# Pentacoordination of boron, carbon, aluminum, and silicon atoms in organic compounds: an *ab initio* study

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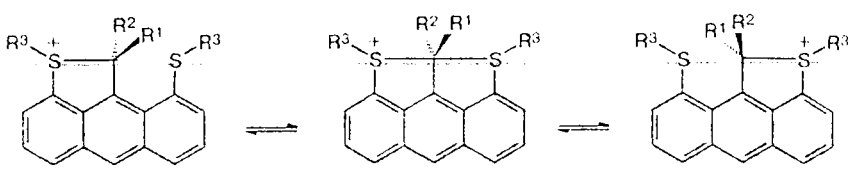
Pentacoordination of boron, carbon, aluminum, and silicon atoms in bicyclic organic compounds of the pentalene type was studied using the *ab initio* RHF/6-31G** and MP2(full)/6-31G** methods. It was shown that the ability of the atom to form pentacoordinate structures increases on going from B to Al and from C to Si atom, *i.e.*, as the number of the element of Groups IIIA and IVA of the periodic system increases. At the same time, the reverse tendencies are observed in the 2nd and 3rd periods of the periodic system, *viz.*, the ability of the atom to form pentacoordinate structures increases on going from C to B and from Al to Si atom.

**Key words:** *ab initio* quantum-chemical calculations; nucleophilic substitution; pentacoordination of boron, carbon, aluminum, and silicon.

Unusual properties of hypervalent (nonclassical) structures formed by the elements of Groups IIIA and IVA of the periodic system, which cannot be explained by the classical theory of the structure of matter using two-center two-electron (2c-2e) bonds, have always attracted the attention of investigators.[1–5] In the last two decades, major efforts have been directed toward elucidating the conditions under which it is possible to stabilize a bipyramidal configuration of valence bonds at pentacoordinate C and Si atoms in organic compounds.[2,3,5–8] It is known that nucleophilic substitution ($S_N2$) reactions at tetracoordinate C [6,9] and Si atoms[3,10,11] occur with inversion of the configuration and the formation of pentacoordinate bipyramidal structures, which always correspond to the transition state (TS) of the reaction[6] in carbon-containing systems and can correspond either to the TS[12,13] or to an intermediate[3,14] in silicon-containing systems. The establishment of the conditions under which the Si atom is capable of forming pentacoordinate structures has led to rapid development of the chemistry of compounds containing pentacoordinate[3–5] and even hexacoordinate silicon atoms.[3,15,16] Up to the present, numerous attempts to isolate or detect intermediates with bipyramidal bond configuration at the pentacoordinate C atom have failed.[1,2,6,7] Nucleophilic substitution reaction at the tetracoordinate C atom in the gas phase proceeds with an internal activation barrier,[6,9] which, as a rule, is not higher than 20 kcal mol$^{-1}$. Previously,[17] the idea was proposed of "freezing" the pentacoordinate structure of TS by steric strain energy by incorporating the structure into the corresponding rigid framework. To this end, salts of 1,8-di(arylthio)anthracene-9-carbinyl cation **1** were synthesized[17] in which the anthracene nucleus in combination with the sulfenyl groups creates steric conditions required to stabilize form **2** containing a fragment with a key pentacoordinate carbon atom (Scheme 1).

However, it was shown in studies by $^1$H NMR spectroscopy that a fast and reversible rearrangement **1a** ⇌ **1b** *via* TS **2** with an activation barrier ($\Delta H^{\neq}$) of

**Scheme 1**




**1a** **2** **1b**

$R^1$, $R^2$ = H, Me; $R^3$ = Ar

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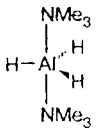
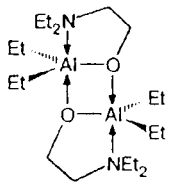
10 to 20 kcal mol$^{-1}$ occurs in these cations and that the barrier height is strongly dependent on the nature of the substituents $R^1$—$R^3$ and the solvent.[17] The fact that structure **2** corresponds to the TS rather than to the energy minimum was explained by large additional steric strain produced in the fragment containing the pentacoordinate carbon atom due to the deviation of the S—C—S angle (it is 163° in cation **2**) from the required value (180°). In accord with the general idea,[17] replacement of the sulfur atom in cation **1** by the oxygen atom should decrease the corresponding angle and lower the activation barrier to reaction **1a** ⇌ **1b**. However, to our knowledge such compounds have not been obtained to date and it is unclear whether or not they can exist.

We failed in finding information on organic compounds containing a fragment with the bipyramidal bond configuration at the pentacoordinate B atom. The possibility for the $S_N2$ reaction to occur at the tetracoordinate B atom has not been studied before.

A bipyramidal bond configuration at the pentacoordinate Al atom is known for the adduct $H_3Al(NMe_3)_2$ (**3**),[18] dimer **4**,[19—21] polymer $[H_3Al(NMe_2CH_2)_2]_n$,[22] and several other compounds.[4,19—21] However, the energetics of the hypervalent bond formation in such structures has not been studied.



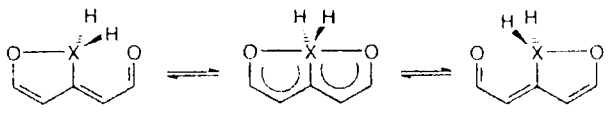

**3**




**4**

In this work, we studied the ability of B, C, Al, and Si atoms to form pentacoordinate structures using *ab initio* calculations by the RHF/6-31G** and MP2(full)/6-31G** methods[23] (hereafter, RHF and MP2, respectively). Relative stabilities of structures **5** and **6** (Scheme 2) were compared. The difference in the total energies of these systems makes it possible to assess the height of the activation barrier to the ($S_N2$) reaction of intramolecular nucleophilic substitution **5a** ⇌ **6** ⇌ **5b** at the X atom and characterizes its ability to form pentacoordinate structures.

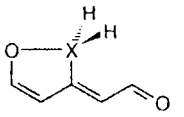
**Scheme 2**



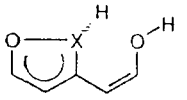

**5a** **6** **5b**

X = $B^-$, C, $Al^-$, Si

To estimate the energy of the "nonvalence" donor-acceptor O···X interaction in structure **5**, we calculated corresponding *trans*-forms **7**, in which this type of interaction does not occur.




**7**




**8**

X = $B^-$, C, $Al^-$, Si

The difference between the total energies of structures **5** and **7** (X = $B^-$, C, $Al^-$, Si) characterizes the lower bound of the energy of donor-acceptor X···O interaction in molecule **5**, whereas the difference between the total energies of structures **6** and **7** (X = $B^-$, C, $Al^-$, Si) can be considered as the lower bound of the energy of the hypervalent X—O bond in structure **6** (X = $Al^-$, Si). For compounds of type **5** with hypervalent B and Al atoms, it is of importance to compare their stability with that of the closest classical analogs of type **8** (X = $B^-$, $Al^-$); the results of *ab initio* calculations of the latter are also presented in this work.

## Calculation procedure

First, the *ab initio* calculations were carried out by the restricted Hartree—Fock (RHF) method. The results obtained were refined using calculations at the second-order Møller—Plesset (MP2) level of perturbation theory with inclusion of correlation of all (valence and core) electrons in the 6-31G** split-valence basis set[23] using the GAUSSIAN-94[24] and GAMESS[25] program packages on RISC-6000, DEC Alpha-Station 500, and Duranga workstations. Full optimization of the geometry of the molecular structures corresponding to the saddle points ($\lambda$ = 1; hereafter $\lambda$ is the number of negative eigenvalues of the Hesse matrix at a given stationary point[26]) and to the energy minima ($\lambda$ = 0) on the potential energy surface (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 (TS) to the neighboring stationary point (a saddle point or a minimum).[26] 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 Figs. 1—6 were obtained using the PC MODEL program.

## Results and Discussion

**Structure of compounds 5—8 (X = $B^-$).** According to our *ab initio* calculations, structures **5**, **7**, and **8** (X = $B^-$) correspond to minima ($\lambda$ = 0), whereas structure **6** (X = $B^-$) corresponds to a saddle point ($\lambda$ = 1) on the PES of the system shown in Scheme 2. The predicted geometric and energy characteristics of these structures are shown in Fig. 1 and listed in Table 1.

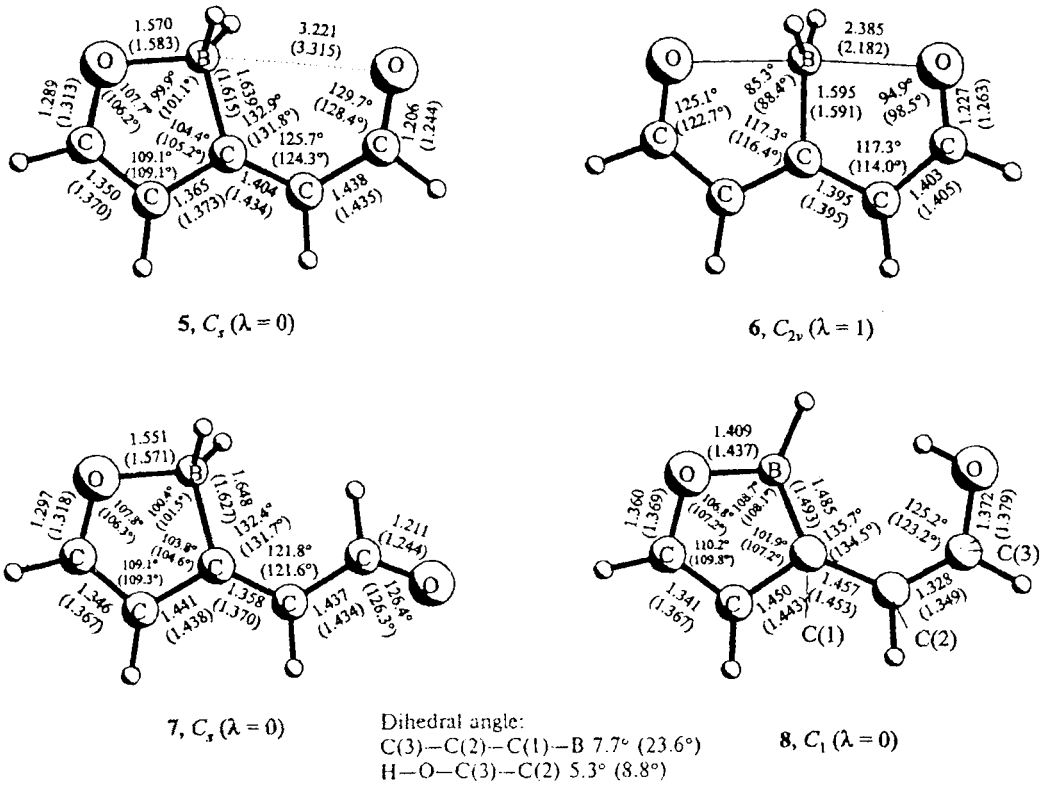



**Fig. 1.** Geometric characteristics of structures **5**, **7**, and **8** (X = $B^-$), corresponding to minima on the PES, and those of TS **6** (X = $B^-$), corresponding to the saddle point, calculated by the RHF and MP2 (figures in parentheses) methods. Here and in Figs. 2—6 the bond lengths (in Å) and bond angles are shown.

**Table 1.** Total energies ($E_{tot}$/au), relative energies ($\Delta E$/kcal mol$^{-1}$), number of negative eigenvalues of the Hessian ($\lambda$), and imaginary or lowest harmonic frequencies ($(i\omega/\omega_1)$/cm$^{-1}$) of structures **5**—**8** (X = $B^-$) and **9**—**12** (Y = B), calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods

| Structure, symmetry | $E_{tot}$ | $\Delta E$ | $\lambda$ | $i\omega/\omega_1$ |
|---|---|---|---|---|
| **5**, $C_s$ | −367.25763 | 0 | 0 | 133 |
| | (−368.40501) | (0) | (0) | (132) |
| **6**, $C_{2v}$ | −367.23578 | 13.7 | 1 | i245 |
| | (−368.38205) | (14.4) | (1) | (i429) |
| **7**, $C_s$ | −367.26932 | −7.3 | 0 | 106 |
| | (−368.41422) | (−5.8) | (0) | (93) |
| **8**, $C_1$ | −367.23488 | 14.3 | 0 | 31 |
| | (−368.39540) | (6.0) | (0) | (67) |
| **9**, $C_s$ | −383.80991 | 0 | 0 | 113 |
| | (−384.99345) | (0) | (0) | (145) |
| **10**, $C_{2v}$ | −383.77393 | 22.6 | 1 | i535 |
| | (−384.97090) | (14.1) | (1) | (i540) |
| **11**, $C_s$ | −383.81819 | −5.2 | 0 | 100 |
| | (−384.99542) | (−1.2) | (0) | (101) |
| **12**, $C_1$ | −383.86381 | −33.4 | 0 | 44 |
| | (−384.03226) | (−24.3) | (0) | (57) |

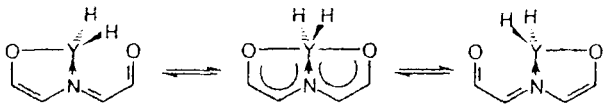
*Note.* 1 au = 627.5095 kcal mol$^{-1}$.

The bond lengths and bond angles in structures **5**, **7**, and **8** (X = $B^-$) calculated in this work are fairly close to the corresponding experimentally determined values[27,28] for organoboron compounds containing a tetracoordinate B atom. It is noteworthy that the geometric parameters of these structures calculated with inclusion of electron correlation are, on the whole, in good agreement with the results of the RHF calculations, though the structures become more delocalized in the first case. The *trans*-isomer **7** is 7.3 (RHF) and 5.8 kcal mol$^{-1}$ (MP2) more energetically favorable than the *cis*-form **5**. This is an indication of the absence of stabilizing donor-acceptor B···O interaction in *cis*-form **5**, which is likely determined by strong electrostatic repulsion between the O atoms and the H atoms bonded to the B atom and carrying a rather large Mulliken charge of −−0.212 (RHF) and −0.208 au (MP2). The classical structure **8** containing a tricoordinate B atom is less stable than structure **5** containing the fragment with the hypervalent B atom (the energy difference is 14.3 (RHF) and 6.0 kcal mol$^{-1}$ (MP2)). The aromatic ring in structure **8** is planar, whereas the substituent deviates out of the ring plane so that the OH group is oriented to the $p_\pi$-orbital of the ring C atom (see Fig. 1).

Structure **6** containing a hypervalent pentacoordinate B atom is the TS of the intramolecular $S_N2$ reaction

**5a** ⇌ **6** ⇌ **5b** (X = $B^-$), the activation barrier to which is 13.7 (RHF) and 14.4 kcal $mol^{-1}$ (MP2). The inclusion of electron correlation leads to a shortening of the rather long hypervalent B—O bond in structure **6** by nearly 0.2 Å and to some increase (by less than 1 kcal $mol^{-1}$) in the barrier height. Most likely, the appreciable length of the three-center hypervalent O—B—O bond is determined by the large negative Mulliken charges on the O atoms (~−0.7 au) in anions **5**—**8** (X = $B^-$). To elucidate how the energy characteristics of the reaction **5a** ⇌ **6** ⇌ **5b** and the geometric parameters of the structures corresponding to stationary points on the PES change on going to neutral compounds, we studied the intramolecular $S_N2$ reaction **9a** ⇌ **10** ⇌ **9b** (Scheme 3, Y = B).

**Scheme 3**

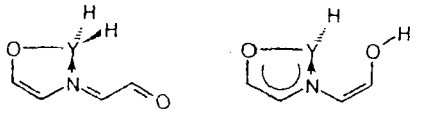


**9a** **10** **9b**

The calculated geometric and energy characteristics of structures **9** and **10** (Y = B) are shown in Fig. 2 and listed in Table 1.

According to calculations, the valence bonds in molecule **9** are shortened as compared to those in structure **5**. The activation barrier to the reaction **9a** ⇌ **10** ⇌ **9b** (Y = B) calculated by the RHF method (22.6 kcal $mol^{-1}$) is much higher than the barrier to the reaction **5a** ⇌ **6** ⇌ **5b**; however, its height remains virtually unchanged (14.1 kcal $mol^{-1}$) when performing calculations by the MP2 method. This is explained by the fact that RHF calculations are unsuitable for description of the coordination (donor-acceptor) B←N bond.

To estimate the relative stability of *cis*-form **9**, we calculated the energies of the *trans*-form **11** and the classical isomer **12** (Y = B), which are analogous to structures **7** and **8**, respectively.



**11** **12**

As in the first case, the *trans*-isomer **11** is more stable than the *cis*-form **9**, though the difference in their energies is smaller than for structures **7** and **8**. In this case, the classical isomer **12** appears to be much more stable (by 33.4 (RHF) and 24.3 kcal $mol^{-1}$ (MP2)) than structure **9** containing a fragment with the hypervalent B

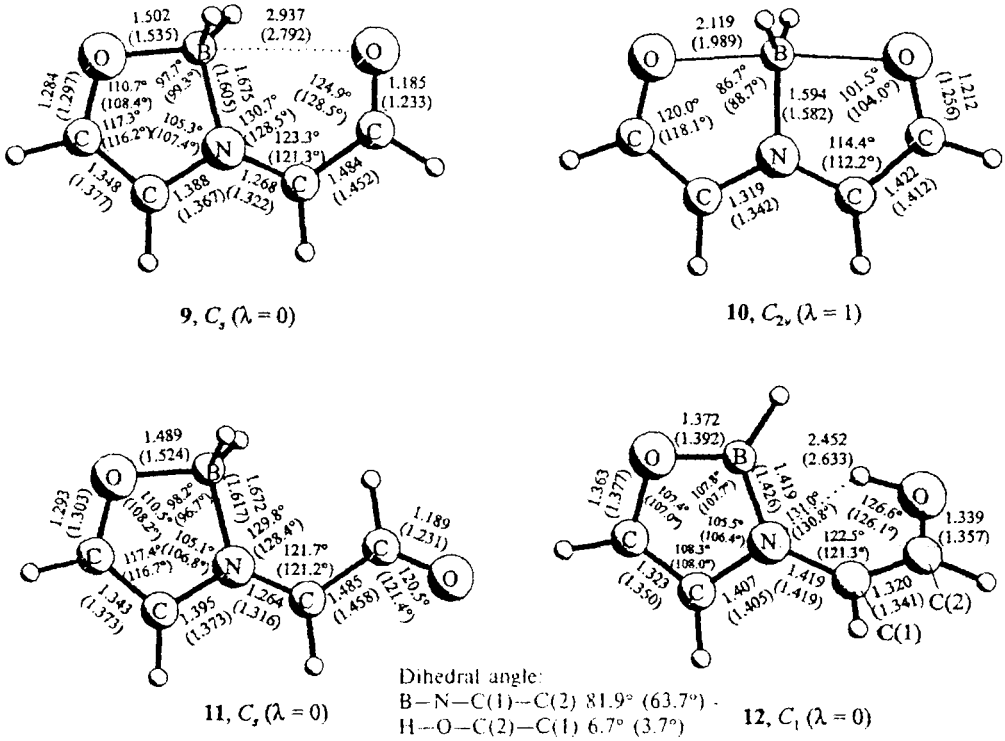
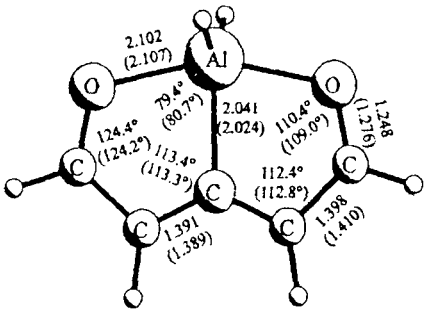
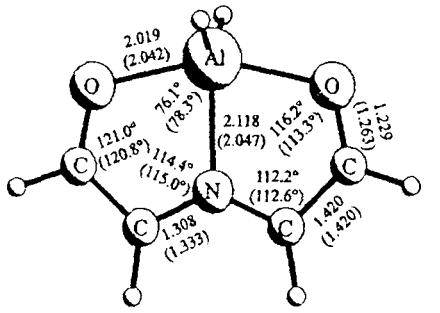


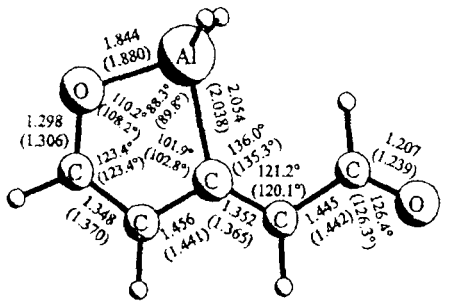

**Fig. 2.** Geometric characteristics of structures **9**, **11**, and **12** (Y = B), corresponding to minima on the PES, and those of TS **10** (Y = B), corresponding to the saddle point, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.



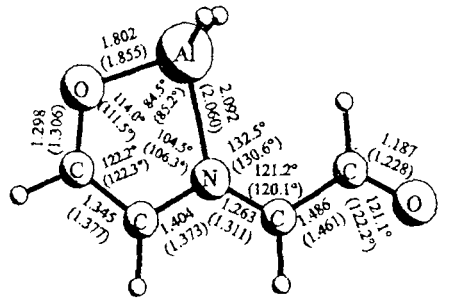

**6**, $C_{2v}$ ($\lambda = 0$)



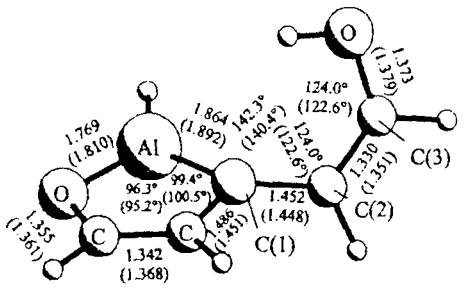

**10**, $C_{2v}$ ($\lambda = 0$)




**7**, $C_s$ ($\lambda = 0$)

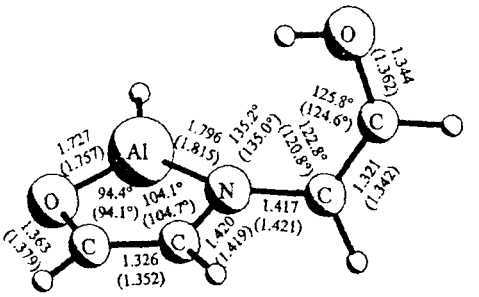



**11**, $C_s$ ($\lambda = 0$)




**8**, $C_1$ ($\lambda = 0$)

Dihedral angle:
Al—C(1)—C(2)—C(3) 21.0° (23.8°)
H—O—C(3)—C(2) 22.5° (17.3°)




**12**, $C_1$ ($\lambda = 0$)

Dihedral angle:
Al—N—C—C 88.2° (78.9°)
H—O—C—C 7.3° (7.8°)

**Fig. 3.** Geometric characteristics of structures **6**—**8** (X = $Al^-$), corresponding to minima on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

**Fig. 4.** Geometric characteristics of structures **10**, **11**, and **12** (X = Al), corresponding to minima on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

atom, which indicates that the hypervalent state is thermodynamically unfavorable as compared with the classical states in similar bicyclic systems.

**Structure of compounds 5—12 (X = $Al^-$, Y = Al).** Compounds **5**—**12** (X = $Al^-$, Y = Al) contain tri-, tetra-, and pentacoordinate Al atoms. According to *ab initio* calculations of reactions **5a** ⇌ **6** ⇌ **5b** (X = $Al^-$) and **9a** ⇌ **10** ⇌ **9b** (Y = Al) in the gas phase, there are no local minima corresponding to the classical *cis*-forms of types **5** and **9** on the PES of these systems. Energy optimization leads to transformation of these structures into stable structures **6** and **10** containing the fragment with the hypervalent X (or Y) atom and corresponding to minima on the PES. The calculated geometric and energy characteristics of these systems are shown in Figs. 3 and 4 and listed in Table 2.

**Table 2.** Total energies ($E_{tot}$/au), relative energies ($\Delta E$/kcal mol$^{-1}$), number of negative eigenvalues of the Hessian ($\lambda$), and lowest harmonic frequencies ($\omega_1$/cm$^{-1}$) of structures **5**—**8** (X = Al$^-$) and **9**—**12** (Y = Al), calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods

| Structure, symmetry | $E_{tot}$ | $\Delta E$ | $\lambda$ | $\omega_1$ |
|---|---|---|---|---|
| **6**, $C_{2v}$ | −584.50958 (−585.63664) | 0 (0) | 0 (0) | 122 (169) |
| **7**, $C_s$ | −584.51965 (−585.63917) | −6.3 (−1.6) | 0 (0) | 90 (82) |
| **8**, $C_1$ | −584.43492 (−585.58424) | 46.8 (32.9) | 0 (0) | 63 (69) |
| **10**, $C_{2v}$ | −601.07334 (−602.23982) | 0 (0) | 0 (0) | 128 (175) |
| **11**, $C_s$ | −601.07247 (−602.22237) | 0.5 (11.0) | 0 (0) | 83 (81) |
| **12**, $C_1$ | −601.06182 (−602.21562) | 7.2 (15.2) | 0 (0) | 38 (52) |

According to calculations, the *trans*-isomer **7** (X = Al$^-$) is more stable than corresponding form **6** (the energy difference is 6.3 (RHF) and 1.6 kcal mol$^{-1}$ (MP2)), whereas the reverse is observed for the neutral compound **10** (Y = Al), *viz.*, structure **10** (Y = Al) is more stable than *trans*-form **11** (by 0.5 (RHF) and 11.0 kcal mol$^{-1}$ (MP2)). This indicates that the hypervalent (three-center) O—Al—O bond in compounds **6** and **10** is extremely weak, which is likely due to the large deviation of the O—Al—O angle from 180°. At the same time, the structurally close classical isomers **8** (X = Al$^-$) and **12** (Y = Al) with a tricoordinate Al atom in both cases appear to be less energetically favorable than their analogs **6** (X = Al$^-$) and **10** (Y = Al) containing the fragment with the hypervalent X (or Y) atom. The structures **8** (X = Al$^-$) and **12** (Y = Al) with $C_1$ symmetry are nonplanar. Their aromatic rings are planar, while the substituent deviates out of the ring plane so that the OH group is oriented by the $p_\pi$-orbital of the ring carbon or nitrogen atoms (see Figs. 3 and 4). The geometric characteristics of stable structures **6**—**8** (X = Al$^-$) and **10**—**12** (Y = Al) calculated in this work are fairly close to the experimentally determined values for the known compounds containing tri-, tetra-, and pentacoordinate Al atoms.[28,29] For instance, the lengths of the valence Al—C and Al—O bonds in compounds containing a tetracoordinate Al atom lie in the range 2.02—2.30 and 1.81—1.88 Å, respectively, while the length of the coordination Al←N bond in molecule **3** (2.088 Å [18]) is in good agreement with the values of 2.118 and 2.047 Å predicted for compound **10** by RHF and MP2 calculations, respectively.

**Structure of compounds 5—7 (X = C).** Compounds **5**—**7** (X = C) contain tetra- and pentacoordinate C atoms. According to calculations, structures **5** and **7** (X = C) correspond to minima ($\lambda$ = 0), whereas structure **6** corresponds to a saddle point ($\lambda$ = 1) on the PES. Their geometric and energy characteristics are shown in Fig. 5 and listed in Table 3.

We failed to find information on experimentally studied compounds similar to **5** and **7**; because of this, structure **5** can be compared only with the analogous structure of 1-*H*-iodophenyl-3-carbomethoxy-4-phenacylidene-5-hydroxy-5-phenylpyrazoline, which also exists in the *cis*-form **13**. Comparison shows that

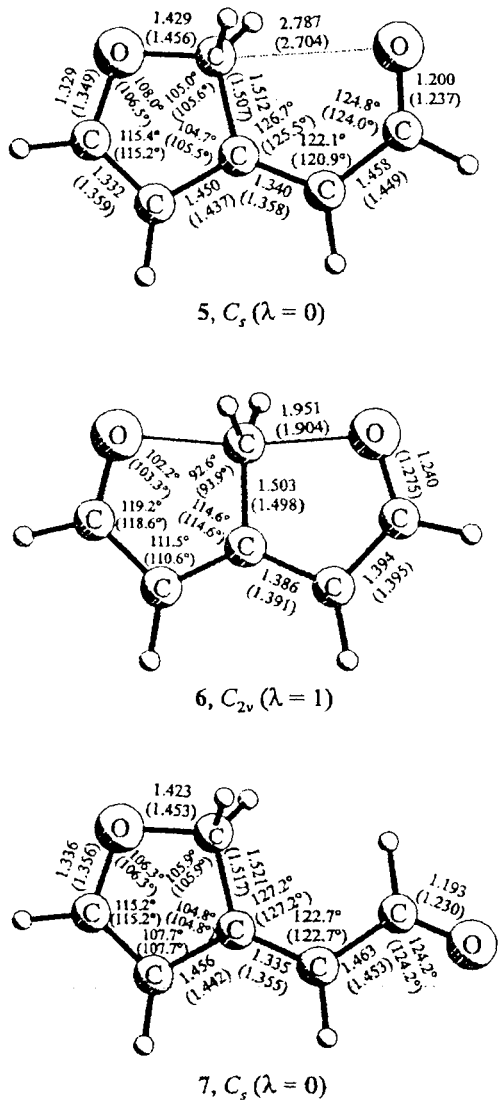
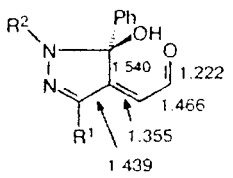



Fig. 5. Geometric characteristics of structures **5** and **7** (X = C), corresponding to minima on the PES, and those of TS **6** (X = C), corresponding to the saddle point, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

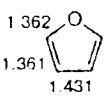
**Table 3.** Total energies ($E_{tot}$/au), relative energies ($\Delta E$/kcal mol$^{-1}$), number of negative eigenvalues of the Hessian ($\lambda$), and imaginary or lowest harmonic frequencies (($i\omega/\omega_1$)/cm$^{-1}$) of structures **5**—**7** (X = C and Si), calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods

| Structure, symmetry | X | $E_{tot}$ | $\Delta E$ | $\lambda$ | $i\omega/\omega_1$ |
|---|---|---|---|---|---|
| **5**, $C_s$ | C | −380.39118 | 0 | 0 | 153 |
| | | (−381.56847) | (0) | (0) | (148) |
| **6**, $C_{2v}$ | C | −380.33243 | 36.9 | 1 | i847 |
| | | (−381.52440) | (27.7) | (1) | (i840) |
| **7**, $C_s$ | C | −380.38563 | 3.5 | 0 | 103 |
| | | (−381.56158) | (4.3) | (0) | (99) |
| **6**, $C_{2v}$ | Si | −631.49053 | 0 | 0 | 206 |
| | | (−632.63260) | (0) | (0) | (196) |
| **7**, $C_s$ | Si | −631.47742 | 8.2 | 0 | 89 |
| | | (−632.61099) | (13.5) | (0) | (85) |

the geometric characteristics of compounds **5** and **13** (data of X-ray diffraction study[30]) are fairly close.




**13**

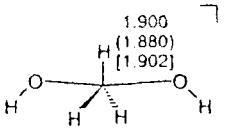



**14**

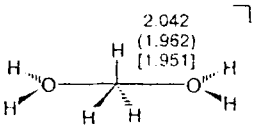
According to calculations, *trans*-isomer **7** (X = C) is 3.5 (RHF) and 4.3 kcal mol$^{-1}$ (MP2) less energetically favorable than *cis*-form **5**, which indicates a rather strong stabilizing donor-acceptor C···O interaction in molecule **5**. It is noteworthy that, despite the presence of a methylene group, the five-membered cycles in structures **5** and **7** (X = C) are planar and their geometric characteristics are close to those of furan (**14**).[31] This suggests an aromatic type of these cycles and shows that the methylene group participates in conjugation.

Structure **6** containing a hypervalent pentacoordinate C atom is a TS of the intramolecular $S_N2$ reaction **5a** ⇌ **6** ⇌ **5b** (X = C), occurring with an energy barrier of 36.9 (RHF) and 27.7 kcal mol$^{-1}$ (MP2). The inclusion of electron correlation leads to lowering of the barrier to the reaction by about 10 kcal mol$^{-1}$ and to shortening of the hypervalent C—O bond in structure **6** by 0.05 Å. The O—C—O angle in molecule **6** (174.2° and 172.2° according to RHF and MP2 calculations, respectively) is about 10° less than the S—O—S angle in cation **1**; however, the calculated barrier to the reaction **5a** ⇌ **6** ⇌ **5b** (X = C) is much higher than the experimental activation barrier to the reaction **1a** ⇌ **2** ⇌ **1b**.[17] It can be assumed that the sterically unstrained hypervalent C—O bond must be much shorter than in structure **6** (X = C), whose geometry is fixed by the rigid framework. In turn, this increases the energy of structure **6** compared to that of **5** (X = C). To estimate the length of the sterically unstrained hypervalent C—O bond, we performed *ab initio* calculations of complexes $Me(OH)_2^-$ (**15**) and $Me(H_2O)_2^+$ (**16**) with $C_2$ symmetry in the gas phase (Scheme 4) by the RHF/6-31G**, MP2(full)/6-31G* (figures in parentheses), and MP2(full)/6-311++G** (figures in brackets) methods. According to calculations, these complexes correspond to the saddle points ($\lambda$ = 1) on the PES and the lengths of the O—C—O bonds are fairly close to those found for molecule **6** (X = C). This indicates that the steric strain in the fragment with the pentacoordinate C atom (structure **6**) is small as compared to that in the model systems **15** and **16** and can not be responsible for the high activation barrier to the reaction **5a** ⇌ **6** ⇌ **5b** (X = C).

**Scheme 4**




**15**, $C_2$ ($\lambda$ = 1)

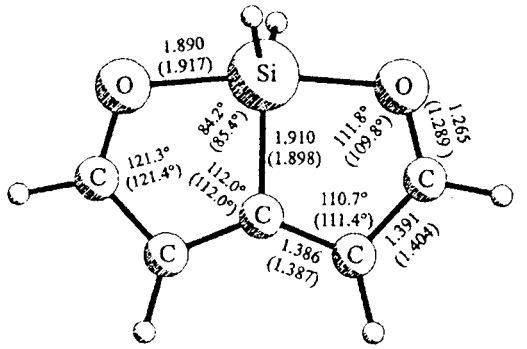



**16**, $C_2$ ($\lambda$ = 1)

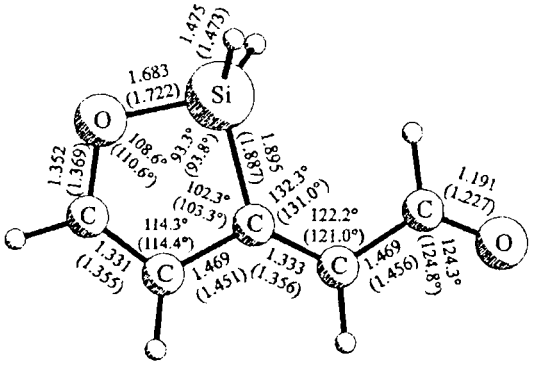
Thus, the results of our calculations suggest that it is impossible to stabilize structure **6** (X = C) containing a pentacoordinate C atom in compounds of type **5**; therefore, further investigations are required to elucidate the ability of the C atom to form pentacoordinate structures.

**Structure of compounds 6 and 7 (X = Si).** Compounds **6** and **7** (X = Si) contain tetra- and pentacoordinate silicon atoms. According to calculations of system **5** (X = Si), there are no compounds with that structure; energy optimization leads to transformation of structure **5** into the stable structure **6** (X = Si) containing a fragment with the hypervalent Si atom and corresponding to a minimum on the PES. Its geometric characteristics are shown in Fig. 6.

Our calculations show that *trans*-isomer **7** (X = Si) is 8.2 (RHF) and 13.5 kcal mol$^{-1}$ (MP2) less energetically favorable than structure **6**. These values can be considered as a lower bound for the energy of the hypervalent (three-center) O—Si—O bond in molecule **6** (X = Si). The inclusion of electron correlation results in strengthening of the hypervalent Si—O bond by a factor of almost 1.5. The energy of the hypervalent Si—O bond (13.5 kcal mol$^{-1}$) predicted by the MP2 method falls into the range of the experimental values of the energies of analogous bonds in silatranes (10—20 kcal mol$^{-1}$).[5] The geometric characteristics of stable structures **6** and **7** (X = Si) calculated in this work are fairly close to the experimentally determined values for compounds containing tetra- and pentacoordinate Si atoms.[5,28,29] For




**6**, $C_{2v}$ ($\lambda = 0$)




**7**, $C_s$ ($\lambda = 0$)

**Fig. 6.** Geometric characteristics of structures **6** and **7** (X = Si), corresponding to minima on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

instance, the lengths of valence Si—C and Si—O bonds in molecules of compounds containing a tetracoordinate Si atom lie in the range 1.88—1.89 and 1.62—1.70 Å, respectively,[5,28,29] which is in good agreement with the bond lengths predicted for structure **7** (X = Si). The length of the coordination Si←O bond in molecule **6** (X = Si) calculated by the RHF and MP2 methods (1.890 and 1.917 Å, respectively) is close to the analogous values for silatranes (1.83—2.027 Å)[5,28,29] and hexakis(dimethylsilylmethoxy)benzene (1.88 Å).[13]

* * *

The calculations performed in this work indicate that the ability of B, C, Al, and Si atoms to form pentacoordinate structures in bicyclic systems of the pentalene type increases as the number of the element in the corresponding group of the periodic system increases, *i.e.*, on going from B to Al and from C to Si. At the same time, the reverse tendencies are observed in the 2nd and 3rd periods of the periodic system, *viz.*, the ability of the atoms to form pentacoordinate structures increases on going from C to B and from Al to Si. The donor-acceptor interaction between the vacant $\sigma^*$-orbital localized on the X (or Y) atom and the lone electron pair of the O atom, which is responsible for the stabilization of the *cis*-form as compared to the *trans*-structure in the case of carbon-containing systems (**5** (X = C)), results in the formation of a rather strong (3c-2e)-hypervalent bond in silicon-containing systems (**6** (X = Si)) and favors the formation of a coordination bond in compounds containing metal atoms (**6** (X = $Al^-$) or **9** (Y = Al)).

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