	163.6	−40.17385	4	140.9	−40.19049	4	144.4	136.2
9	C_{2v}	$^1A_1$	−40.04437	3	157.3	—	—	—	−40.19947	3	138.8	132.2
10	C_{2v}	$^1A_1$	−40.05875	2	148.3	−40.19101	2	130.1	−40.20994	2	132.2	127.6
11	C_{4v}	$^1A_1$	−40.08533	3	131.6	−40.21241	3	116.5	−40.23102	3	119.0	110.0
12	C_s	$^1A'$	—	—	—	—	—	—	−40.23158	2	118.6	110.9
13	C_s	$^1A'$	−40.09488	1	125.6	−40.21620	1	114.3	−40.23668	1	115.4	110.1

[a] Here and in Tables 2 and 3, E_{tot}/au is the total energy (1 au = 627.5095 kcal mol^{-1}), λ is the number of negative eigenvalues of the Hessian, ΔE/kcal mol^{-1} is the relative energy, and ΔE_{ZPE}/kcal mol^{-1} is the relative energy with inclusion of *ZPE* correction.

[b] See Ref. 24.

[c] See Ref. 25.

[d] This work.



1, T_d ($\lambda = 0$) **2**, D_{4h} ($\lambda = 4$) **9**, C_{2v} ($\lambda = 3$)

10, C_{2v} ($\lambda = 2$) **11**, C_{4v} ($\lambda = 3$)

12, C_s ($\lambda = 2$) **13**, C_s ($\lambda = 1$)

Fig. 1. Geometric characteristics of structures **1**, **2**, and **9**—**13** with tetracoordinated carbon atom corresponding to different stationary points on the PES of methane, calculated by the CCD(full)/6-311++G** method. Hereafter, the bond lengths (in Å) and bond angles (in degrees) are given.

consideration of planar distortions of the structure only, where all atoms are in the same plane. In this case, there is only one point corresponding to the planar form **2** and eight points corresponding to equivalent planar structures **9a,b,c,d** and **10a,b,c,d** with C_{2v} symmetry. Analysis of the evolution of the eigenvectors corresponding to negative eigenvalues of the Hesse matrix along the gradient lines connecting stationary points **2**, **9a—d**, and **10a—d** shows that if the space is confined in the above-mentioned fashion, then structures **9a—d** are "transition states" between structures **10a—d** (Fig. 2). Pyramidal distortions of structures **2**, **9a—d**, and **10a—d** lead to two sets of pyramidal structures (**11a**, **12a—d**, and **13a—d** and **11b**, **12e—h**, and **13e—h**, respectively). As in the preceding case, the forms **12** are "transition states" between structures **13** in the confined space under consideration. Schematically, the distribution of stationary points and gradient lines connecting them on the PES of methane in the configuration space region between two tetrahedral forms is shown in Fig. 2. It should be noted that the distribution of nondegenerate stationary points shown in Fig. 2 is in agreement with the Morse relations.[33]

Based on the results of *ab initio* calculations, it can be concluded that there are eight equivalent true transition states **13a—h** corresponding to eight equivalent pathways of the inversion of tetrahedral methane

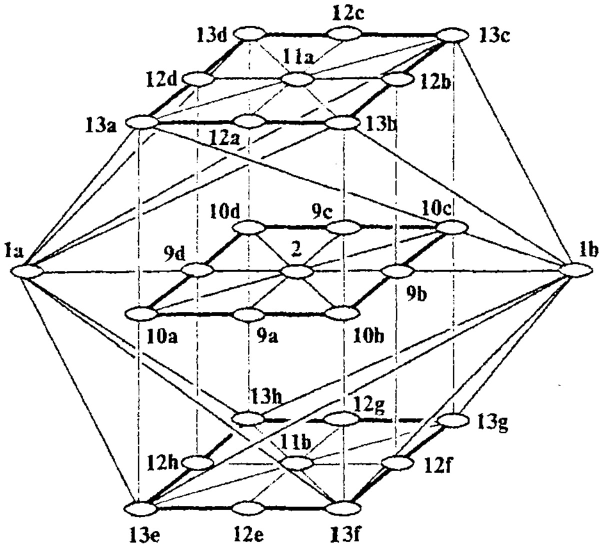
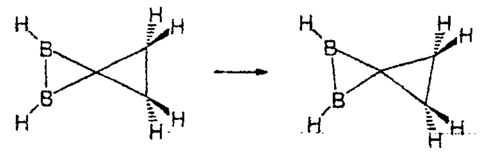


Fig. 2. Graph of inversion **1a** $\rightleftharpoons$ **1b**. The ovals and solid lines connecting them respectively denote the stationary points on the PES of methane and the gradient lines issuing from the stationary points along the directions of negative eigenvalues of the Hessian.

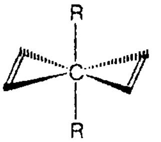
1a $\rightleftharpoons$ **13** $\rightleftharpoons$ **1b**. The high relative energies (≥100 kcal mol^{-1}) of all structures corresponding to the stationary points on the PES compared to the energy of the tetrahedral structure indicate that it is impossible to stabilize nonclassical systems with tetracoordinated carbon atom by means of steric interactions only (without involvement of electronic stabilization). In the case of stereoelectronic stabilization of planar structures with tetracoordinated carbon atom, the structures of the types **9** or **10** with C_{2v} symmetry will be more stable than the systems with D_{4h} symmetry because of secondary σ-interactions[5,18,34] between the ligands. The stabilizing distortion **14** $\rightleftharpoons$ **15** we found recently[11] can be taken as a good example supporting this conclusion.



14, C_{2v} **15**, C_s

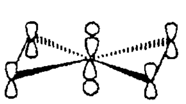
Analogous conclusion can also be drawn for compounds with pyramidal structure. However, in this case the primary π-interactions (conjugation) between the atoms in basal plane are much stronger than secondary σ-interactions.[5,18]

System $CB_4H_4Li_2$ with octahedral environment of hexacoordinated carbon center. The $CFe_6(CO)_6{}^{2-}$ and $CRu_6(CO)_{17}$ carbonyl clusters of iron[35] and ruthenium,[35] respectively, as well as the $[(Ph_3PAu)_6C]^{2+}$ complex of gold[36] and other organometallic compounds (see Refs. 5, 9, and 21) with hexacoordinated carbon atoms have long been obtained and studied in detail. It was also theoretically predicted that minima on the PES of CH_6 and CLi_6 systems correspond to the CH_6^{2+} and CLi_6^{2+} dications (see Refs. 22 and 37, respectively). However, these examples are few and so it is impossible to establish reliably the stereoelectronic conditions for hexacoordination of the carbon atom. Because of this, the search for compounds with hexacoordinated C atom is topical. Previously,[38] it was proposed that the systems with "planar" tetracoordinated carbon atom can be used as basic models in the search for stable compounds with hexacoordinated carbon center. This assumption has been analyzed taking hypothetical organic compounds of the type **16** (R = H, F, Me) as examples.



16, D_{2h}

However, the *ab initio* calculations[38] indicated that none of these structures corresponds to a minimum on the PES. This is due to the occupation of antibonding molecular orbitals, as is shown below taking structures of the types **17**—**19** as examples.



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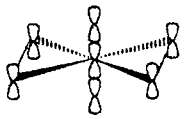

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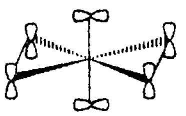

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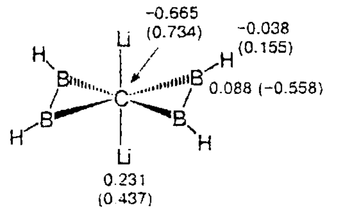
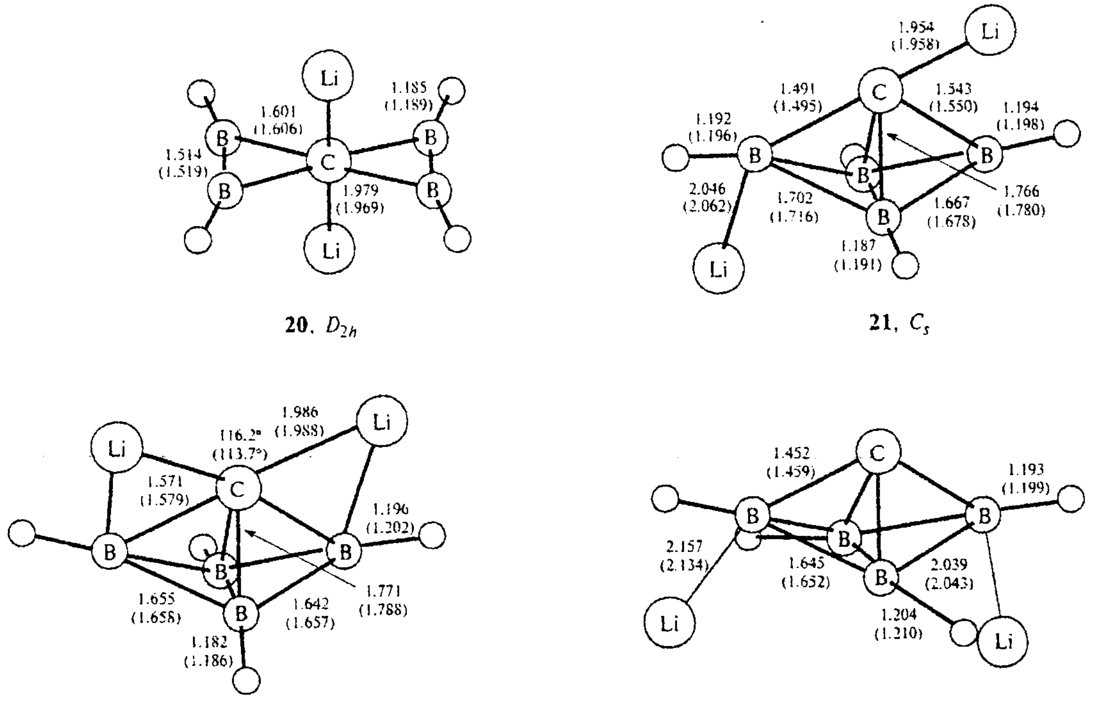
It can be expected that no destabilization will be observed in systems in which the antibonding orbitals remain unoccupied. According to the results of our *ab initio* calculations, the structure of the dilithium salt **20** with a hexacoordinated carbon center corresponds to an energy minimum (λ = 0) on the PES (here, given are the corresponding atomic charges calculated by the MP2/DZ and MP2/TZ (figures in parentheses) methods).



20

The lengths of axial C—Li bonds (~2.00 Å) lie within the limits of experimentally (1.959 Å)[39] and theoretically (2.000±0.004 Å)[40] determined values for the ordinary covalent C—Li bonds. The electron density distribution in system **20** also corresponds to covalent bonding rather than to zwitterionic bonding usually assumed for such systems. The degree of charge transfer between the apical and equatorial fragments increases appreciably if the calculations are performed in the TZ basis set rather than in the DZ basis set, namely, each lithium center accepts a charge of 0.2 *e* (DZ) and 0.4 *e* (TZ).



20, D_{2h} **21**, C_s

22, C_2 **23**, C_2

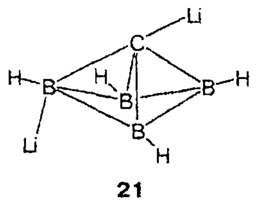
Fig. 3. Geometric characteristics of structures **20**—**23** corresponding to minima (λ = 0) on the PES of the $CB_4H_4Li_2$ system calculated by the MP2/DZ and MP2/TZ (figures in parentheses) methods.

Table 2. Results of MP2 calculations of structures **20—31**

Structure	Symmetry	Basis set	E_{tot}	λ	*ZPE*	$\omega_1(i\omega)$
20	D_{2h}	DZ	−154.29061	0	0.05622	65.5
		TZ	−154.44650	0	0.05497	68.15
21	C_s	DZ	−154.33227	0	0.05859	82.7
		TZ	−154.48763	0	0.05740	73.1
22	C_2	DZ	−154.33127	0	0.05945	41.8
		TZ	−154.48671	0	0.05874	28.9
23	C_2	DZ	−154.33270	0	0.05965	189.8
		TZ	−154.48710	0	0.05841	181.0
24	C_{2v}	DZ	−139.24724	0	0.05831	112.8
25	D_{2h}	DZ	−139.14421	0	0.05032	119.7
		TZ	−139.32902	1	0.04687	(i442.3)
26	C_2	DZ	−139.17271	0	0.05338	308.4
		TZ	−139.35738	0	0.05116	309.8
27	C_s	DZ	−139.11161	0	0.05198	254.1
		TZ	−139.30139	0	0.04976	230.3
28	D_{2h}	DZ	−296.93857	0	0.06192	102.4
		TZ	−297.18305	0	0.06058	103.7
29	D_{2h}	DZ	−336.61879	0	0.03705	116.6
		TZ	−336.89904	0	0.03621	120.0
30	C_{2v}	DZ	−193.36366	0	0.05376	163.3
		TZ	−193.52119	0	0.05260	173.5
31	C_{2v}	DZ	−213.20889	0	0.04167	239.1
		TZ	−213.38482	0	0.04075	238.7

Note. Here and in Table 3 *ZPE*/au is the zero-point vibrational energy and ω_1/cm^{-1} and $i\omega$/cm^{-1} are the lowest and imaginary harmonic vibrational frequencies, respectively.

It should be noted that, despite a rather high stability, structure **20** is not the most energetically favorable $CB_4H_4Li_2$ isomer. According to calculations, more stable are forms **21—23**. The calculated geometric and energy characteristics of structures **20—23** are shown in Fig. 3 and listed in Table 2.



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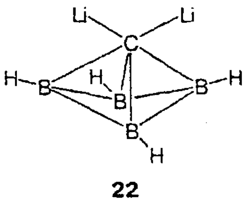

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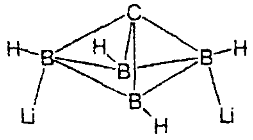
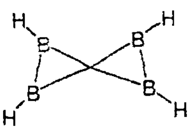


23

It was of importance to establish how the apical lithium atoms affect the stability and geometry of planar basal fragment in structure **20**. To this end, we studied the tetraboraspiropentane basal fragment in molecule **24** and dianion **25**. According to *ab initio* calculations, the basal fragment in the triplet ($^3B_1$) ground state of planar form **24** is stable (λ = 0), whereas the singlet states are characterized by higher energies and correspond to the stationary points with $\lambda \geq 1$.



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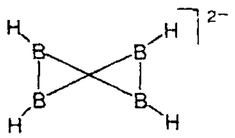

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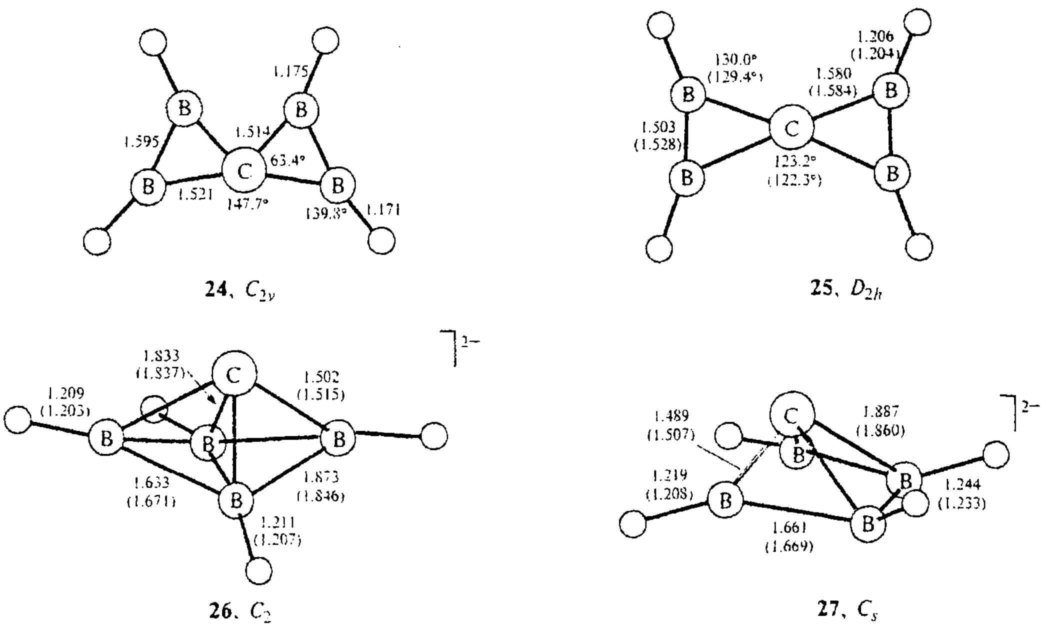
The geometric characteristics of tetraboraspiropentane **24** (Fig. 4) differ appreciably from those of structure **20**. At the same time, the geometry of dianion **25** (see Fig. 4) is much like that of the basal fragment in structure **20**, namely, the B—C bonds in molecule **20** are only slightly lengthened as compared to those in dianion **25** because of a minor weakening of the bonding to boron atoms due to the interaction between the carbon center and axial ligands. According to the MP2/DZ calculations, the planar form **25** of the tetraboraspiropentane dianion corresponds to an energy minimum (λ = 0) on the PES of the $CB_4H_4^{2-}$ system. The other two isomers, **26** and **27** (see Fig. 4), are also stable (λ = 0). The deepest minimum corresponds to a carbene-type pyramidal dianion **26** with C_2 symmetry. The energy of dianion **25** is ~18 kcal mol^{-1} higher than that of dianion **26**. However, the most unstable is the carbene-type iso-



24, C_{2v} **25**, D_{2h} **26**, C_2 **27**, C_s

Fig. 4. Geometric characteristics of structures **24—27** corresponding to the PES minima (λ = 0) calculated by the MP2/DZ and MP2/TZ (figures in parentheses) methods. According to MP2/DZ calculations, structure **25** corresponds to a saddle point (λ = 1).

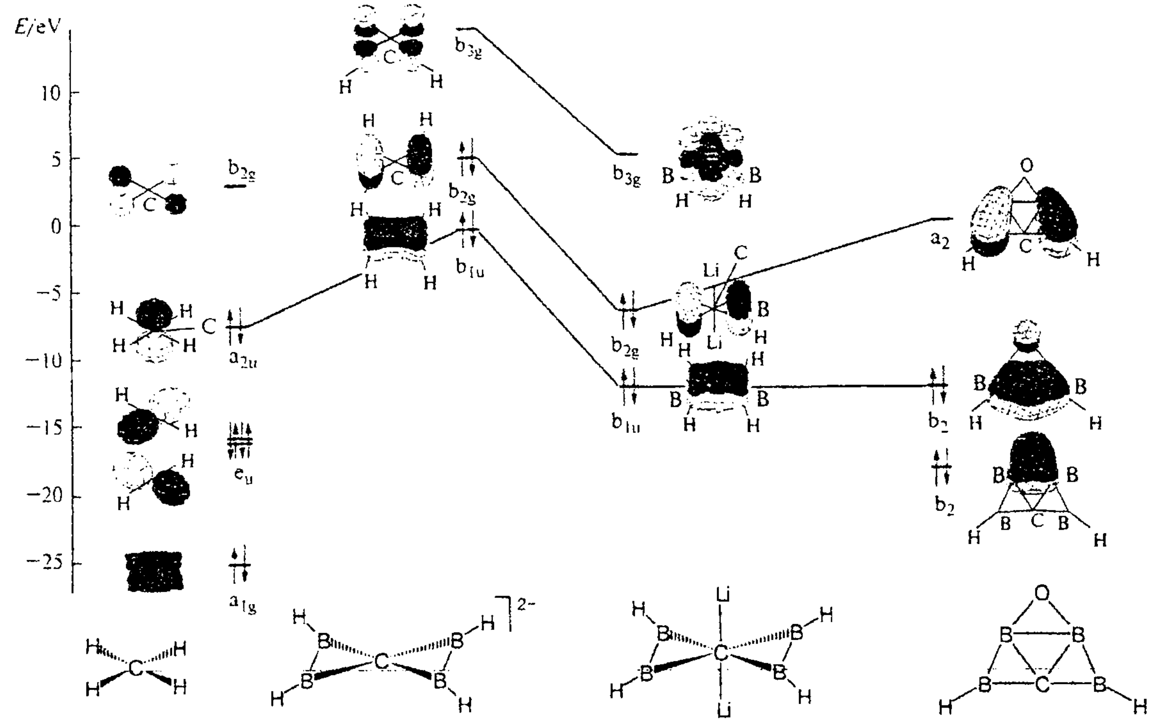


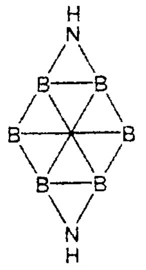
Fig. 5. The π-MO correlation diagram for planar systems with tetracoordinated carbon atom.

mer **27**, whose energy is ~38 kcal mol^{-1} higher than that of dianion **26**. At the same time, according to the MP2/TZ calculations, the planar structure **25** corresponds to a saddle point (λ = 1) rather than to a minimum. However, these calculations leave the relative stability pattern of isomers **25**—**27** virtually unchanged.

Comparison of the π-MO correlation diagrams for systems **2** and **25** (Fig. 5) shows that the boron atoms surrounding the carbon center are responsible for delocalization of the lone electron pair of the carbon atom and for the formation of the b_{1u} multicenter orbital. However, unlike the previously considered system **3** in which such an interaction favors stabilization of the system, in this case the position of the energy level of the delocalized orbital is appreciably shifted toward higher energies, which can be the reason for instability of the planar structure of dianion **25**. The MO correlation diagram pattern obtained for dianion **25** remains unchanged on going to the dilithium compound **20**; however, the inclusion of lithium atoms in the system causes a decrease in the energy of all (σ and π) orbitals, thus resulting in the stabilizing effect.

Thus, despite the fact that the isolated planar structure of dianion **25** is unstable, it appears to be stabilized as the basal fragment in structure **20** in the presence of lithium counterions which can strongly affect the stability and structural parameters of the systems under study.[41,42]

Systems with a "planar" hexacoordinated carbon center. Previously,[11] it has been shown taking structures **3—5** as examples that expansion of one of the cycles by introduction of electron-donor groups substantially stabilizes the systems with "planar" carbon atom and leads to the appearance of additional possibilities for this atom to form coordination bonds. In this work, we studied heterocyclic compounds **28** and **29** as the simplest systems with a planar hexacoordinated carbon center.



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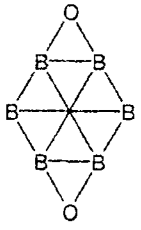

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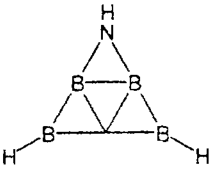

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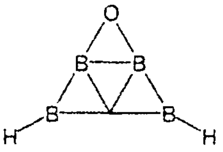

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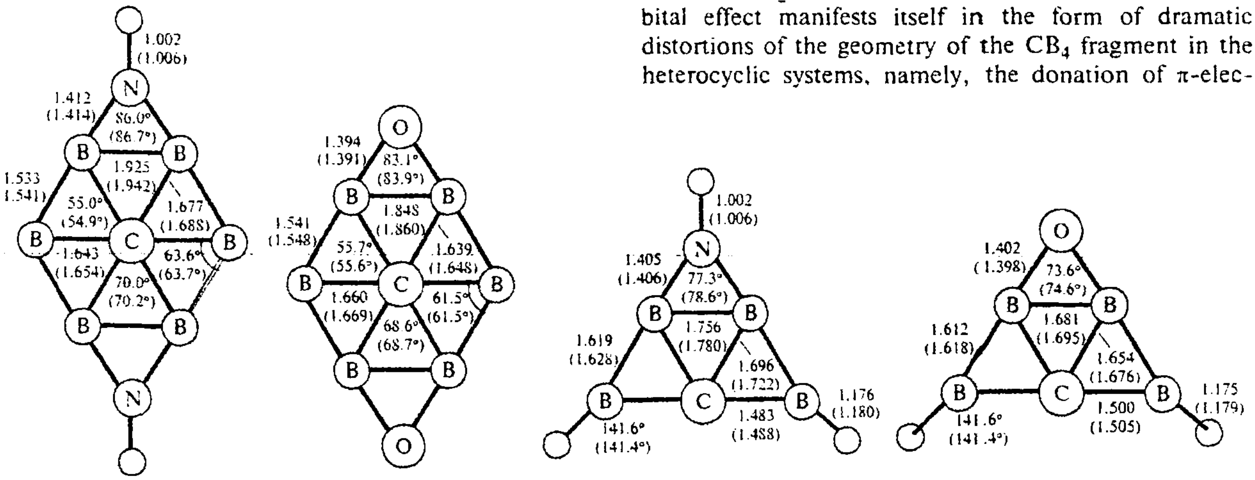
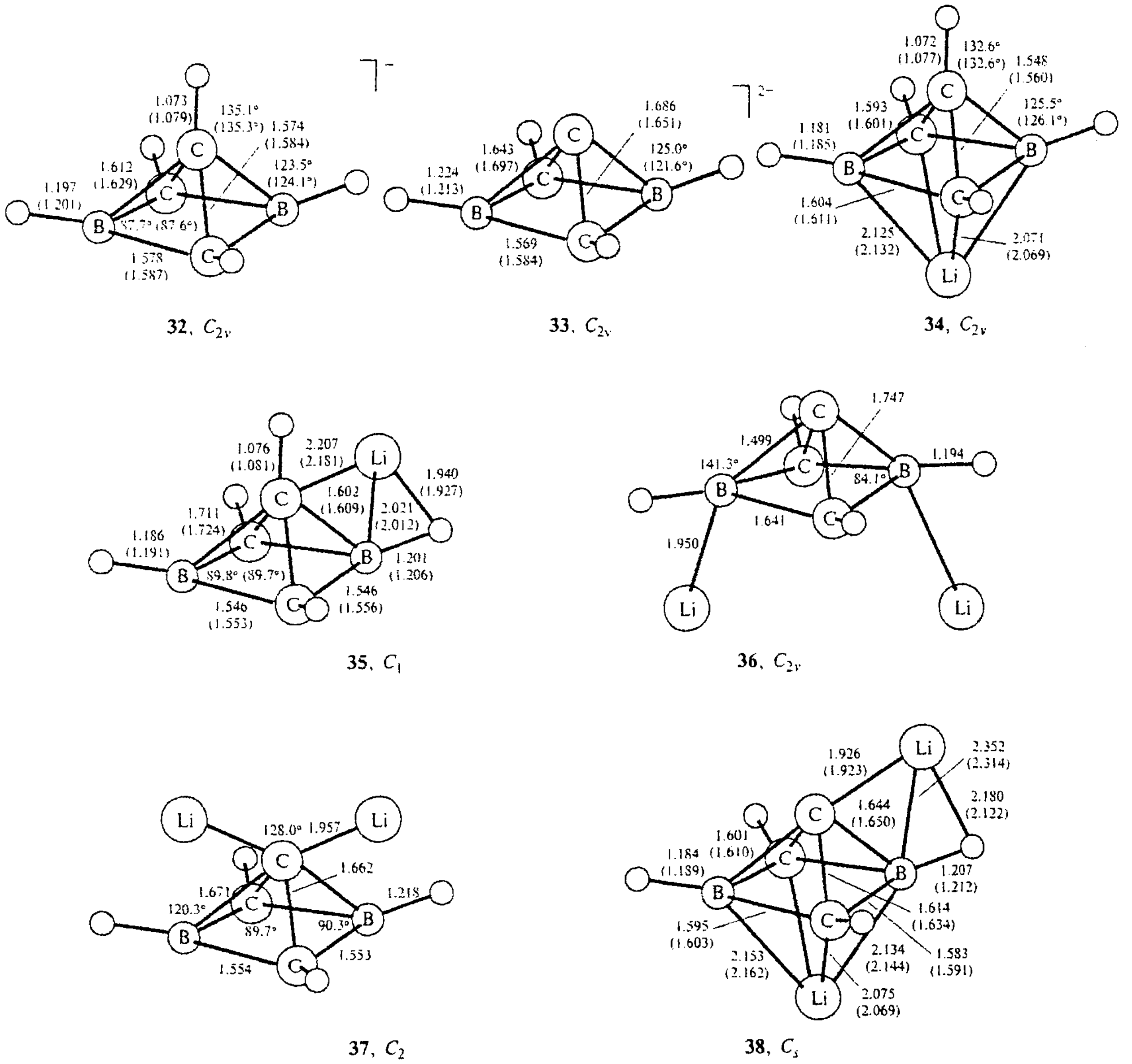
According to calculations (Fig. 6, see Table 2), structures **28** and **29** correspond to stable molecular systems (λ = 0). The lengths of six B—C bonds in molecules **28** and **29** (1.64—1.67 Å) lie within the limits characteristic of the ordinary B—C bonds (~1.6—1.7 Å).[43,44] It is of interest to compare the values of geometric and electronic characteristics of the nitrogen- and oxygen-containing heterocycles (**30** and **31**, respectively) with "planar" tetracoordinated carbon atom and those of the corresponding parameters of molecules **28** and **29**. According to calculations, both structures **30** and **31** correspond to deep energy minima (λ = 0) on the PES (see Fig. 6 and Table 2). The B—N and B—O bond lengths in molecules **30** and **31** are nearly the same as those in molecules **28** and **29**, whereas the B—C bonds in the hexacoordinated structures **28** and **29** are lengthened as compared to those in molecules **30** and **31**, which is due to the passage from the one-center MO to the multicenter MO. The orbital correlation diagram (see Fig. 5) illustrates well the drastic increase in the stability of planar heterocyclic systems compared to dianion **25** and the lithium derivative **20**. The stabilizing effect due to delocalization of the lone electron pair of the carbon atom in heterocyclic systems is increased by additional stabilization due to the donation of a pair of π-electrons of the heteroatom to the vacant p_z-orbitals of the boron atoms bonded to the heteroatom, which results in the formation of a strongly stabilized $1b_2$ multicenter orbital. Structurally, this orbital effect manifests itself in the form of dramatic distortions of the geometry of the CB_4 fragment in the heterocyclic systems, namely, the donation of π-elec-



28, D_{2h} **29**, D_{2h} **30**, C_{2v} **31**, C_{2v}

Fig. 6. Geometric characteristics of planar structures **28—31** corresponding to the PES minima calculated by the MP2/DZ and MP2/TZ (figures in parentheses) methods.



32, C_{2v} **33**, C_{2v} **34**, C_{2v}

35, C_1 **36**, C_{2v}

37, C_2 **38**, C_s

Fig. 7. Geometric characteristics of the structures of pyramidal systems **32—38** corresponding to the PES minima (λ = 0), calculated by the MP2/DZ and MP2/TZ (figures in parentheses) methods.

trons is accompanied by a pronounced weakening of the interaction between the spiro-carbon atom and two boron centers bonded to the heteroatom while strengthening of the other two C—B bonds occurs simultaneously.

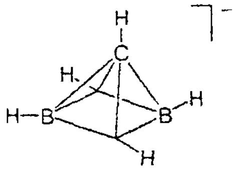
Stabilization of "pyramidal" hypercoordinated carbon atom in lithium salts. In the preceding sections of this work we have shown that lithium salts are convenient reagents for stabilization of the structures with "planar" carbon atom. In this connection, the idea of stabilizing the systems with yet another type of nonclassical bond orientation, namely, "pyramidal" carbon center, seems attractive. To date, the existence of this type of neutral and cationic systems has received reliable experimental and theoretical confirmation[5,14,15,21]; however, anionic systems with a "pyramidal" carbon atom and the effect of counterions on their stability have been little studied. In this work, we considered this problem taking the two simplest boron-containing anionic pyramidal systems **32** and **33** as examples and studied the effect of lithium counterions on their stability and structural parameters.

Anions **32** and **33** satisfy the "8e rule"[5] and correspond to rather deep energy minima (λ = 0) on the PES. The calculated geometric and energy characteristics of structures **32** and **33** are shown in Fig. 7 and listed in Table 3.

Table 3. Results of MP2 calculations of structures **32—38**

Structure	Symmetry	Basis set	E_{tot}	ZPE	ω_1
32	C_{2v}	DZ	−166.40124	0.07270	309.2
		TZ	−166.55411	0.07016	246.2
33	C_{2v}	DZ	−165.55360	0.05842	418.4
		TZ	−165.76500	0.05653	309.6
34	C_{2v}	DZ	−173.91790	0.07828	356.0
		TZ	−174.06649	0.07591	339.7
35	C_1	DZ	−173.86964	0.07570	201.7
		TZ	−174.02431	0.07410	213.6
36	C_{2v}	DZ	−180.72139	0.06565	116.5
37	C_2	DZ	−180.75410	0.06564	22.9
38	C_s	DZ	−180.78468	0.06743	129.4
		TZ	−180.95173	0.06566	112.8

Note. For all structures, the stationary point index $\lambda = 0$.



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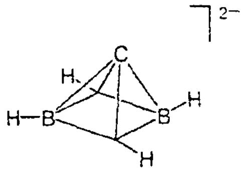

33

Pyramidal structures **32** and **33** contain a pentacoordinated and a tetracoordinated carbon atom, respectively. The cycles in the basal planes are virtually planar. The inclusion of lithium cation in system **32** results in the formation of two isomers, **34** and **35** (see Fig. 7), which differ in position of the coordination site of the counterion. In structure **34**, the Li atom lying below the basal plane is coordinated to complete the environment to the square bipyramid configuration. In isomer **35**, this atom is coordinated to the apical CH group, thus forming the structure with hexacoordinated carbon center. The energy of structure **35** is only ~5 kcal mol^{-1} higher than that of isomer **34**. Introduction of lithium cations in the system has little effect on the geometric parameters of initial pyramidal structures. As in the case of system **20**, the lithium compounds **34** and **35** have no pronounced zwitterionic character and their formation is also accompanied by a pronounced stabilizing effect due to a decrease in the energy of all orbitals in the resulting system (see the preceding example). As previously, the pattern of the MO correlation diagram remains (qualitatively) unchanged.

Consideration of the effect of counterions, as applied to dianion **33**, gives analogous results. In this case, three isomers, **36—38** (see Fig. 7), can be formed. The most stable among them is isomer **38** in which the lithium atoms are coordinated on the opposite sides of the basal plane. No pronounced distortions of the geometry of initial pyramidal system and charge transfer is observed in structures **37** and **38**, which means that these systems can be characterized as covalent compounds. Having virtually no effect on structural characteristics of the systems with hypercoordinated carbon atom, the counterions substantially increase their stability. Because of this, lithium salts are rather convenient for experimental study of nonclassical structures.

* * *

The complete topological structure of the methane PES obtained in this work shows that, first, the pathway of inversion **1a** $\rightleftharpoons$ **1b** of the tetrahedral structure includes eight equivalent gradient lines. This indicates that even such a simple system like methane is characterized by a very complicated inversion pathway. Second, high energies (≥100 kcal mol^{-1}) of the structures corresponding to all stationary points compared to that of the tetrahedral form indicate that it is impossible to stabilize nonclassical systems with tetracoordinated carbon atom by means of steric interactions only (without involvement of electronic stabilization). Third, nuclear motions should be taken into account in order to rigorously consider the methane inversion because of the flattened shape of its PES in the region of pyramidal structures.

Aromaticity[4,11] of planar systems **3—5** and **28—31** with tetra- and hexacoordinated carbon centers is of fundamental importance for their stabilization. The fact that these systems correspond to rather deep minima on the PES indicates that they can be the subject of synthetic studies.

According to *ab initio* calculations, pyramidal systems **32—38** with hypercoordinated carbon atom, which satisfy the "8e rule," correspond to rather deep minima on the corresponding PES and can also be detected experimentally.

Lithium counterions are of fundamental importance for stabilization of systems with hypercoordinated carbon atom.

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