Intramolecular nucleophilic S_N2 substitution at the tetrahedral carbon atom: an *ab initio* study

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Pentacoordination of carbon atom in bicyclic organic compounds of the pentalene type was studied by the *ab initio* RHF/6-31G** and MP2(full)/6-31G** methods. It was shown that intramolecular S_N2 reactions with energy barriers within the energy scale of NMR spectroscopy can occur in systems in which a linear orientation of the attacking and leaving groups is realized. The barrier to the intramolecular nucleophilic substitution reaction in 2,3-dihydro-3-formylmethylenefuran is 36.9 (RHF) and 27.7 kcal mol^{-1} (MP2) and decreases to 16.4 and 19.4 kcal mol^{-1}, respectively, in the case of diprotonation at the O atoms in this system. For model pentalene type compounds containing electron-deficient B atoms in the ring, the *ab initio* calculations predict a further decrease in the barrier height (down to less than 10 kcal mol^{-1}).

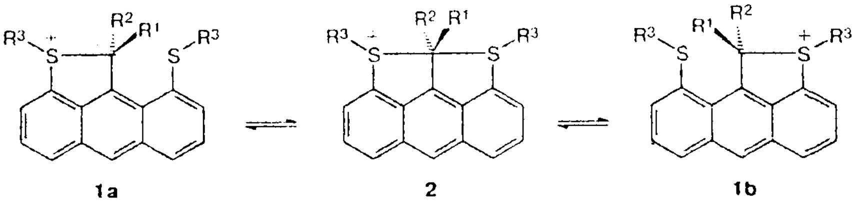
Key words: *ab initio* quantum-chemical calculations, reaction pathway, nucleophilic substitution, pentacoordination of carbon atom.

Intermolecular nucleophilic substitution reactions (S_N2) at the tetracoordinate C atom in the gas phase occur with inversion of the configuration and intermediate formation of pentacoordinate bipyramidal structures,[1—3] which, as has been shown in numerous theoretical studies,[3—6] always correspond to the transition state (TS) of the reaction. As a rule, the internal activation barrier corresponding to these TS in the gas phase does not exceed 20 kcal mol^{-1}. The relatively low activation barrier suggests that in the corresponding intramolecular S_N2 reaction it can be partially compensated by the strain energy of the initial structure by incorporating the fragment with the bipyramidal bond configuration at the pentacoordinate C atom into a rigid framework.

The idea of "freezing" of the pentacoordinate structure of TS was proposed for the first time in 1973.[7,8] Salts of 1,8-di(arylthio)anthracene-9-carbinyl cation **1** (Scheme 1, R^1, R^2 = H, Me; R^3 = Ar) were synthesized, in which the anthracene nucleus and the sulfenyl groups create the required steric conditions for the formation of form **2** with the pentacoordinate C atom, and it was shown by ^{1}H NMR spectroscopy that the activation barrier to the degenerate alkylotropic rearrangement **1a** $\rightleftharpoons$ **1b** *via* TS **2** decreases to ~10—20 kcal mol^{-1} and is strongly dependent on the nature of substituents R^1—R^3 and the type of solvent.[7]

The fact that structure **2** corresponds to the transition state rather than to the energy minimum was explained[7] by the large additional steric strain produced in the fragment containing the pentacoordinate carbon atom due to the deviation of the S—C—S angle (~163° in structure **2**) from 180°. In fact, our preliminary *ab initio* (MP2(full)/6-31G**) calculations of intramolecular nucleophilic substitution reactions in model system **3** (**3a** $\rightleftharpoons$ **3b**, Scheme 2) showed that the S—C—S angle in structure **4** with C_{2v} symmetry and a planar bicyclic framework is equal to ~161°. However, the structure with C_{2v} symmetry is not the TS of the reaction **3a** $\rightleftharpoons$ **3b**. Despite the long C—S bond, the absence of the anthracene nucleus allows the system to adopt the configuration with a S—C—S angle of ~179°, which

Scheme 1



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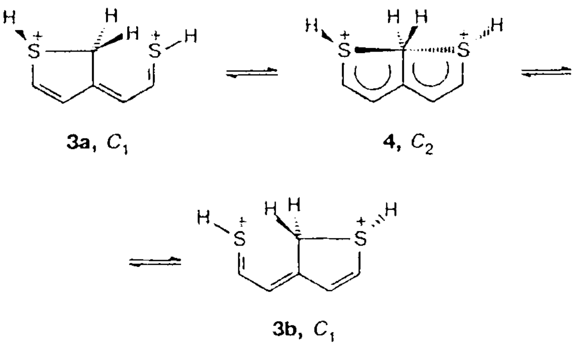
is optimum for the occurrence of the S_N2 reaction, due to the deviation of both C—S bonds in opposite directions from the plane of the five-membered rings by more than 30° and the rotation of the methylene group by about 40°.

Scheme 2



3a, C_1 **4**, C_2 **3b**, C_1

The strongly distorted nonplanar form **4** with C_2 symmetry, corresponding to the rather high energy barrier (~40 kcal mol^{-1}), becomes the true TS of the reaction **3a** $\rightleftharpoons$ **4** $\rightleftharpoons$ **3b**.

Up to the present, attempts to detect organic intermediates with a pentacoordinate C atom and bipyramidal bond configuration using the substituents R^1—R^3 and solvents of different natures failed.[2,3,6–8] It is logical to assume that replacement of the S atom in cation **1** by an O atom will lead to decrease in the corresponding angle in the planar bicyclic form and in the activation barrier to the reaction **1a** $\rightleftharpoons$ **1b**, or even to stabilization of structure **2**. However, we failed to find information either on experimental or on theoretical studies of this type of compounds.

The aim of this work was to perform a quantum-chemical study (using the RHF/6-31G** and MP2(full)/6-31G** [9–11] methods) of the energetics and mechanism of the intramolecular nucleophilic substitution (S_N2) reaction **5a** $\rightleftharpoons$ **6** $\rightleftharpoons$ **5b** (Scheme 3) at the C atom and the tendencies to form fragments with the pentacoordinate C atom in structure **6** upon variation of the substituents X (X = O, OH^+, F^+), Y (Y = C, B), and Z (Z = C, B), which affect not only the spatial structure of the reaction site, but also the electronic structure of the entire conjugated system. To estimate the energy of the "nonvalence" donor-acceptor C···X interaction in *cis*-structures **5**, we calculated the corresponding sterically unstrained *trans*-forms **7**.

Differences between the total energies of structures **5** and **7** can be considered as the lower bounds of the energies of the donor-acceptor X···C interaction (X = O, OH^+, F^+) in systems **5**.

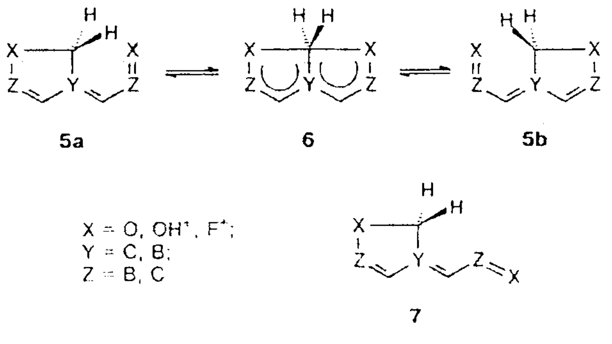
Calculation procedure

The *ab initio* calculations were carried out by the restricted Hartree—Fock (RHF) method and at the second-order Møller—Plesset (MP2(full)) level of perturbation theory with inclusion of correlation of all (valence and core) electrons with the split-valence 6-31G** (DZ) basis set[9] for systems **5**—**7** and with the 6-311++G** (TZ) basis set[9] for the simplest ionic models of nucleophilic substitution at the tetrahedral C atom using the GAUSSIAN-94[10] and GAMESS[11] programs on RISC-6000, DEC Alpha-Station 500, and Duranga workstations. Full optimization of the geometry of the molecular structures corresponding to the saddle points (λ = 1; hereinafter λ is the number of negative eigenvalues of the Hesse matrix at a given stationary point[12]) and to the energy minima (λ = 0) on the potential energy surface (PES) was 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).[12] The initial direction of the gradient line was specified by minor displacement (1/100 of the length of the normalized transition vector) along the direction of the transition vector. Graphic images of the molecular forms were obtained using the PC MODEL[13] program (the PLUTO mode), for which Cartesian atomic coordinates taken from the *ab initio* calculations served as input parameters.

Results and Discussion

To elucidate the effect of the spatial structure of the reaction site on the energy characteristics of the S_N2 reaction, the intermolecular nucleophilic substitution reactions **8a** $\rightleftharpoons$ **9** $\rightleftharpoons$ **8b** (Scheme 4) were ini-

Scheme 3

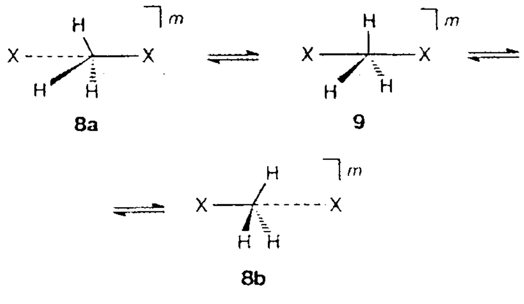


5a **6** **5b**

X = O, OH^+, F^+;
Y = C, B;
Z = B, C

7

Scheme 4

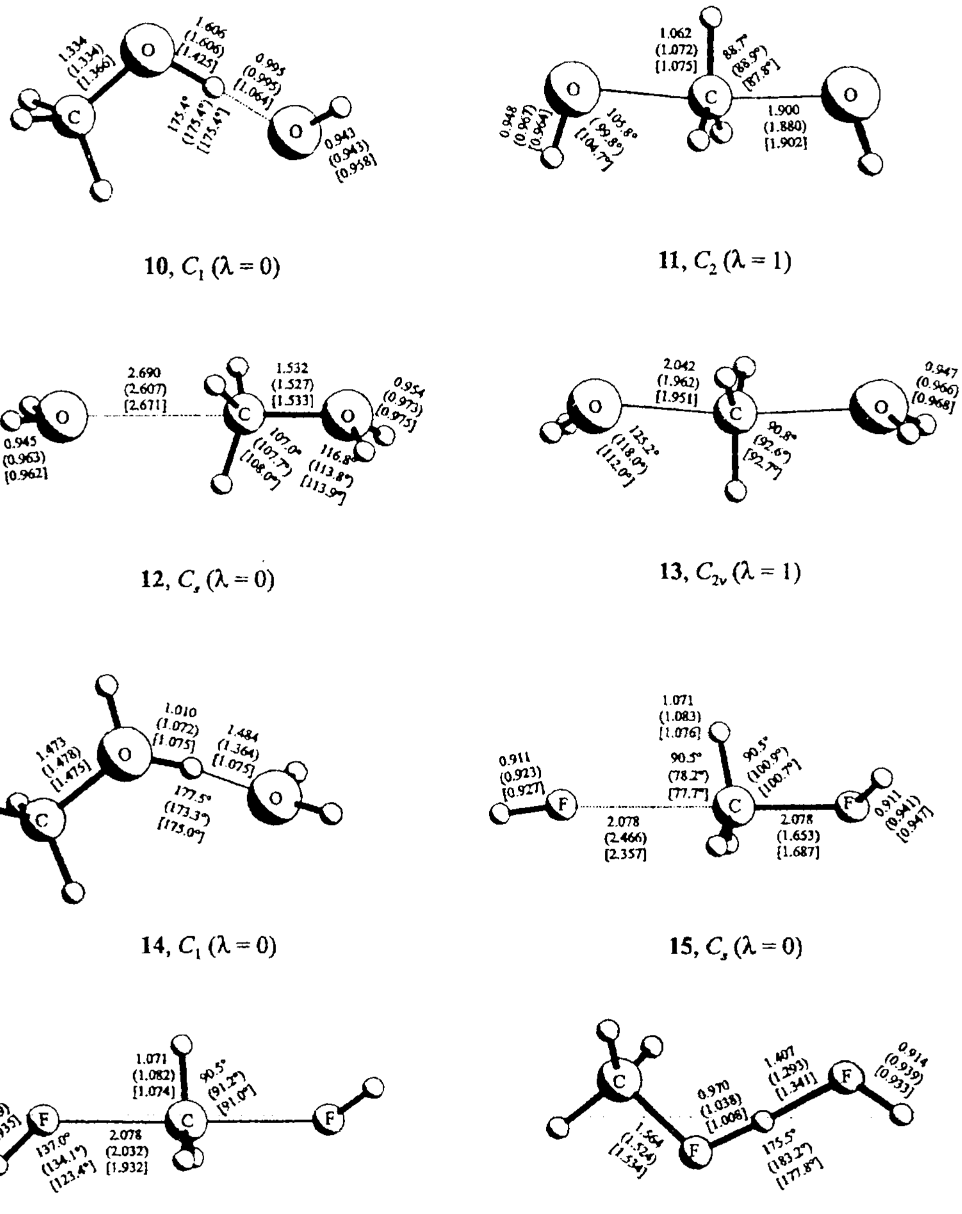


8a **9** **8b**

X = OH, m = −1; X = OH_2, m = +1; X = FH, m = +1 tially studied. Ssystem **8** is sterically unstrained and its geometric parameters are determined only by the electronic effects in TS **9**.

Pathway of nucleophilic substitution reaction $OH^- + H_3COH \rightleftharpoons HOCH_3 + OH^-$. Our *ab initio* calculations showed that this reaction begins with the formation of the stabilized hydrogen-bonded pre-reaction complex **10** corresponding to a minimum (λ = 0) on the PES and proceeds *via* the TS corresponding to structure **11** with C_2 symmetry (Scheme 5) and almost aligned apical C—O bonds (the interbond angle is close to 180°, Fig. 1). The predicted geometric and energy characteristics of systems **10** and **11** are shown in Fig. 1 and listed in Table 1.

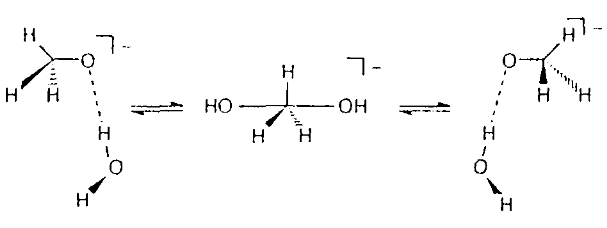
The pre-reaction complex **10** is an associate of a water molecule and a methylate anion bound by a strong



10, C_1 (λ = 0)
11, C_2 (λ = 1)
12, C_s (λ = 0)
13, C_{2v} (λ = 1)
14, C_1 (λ = 0)
15, C_s (λ = 0)
16, C_2 (λ = 1)
17, C_s (λ = 0)

Fig. 1. Geometric characteristics of structures **10**, **12**, **14**, **15**, and **17**, corresponding to minima, and those of transition structures **11**, **13**, and **16**, corresponding to saddle points on the PES, calculated by the RHF/6-31G**, MP2(full)/6-31G** (figures in parentheses), and MP2(full)/6-311++G** (figures in brackets) methods. Here and in Figs. 2—7 the bond lengths (in Å) and bond angles are given.

Scheme 5



10a, C_1 **11**, C_2 **10b**, C_1

hydrogen bond. According to calculations, the energy of this bond is 25.4, 30.3, and 22.6 kcal mol^{-1} at the RHF/DZ, MP2/DZ, and MP2/TZ levels, respectively. The last value is rather close to the experimentally determined energy of the H-bond in this system (23.9 kcal mol^{-1}).[14]

The bond lengths and bond angles in structure **11** calculated in this work are in good agreement with the results of previous calculations.[16,17] The rather high energy barrier to the S_N2 reaction **10a** $\rightleftharpoons$ **11** $\rightleftharpoons$ **10b**, *viz.*, 62.6 (RHF/DZ), 59.1 (MP2/DZ), and 48.9 kcal mol^{-1} (MP2/TZ), is determined by the high stabilization energy of complex **10** rather than by stereoelectonic effects in TS **11**. Noteworthy is that the geometric parameters of TS **11** calculated with inclusion of electron correlation are, on the whole, in good agreement with those predicted by calculations in the Hartree—Fock approximation, whereas for complex **10** these values differ appreciably (see Fig. 1).

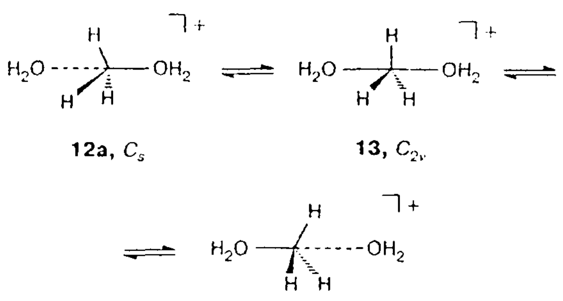
Table 1. Total (E_{tot}/au) and relative (ΔE/kcal mol^{-1}) energies, number of negative eigenvalues of the Hessian (λ), zero-point harmonic vibrational energies (*ZPE*/au), and imaginary or lowest harmonic frequencies ((iω/ω_1)/cm^{-1}) of structures **10—17**, calculated by the RHF/6-31G**, MP2(full)/6-31G** (figures in parentheses), and MP2(full)/6-311++G** methods (figures in brackets)

Structure, symmetry	E_{tot}	ΔE	λ	*ZPE*	iω/ω_1
10, C_1	−190.45363	0	0	0.06542	58
	(−191.00716)	(0)	(0)	(0.06246)	(96)
	[−191.1935]	[0]	[0]	[0.06081]	[53]
11, C_2	−190.35318	62.6	1	0.06457	i744
	(−190.91305)	(59.1)	(1)	(0.06178)	(i597)
	[−191.11565]	[48.9]	[1]	[0.06031]	[i677]
12, C_s	−191.40005	0	0	0.09389	35
	(−191.94081)	(0)	(0)	(0.09032)	(34)
	[−192.10830]	[0]	[0]	[0.08931]	[26]
13, C_{2v}	−191.38515	9.3	1	0.09017	i361
	(−191.92282)	(11.3)	(1)	(0.08906)	(i506)
	[−192.08786]	[12.8]	[1]	[0.08806]	[i520]
14, C_1	−191.42529	0	0	0.09474	116
	(−191.97261)	(0)	(0)	(0.09053)	(118)
	[−192.13642]	[0]	[0]	[0.08984]	[127]
15, C_s	−239.32310	0	0	0.06172	36
	(−239.82928)	(0)	(0)	(0.06148)	(94)
	[−240.03618]	[0]	[0]	[0.06055]	[77]
16, C_2	239.32310	0	0	0.06172	36
	(−239.32310)	(2.3)	(1)	(0.06138)	(i242)
	[−240.03242]	[1.8]	[1]	[0.05894]	[i265]
17, C_s	−239.33687	0	0	0.06500	64
	(−239.85522)	(0)	(0)	(0.06286)	(73)
	[−240.07179]	[0]	[0]	[0.06194]	[63]

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

Pathway of nucleophilic substitution reaction $H_2O + H_3COH_2^+ \rightleftharpoons H_2OCH_3^+ + H_2O$. According to calculations, the degenerate reaction $H_2O + H_3COH_2^+ \rightleftharpoons H_2OCH_3^+ + H_2O$ (Scheme 6) begins with the formation of the pre-reaction complex **12** with C_s symmetry, which corresponds to a minimum (λ = 0) on the PES.

Scheme 6



12a, C_s **13**, C_{2v}

12b, C_s

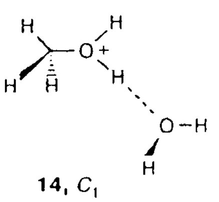
Stability of complex **12** is determined by donor-acceptor interactions of the O atom of the water molecule with all three H atoms of the methyl group (H-bonds) and with the C atom as well, which is indicated by the arrangement of the water molecule relative to the cation (see Fig. 1). The formation energy of the pre-reaction complex **12** calculated without inclusion of the basis set superposition error (*BSSE*) (see Ref. 12, notes to the calculation procedure) is 11.5 (RHF/DZ), 12.7 (MP2/DZ), and 11.4 kcal mol^{-1} (MP2/TZ), which is rather close to the experimental energy of the H-bond between the oxonium cation and methanol molecule (11.9 kcal mol^{-1}).[14]

The transition state of this reaction corresponds to structure **13** with C_{2v} symmetry and almost aligned apical C—O bonds. As in the anionic form **11**, the interbond angle is close to 180° (see Fig. 1). The geometric and energy characteristics of systems **12**, **13**, and protonated methanol calculated in this work (see Fig. 1 and Table 1) are in good agreement with the results of *ab initio* calculations of the same complexes performed by other authors.[18,19]

The calculated energy barrier to the S_N2 reaction **12a** $\rightleftharpoons$ **13** $\rightleftharpoons$ **12b**, which is equal to 9.3 (RHF/DZ), 11.3 (MP2/DZ), and 12.8 kcal mol^{-1} (MP2/TZ), is the internal barrier to transfer of the CH_3

group between two water molecules. Most likely, its height is minimum in the case of methyl group transfer between two oxygen centers in the absence of steric strain.

However, it should be noted that the experimentally detected complex **14** [20,21] possesses the highest stability. Its energy is more than 15.8 (RHF/DZ), 19.9 (MP2/DZ), and 17.6 kcal mol^{-1} (MP2/TZ) lower than that of the pre-reaction complex **12**.

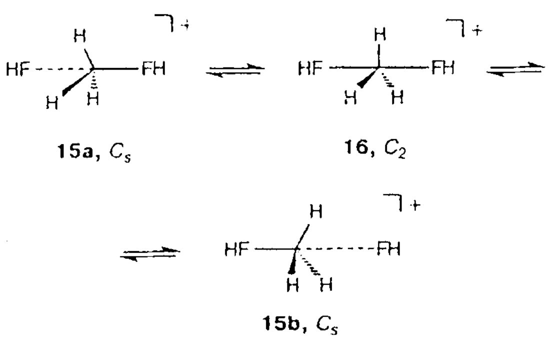


14, C_1

The experimentally determined energy of the formation of a complex between protonated methanol and water is 11.9 kcal mol^{-1}.[21] We have found that the energy of the H-bond in structure **14** is much higher, *viz.*, 27.8 (RHF/DZ), 33.1 (MP2/DZ), and 29.4 kcal mol^{-1} (MP2/TZ), which is close to the experimental energy of the strong H-bond in the $(H_2O)_2H^+$ cation (31.6 kcal mol^{-1}).[20]

Pathway of nucleophilic substitution reaction $HF + H_3CFH^+ \rightleftharpoons HFCH_3^+ + FH$. According to calculations, this reaction, analogously to the two preceding reactions, begins with the formation of the pre-reaction complex **15** with C_s symmetry ($\lambda = 0$), whose stability is also determined by H-bonds formed by the F atom of the hydrogen fluoride molecule with all three H atoms of the methyl group and by its donor-acceptor interaction with the C atom.

Scheme 7

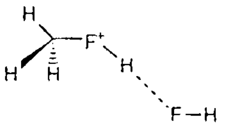


15a, C_s **16**, C_2 **15b**, C_s

This is confirmed by a nearly exact arrangement of the hydrogen fluoride molecule along the axis of the C—F bond of the protonated form of fluoromethane (see Fig. 1). The formation energy of complex **15** calculated without inclusion of *BSSE* is equal to 13.3, 14.0, and 10.7 kcal mol^{-1} at the RHF/DZ, MP2/DZ, and MP2/TZ levels of theory, respectively.

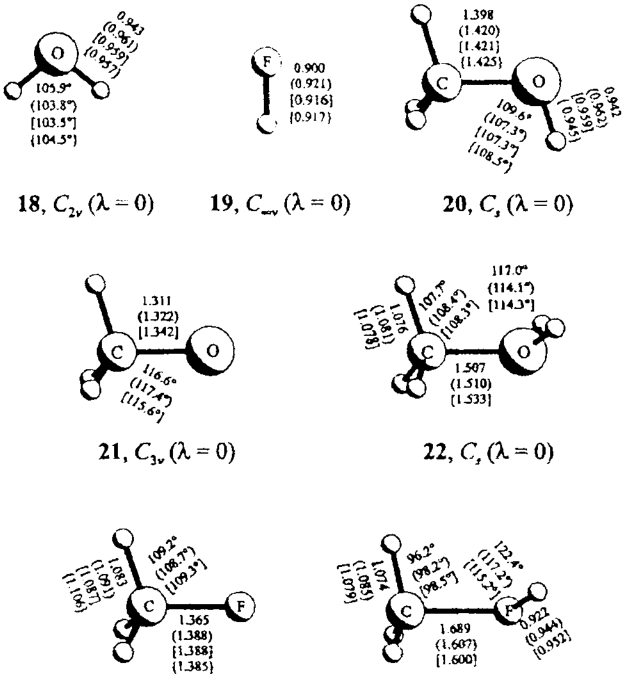
The transition state of this reaction corresponds to structure **16** with C_2 symmetry and nearly aligned apical C—F bonds. The angle between the bonds, as in systems **11** and **13**, is close to 180° (see Fig. 1). The calculated energy barrier to the S_N2 reaction **15a** $\rightleftharpoons$ **16** $\rightleftharpoons$ **15b** (0, 2.3, and 1.8 kcal mol^{-1} according to RHF/DZ, MP2/DZ, and MP2/TZ calculations, respectively), which is the barrier to methyl group transfer between two HF molecules, is much lower than the internal activation barrier to the reaction $F^- + H_3CF \rightleftharpoons FCH_3 + F^-$ (see Ref. 5). Most likely, its height is minimum in the case of methyl group transfer between two fluoride centers in the absence of steric strain.

As in two preceding cases, complex **17** with the FH...F bond possesses the highest stability, *viz.*, its energy is 8.6 (RHF/DZ), 16.3 (MP2/DZ), and 22.3 kcal mol^{-1} (MP2/TZ) lower than that of the pre-reaction complex **15**. According to calculations, the energy of the H-bond in structure **17** is 22.0, 30.3, and 33.0 kcal mol^{-1} at the RHF/DZ, MP2/DZ, and MP2/TZ levels of theory, respectively, which is close to the experimental energy of the strong H-bond in the $(MeF)_2H^+$ cation (32±2 kcal mol^{-1}).[21]



17, C_s

The results of calculations of water, HF, methanol, and fluoromethane molecules and their protonated forms (structures **18—24**) are shown in Fig. 2 and listed in Table 2. The geometric and energy characteristics of protonated fluoromethane calculated in this work are in good agreement with the values obtained recently for this complex by the QCISD/6-31G* method.[22]



18, C_{2v} ($\lambda = 0$) **19**, $C_{\infty v}$ ($\lambda = 0$) **20**, C_s ($\lambda = 0$)

21, C_{3v} ($\lambda = 0$) **22**, C_s ($\lambda = 0$)

23, C_{3v} ($\lambda = 0$) **24**, C_s ($\lambda = 0$)

Fig. 2. Geometric characteristics of structures **18—24**, corresponding to minima on the PES, calculated by the RHF/6-31G**, MP2(full)/6-31G** (figures in parentheses), and MP2(full)/6-311++G** (figures in brackets) methods and experimental data[15] (figures in braces).

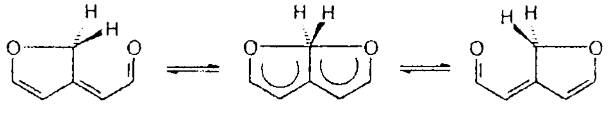
Table 2. Total energies (E_{tot}/au), zero-point harmonic vibrational energies (*ZPE*/au), and the first three lowest harmonic frequencies (ω_1, ω_2, ω_3/cm^{-1}) for structures **18—24**, calculated by the RHF/6-31G**, MP2(full)/6-31G** (figures in parentheses) and MP2(full)/6-311++G** methods (figures in brackets)

Structure, symmetry	E_{tot}	*ZPE*	ω_1	ω_2	ω_3
18, C_{2v}	−76.02361	0.02319	1770	4146	4262
	(−76.22245)	(0.02191)	(1683)	(3897)	(4035)
	[−76.29945]	[0.02173]	[1628]	[3891]	[4010]
			1594.78[a]	3656.65[a]	3755.79[a]
19, $C_{\infty v}$	−100.01169	0.01023	4492		
	(−100.19464)	(0.00955)	(4191)		
	[−100.29794]	[0.00957]	[4201]		
			4141.031[a]		
20, C_s	−115.04671	0.05513	343	1074	1095
	(−115.38984)	(0.05217)	(312)	(1157)	(1189)
	[−115.49038]	[0.05303]	[347]	[1083]	[1118]
			270.0[a]	1033.5[a]	1074.5[a]
21, C_{3v}	−114.38954	0.03804	1299	1311	1597
	(−114.73635)	(0.03660)	(1269)	(1257)	(1516)
	[−114.85801]	[0.03596]	[1164]	[1184]	[1444]
22, C_s	−115.35744	0.06844	236	652	825
	(−115.69736)	(0.06619)	(261)	(741)	(861)
	[−115.79001]	[0.06553]	[282]	[764]	[858]
23, C_{3v}	−139.03974	0.04210	1186	1307	1633
	(−139.48519)	(0.04003)	(1078)	(1216)	(1517)
	[−139.36744]	[0.04074]	[1115]	[1230]	[1566]
			1076.73[a]	1247.45[a]	1495.50[a]
24, C_s	−139.29013	0.05119	163	382	792
	(−139.61226)	(0.05056)	(204)	(610)	(881)
	[−139.72125]	[0.04977]	[199]	[548]	[851]

[a] Experimental data were taken from Ref. 14.

Intramolecular nucleophilic substitution in 2,3-dihydro-3-formylmethylenefuran. According to calculations, the *cis*- and *trans*-forms of 2,3-dihydro-3-formylmethylenefuran (**25** and **27**, respectively, see Scheme 8) correspond to the minima (λ = 0), whereas structure **26** corresponds to a saddle point (λ = 1) on the PES.

Scheme 8

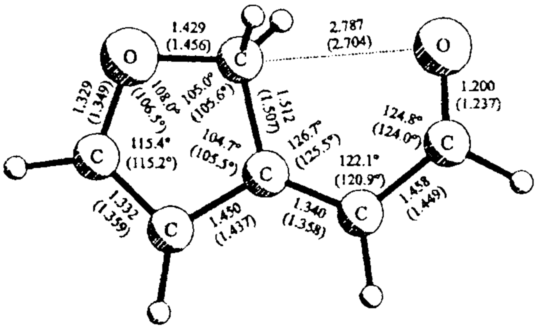


25a, C_s **26**, C_{2v} **25b**, C_s

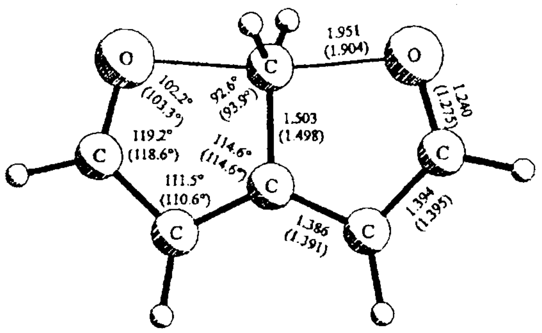
The calculated geometric and energy characteristics of structures **25—27** are shown in Fig. 3 and listed in Table 3. No experimental data on structures similar to systems **25** or **27** have been reported. To some extent the formylmethylene fragment in compound **25** can be compared with a similar fragment in the molecule of 1-H-iodophenyl-3-carbomethoxy-4-phenacylidene-5-hydroxy-5-phenylpyrazoline,[23] which also exists in the *cis*-form.

Despite the presence of a methylene site, the five-membered ring in molecule **25** is planar and geometrically close to the furan ring,[23] which indicates its pseudoaromaticity and can be explained by involvement of the antisymmetric combination of the orbitals of the CH_2 group hydrogens in conjugation. According to calculations, the *trans*-isomer **27** (see Fig. 3) is less stable than the *cis*-form **25**, *viz.*, the difference in their energies is 3.5 (RHF/DZ) and 4.3 kcal mol^{-1} (MP2/DZ). This indicates a rather strong stabilizing donor-acceptor C···O interaction in system **25**, which compensates for the steric strain in this form.

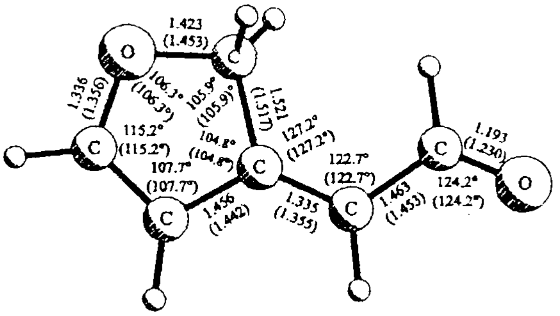
Structure **26** with the hypervalent pentacoordinate C atom is the TS of the intramolecular S_N2 reaction **25a** $\rightleftharpoons$ **26** $\rightleftharpoons$ **25b** with an energy barrier of 36.9 (RHF) and 27.7 kcal mol^{-1} (MP2). The inclusion of electron correlation leads to lowering of the barrier to the reaction by about 10 kcal mol^{-1} and to shortening of the length of the hypervalent C—O bond in TS **26** by 0.05 Å. The O—C—O angle in structure **26** is 174.8° (RHF) and 172.2° (MP2). This is about 10° smaller than the similar angle in cations **1**; however, the calculated barrier to reaction **25a** $\rightleftharpoons$ **26** $\rightleftharpoons$ **25b** is much higher than the experimental activation barriers to reactions



25, C_s ($\lambda = 0$)



26, C_{2v} ($\lambda = 1$)



27, C_s ($\lambda = 0$)

Fig. 3. Geometric characteristics of structures **25** and **27**, corresponding to minima, and those of transition structure **26**, corresponding to a saddle point on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

1a $\rightleftharpoons$ **2** $\rightleftharpoons$ **1b**. Comparison of geometric characteristics of the hypervalent O—C—O bond in structure **26** and in the sterically unstrained TS **11** (*cf.* Figs. 1 and 3) shows that they are very close. This indicates that, in fact, the steric strain in the fragment containing the pentacoordinate C atom in TS **26** is small as compared to that in the "ideal" structure and cannot be responsible for the high activation barrier to the reaction **25a** $\rightleftharpoons$ **26** $\rightleftharpoons$ **25b**. The lower barrier to intramolecular S_N2 reaction in the case of cations **1** is due to electronic factors, *viz.*, a higher nucleophilicity and nucleofugacity of the attacking and leaving groups, respectively. Nucleofugacity of the leaving group in system **25** can be appreciably increased by protonation of the O atom. To retain the symmetry and to exclude attendant side proton transfers in the case of monoprotonation,[25] we calculated the diprotonated form **28**.

Intramolecular nucleophilic substitution in dication 28. According to calculations, the *cis*- and *trans*-structures (**28** and **31**, respectively) correspond to minima ($\lambda = 0$), whereas structures **29** and **30** correspond to saddle points ($\lambda = 1$) on the PES; their calculated geometric and energy characteristics are shown in Fig. 4 and listed in Table 3.

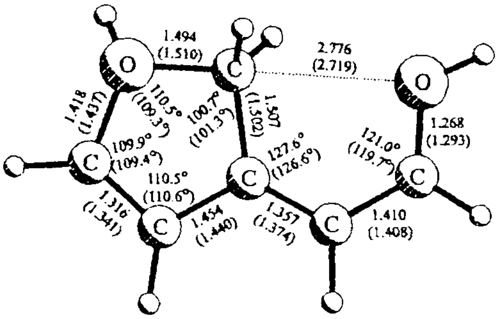
Dication **28** is nearly planar (except for the H atom at the oxonium O atom with a pyramidalized bond configuration, the out-of-plane deviations of the atoms do not exceed 1°).

Structure **29** with the hypervalent pentacoordinate C atom is the TS of an intramolecular S_N2 reaction with an energy barrier of 16.4 (RHF) and 19.4 kcal mol^{-1} (MP2). The inclusion of electron correlation leads to some increase in the barrier to reaction and to a shortening of the hypervalent C—O bond in TS **29** by 0.13 Å. The O—C—O angle in structure **29**, which is equal to 177.0° (RHF) and 179.8° (MP2), is very close to 180°. Comparison of the geometric characteristics of the fragments containing the hypervalent O—C—O bond in structure **29** and in the sterically unstrained TS **13** (*cf.* Figs. 1 and 4) shows that the bond in TS **29** is slightly lengthened due to the large positive charge in the system. The pathway of this nucleophilic substitution reaction passes through two more TS with C_s symmetry, *viz.*, **30a** and **30b**, at which the system arrives by moving from TS **29** and bypassing other stationary points on the PES. Such a PES topology is known (the gradient pathway of analogous reactions has been considered in detail[12]) and the pathway of intramolecular nucleophilic substitution can be described by Scheme 9. Structure **30a** is the TS in the case of inversion of the pyramidal bond configuration at the cyclic O atom (**28a** $\rightleftharpoons$ **30a** $\rightleftharpoons$ **28b**), whereas structure **30b** is the TS in the case of analogous inversion of the bond configuration in topomeric form **28c** (**28c** $\rightleftharpoons$ **30b** $\rightleftharpoons$ **28d**). According to calculations, the corresponding *trans*-isomer **31** is 4.0 (RHF) and 3.2 kcal mol^{-1} (MP2) less stable than the *cis*-isomer **29**. This indicates that there is a rather strong stabilizing donor-acceptor n_O-σ^*_{C-O}-interaction in dication **28**, analogous to that in molecule **25**.

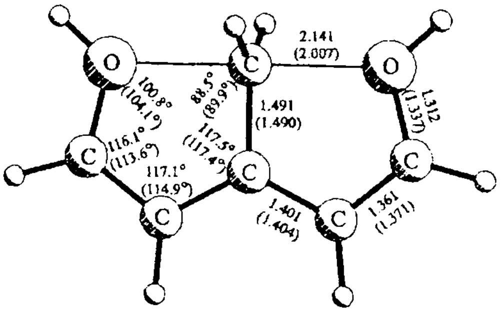
Intramolecular nucleophilic substitution in fluorine-substituted dication 32. Nucleofugacity of the leaving group can be increased to the greatest extent by replacement of the OH$^+$ group in dication **28** by the isoelec-

Table 3. Total (E_{tot}/au) and relative (ΔE/kcal mol^{-1}) energies, number of negative eigenvalues of the Hessian (λ), zero-point harmonic vibrational energies (*ZPE*/au), and imaginary or lowest harmonic frequencies (($i\omega/\omega_1$)/cm^{-1}) for structures **25—40**, calculated by the RHF/6-31G** and MP2(full)/6-31G** methods (figures in parentheses)

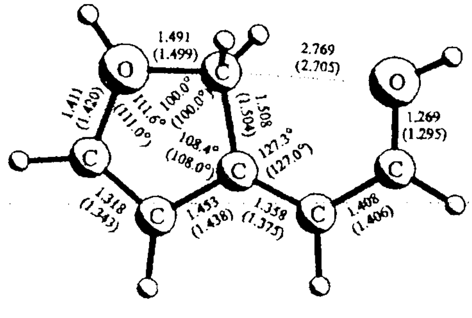
Structure, symmetry	E_{tot}	ΔE	λ	*ZPE*	$i\omega/\omega_1$
25, C_s	−380.39118 (−381.56847)	0 (0)	0 (0)	0.11639 (0.10993)	153 (148)
26, C_{2v}	−380.33243 (−381.52440)	36.9 (27.7)	1 (1)	0.11403 (0.10846)	i847 (i840)
27, C_s	−380.38563 (−381.56158)	3.5 (4.3)	0 (0)	0.11612 (0.10938)	103 (99)
28, C_1	−380.89851 (−382.05948)	0 (0)	0 (0)	0.14237 (0.13487)	136 (132)
29, C_{2v}	−380.87235 (−382.02854)	16.4 (19.4)	1 (1)	0.13869 (0.13209)	i334 (i558)
30, C_s	−380.89781 (−382.05770)	0.4 (1.2)	1 (1)	0.14134 (0.13408)	i337 (i409)
31, C_1	−380.89217 (−382.05434)	4.0 (3.2)	0 (0)	0.14227 (0.13494)	98 (96)
32, C_s	−428.76572 (−429.89538)	0 (0)	0 (0)	0.11244 (0.10719)	130 (130)
33, C_{2v}	−428.76216 (−429.88436)	2.2 (6.9)	1 (1)	0.11037 (0.10595)	i103 (i371)
34, C_s	−428.75801 (−429.88836)	4.8 (4.4)	0 (0)	0.11251 (0.10722)	94 (78)
35, C_s	−416.06850 (−417.15990)	0 (0)	0 (0)	0.10821 (0.10438)	112 (102)
36, C_{2v}	−416.06850 (−417.15478)	0 (3.2)	0 (1)	0.10821 (0.10349)	112 (i268)
37, C_s	−403.20761 (−404.27852)	0 (0)	0 (0)	0.10484 (0.10076)	122 (115)
38, C_{2v}	−403.19474 (−404.26163)	8.1 (10.6)	1 (1)	0.10292 (0.09971)	i250 (i440)
39, C_s	−416.05718 (−417.15151)	4.9 (5.3)	0 (0)	0.10891 (0.10432)	76 (65)
40, C_s	−403.20432 (−404.27476)	2.1 (2.4)	0 (0)	0.10455 (0.10053)	88 (73)



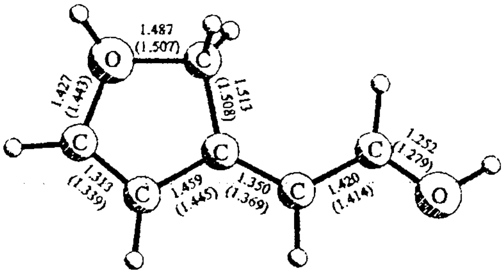
28, C_1 (λ = 0)



29, C_{2v} (λ = 1)



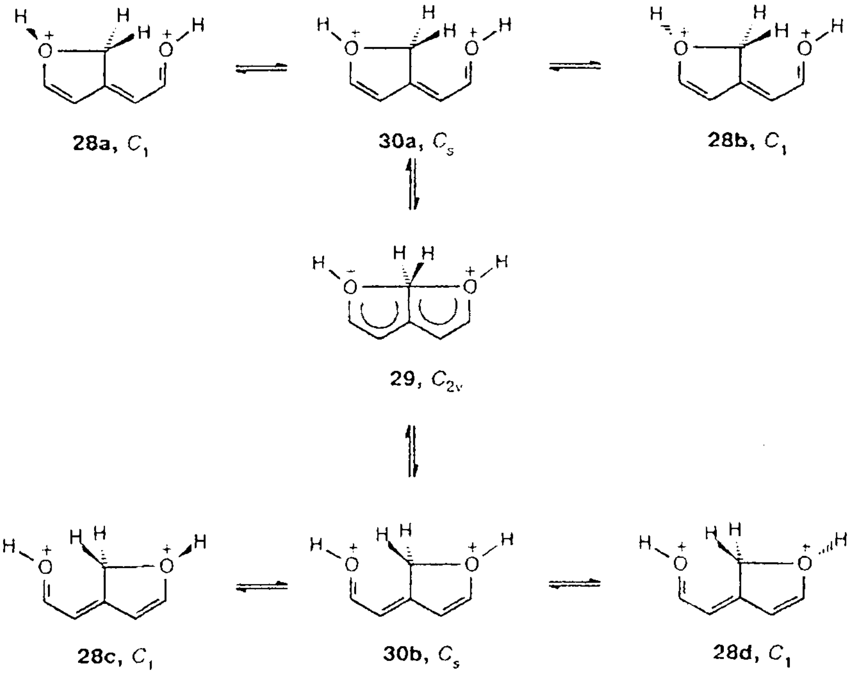
30, C_s (λ = 1)



31, C_1 (λ = 0)

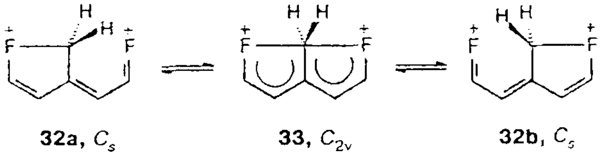
Fig. 4. Geometric characteristics of structures **28** and **31**, corresponding to minima, and those of transition structures **29** and **30**, corresponding to saddle points on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

Scheme 9



tronic F$^+$ center. Our calculations showed that the *cis*- and *trans*-forms (**32** and **34**, respectively) correspond to minima ($\lambda = 0$), whereas structure **33** corresponds to a saddle point ($\lambda = 1$) on the PES (Scheme 10); their calculated geometric and energy characteristics are shown in Fig. 5 and listed in Table 3.

Scheme 10

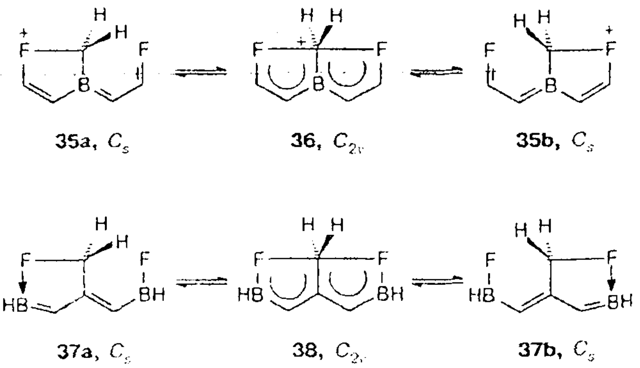


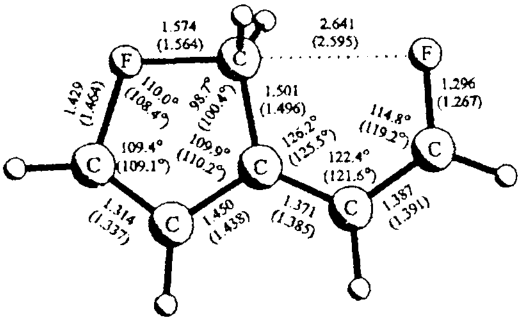
Despite the presence of the methylene group, the five-membered cycle in structure **32** is planar, which indicates its pseudoaromaticity and involvement of the lone electron pair of the cyclic F atom in π-conjugation.

Structure **33** with a hypervalent pentacoordinate C atom and planar bicyclic fragment is the TS of an intramolecular S_N2 reaction with an energy barrier of only 2.2 (RHF) and 6.9 kcal mol^{-1} (MP2). As in the preceding case, the inclusion of electron correlation slightly increases the barrier to reaction and leads to a shortening of the hypervalent C—F bond in TS **33** by 0.14 Å. The F—C—F angle in structure **33**, which is 175.6° (RHF) and 181.2° (MP2), slightly differs from 180°. Comparison of the geometric characteristics of the fragments containing the hypervalent F—C—F bond in dication **33** and in the sterically unstrained TS **16** (*cf.* Figs. 1 and 5) shows that in TS **33** this bond is slightly lengthened due to the large positive charge in the system. As in all preceding cases, there is a rather strong stabilizing donor-acceptor σ^*_{C-F}—n_F-interaction in *cis*-form **32**, due to which this form is 4.8 (RHF) and 4.4 kcal mol^{-1} (MP2) energetically more favorable than *trans*-isomer **34**.

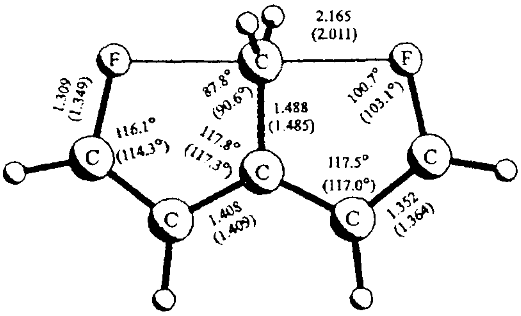
Intramolecular nucleophilic substitution in boron-fluorine-substituted cation 35 and neutral compound 37. The hypervalent bond in the dicationic TS **29** and **33** is slightly longer than in their intermolecular cationic analogs **13** and **16**, which can be explained by the larger positive charges in the former two systems. Therefore a decrease in the charge of the system can lead to shortening of the hypervalent bond and, as a consequence, to

Scheme 11

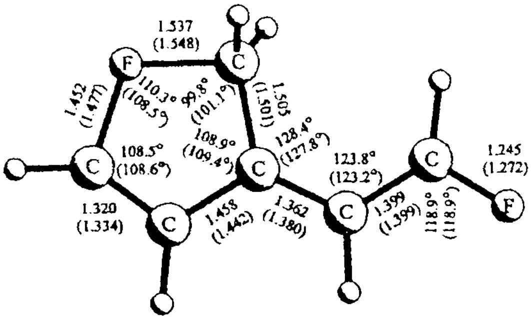




32, C_s ($\lambda = 0$)



33, C_{2v} ($\lambda = 1$)

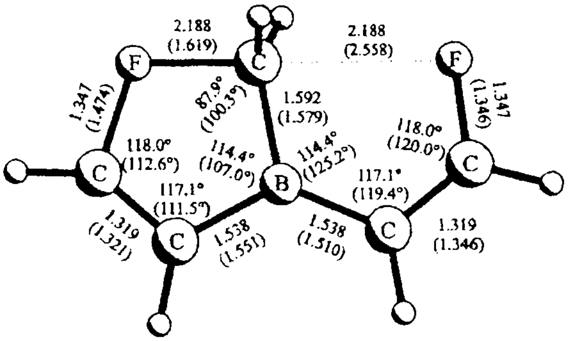


34, C_s ($\lambda = 0$)

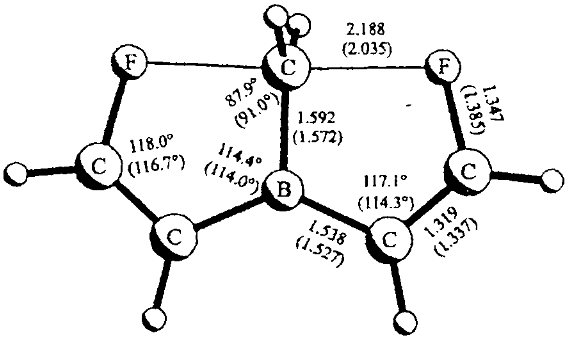
Fig. 5. Geometric characteristics of structures **32** and **34**, corresponding to minima, and those of transition structure **33**, corresponding to a saddle point on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

lowering of the activation barrier to the corresponding intramolecular nucleophilic substitution reaction.

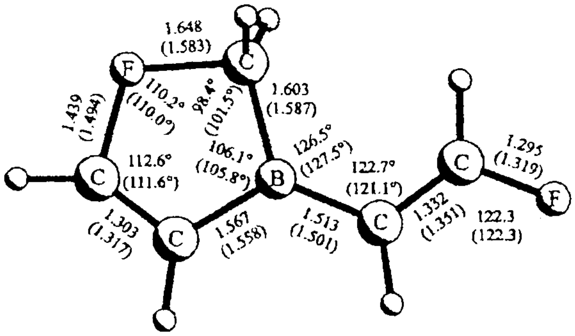
In this connection we studied reactions **35a** $\rightleftharpoons$ **36** $\rightleftharpoons$ **35b** and **37a** $\rightleftharpoons$ **38** $\rightleftharpoons$ **37b** (Scheme 11) for the hypothetical boron-fluorine-substituted compounds **35** and **37**. Our calculations show (see Figs. 6 and 7 and Table 3) that structures **35** and **37** correspond to minima ($\lambda = 0$), whereas structures **36** and **38** correspond to saddle points ($\lambda = 1$) on the PES.



35, C_s ($\lambda = 0$)



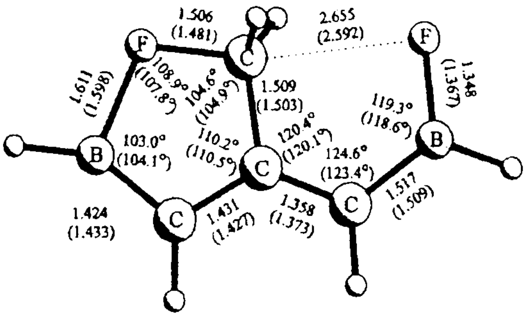
36, C_{2v} ($\lambda = 1$)



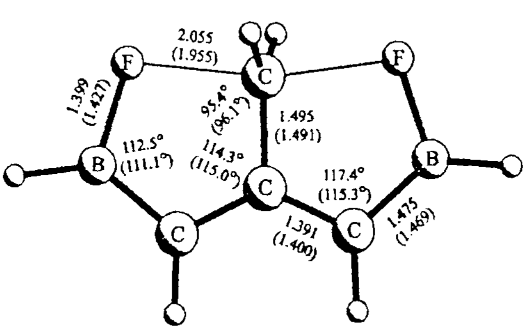
39, C_s ($\lambda = 0$)

Fig. 6. Geometric characteristics of structures **35** and **39**, corresponding to minima, and those of transition structure **36**, corresponding to a saddle point on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

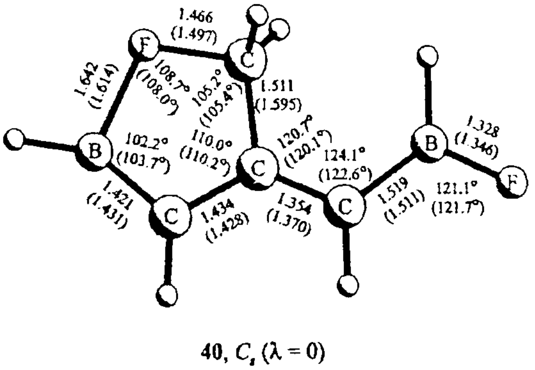
In both cases, the mirror plane is conserved in the course of reactions in the systems and the heavy-atom



37, C_s (λ = 0)



38, C_{2v} (λ = 1)



40, C_s (λ = 0)

Fig. 7. Geometric characteristics of structures **37** and **40**, corresponding to minima, and those of transition structure **38**, corresponding to a saddle point on the PES, calculated by the RHF/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods.

framework remains planar, which indicates aromaticity of the five-membered cycles. Let us dwell on the B—F and F—C bond lengths in the hypothetical compounds **35** and **37**. In cation **35** (see Fig. 6), one of the F—C bonds is ordinary, whereas the other bond is lengthened (its length is close to that of the dative, or donor-acceptor, bond). A reverse situation is observed in the neutral molecule **37**, *viz.*, the methylene C atom forms an ordinary F—C bond with the F atom, whereas the B←F bond is a donor-acceptor bond.

Symmetric structures **36** and **38** with the hypervalent pentacoordinate C atoms are the TS of intramolecular S_N2 reactions with extremely low energy barriers of 0 (RHF) and 3.2 kcal mol^{-1} (MP2) for the first structure and 8.1 (RHF) and 10.6 kcal mol^{-1} (MP2) for the second structure. In both cases, the inclusion of electron correlation leads to an increase in the barriers to the reactions and to a slight shortening of the hypervalent C—F bond in the TS. The F—C—F angle in structure **36** (175.8° and 182.0° at the RHF and MP2 levels, respectively) is much closer to 180° than that in TS **38**, in which it is 190.8° (RHF) and 192.2° (MP2). Most likely, it is such a large deviation of the F—C—F angle from 180° that leads to the the higher energy barrier to reaction for compound **37** compared to that for structure **35**. Because of the strong stabilizing donor-acceptor C···F interaction, *cis*-isomers **35** and **37** (see Figs. 6 and 7) are more stable than the *trans*-isomers **39** and **40** (by 4.9 (RHF), 5.3 (MP2) and 2.1 (RHF), 2.4 kcal mol^{-1} (MP2), respectively).

* * *

Based on the results of our calculations, one can draw the following conclusions.

Intramolecular nucleophilic S_N2 reactions with activation barriers within the energy scale of NMR spectroscopy can occur in the systems in which steric conditions for linear orientation of the attacking and leaving groups are realized.

Catalysis of intramolecular reactions with Brønsted or Lewis acids makes it possible to lower the energy barrier due to the increase in nucleofugacity of the leaving group.

In cationic systems, it is possible to avoid the increase in the energy barrier to intramolecular S_N2 reaction due to electrostatic effects by using model compounds containing electron-deficient atoms.

A further lowering of the energy barrier to S_N2 reaction in systems of type **25** can be achieved by benzoannelation (introduction of an anthracene nucleus), which imparts rigidity to the spatially "mated" system of bonds, as well as by the addition of appropriate substituents to the carbon atoms.

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References

1. S. L. Craig and J. I. Brauman, *Science*, 1997, **276**, 1536 (see also references cited therein).
2. G. A. Olah, G. K. Surya Prakash, and R. E. Williams, *Hypercarbon Chemistry*, J. Wiley and Sons, New York, 1987.

3. V. I. Minkin, B. Ya. Simkin, and R. M. Minyaev, *Quantum Chemistry of Organic Compounds. Mechanisms of Reactions*, Springer-Verlag, Berlin, 1990, Ch. 5.
4. S. Harder, A. Streitweieser, J. T. Petty, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1995, **117**, 3253.
5. M. N. Glukhovtsev, A. Pross, and L. Radom, *J. Am. Chem. Soc.*, 1996, **118**, 6273.
6. S. Wolf, K. Yang, N. Weinberg, Z. Shi, Y.-H. Hsieh, R. D. Sharma, S. Ro, and C.-K. Kim, *Chem. Eur. J.*, 1998, **4**, 886 (see also references cited therein).
7. J. C. Martin and R. J. Basalay, *J. Am. Chem. Soc.*, 1973, **95**, 2572.
8. J. C. Martin, *Science*, 1983, **221**, 509.
9. J. B. Foresman and E. Frisch, *Exploring Chemistry with Electronic Structure Methods*. 2nd ed., Gaussian, Inc., Pittsburgh (PA), 1996, 302 pp.
10. M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. AlLaham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94, Revision B.3*, Gaussian, Inc., Pittsburgh (PA), 1995.
11. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *GAMESS, Version 1996*, *J. Comput. Chem.*, 1993, **14**, 1347.
12. R. M. Minyaev, *Usp. Khim.*, 1994, **63**, 939 [*Russ. Chem. Rev.*, 1994, **63**, 883 (Engl. Transl.)].
13. *PC MODEL*, Selena Software, Bloomington (IN), 1987.
14. M. Meot-Ner (Mautner), *J. Phys. Chem.*, 1986, **90**, 6687.
15. K. S. Krasnov, N. V. Filippenko, V. A. Bobkova, N. L. Lebedeva, E. V. Morozov, T. I. Ustinova, and G. A. Romanova, *Molekulyarnye postoyannye neorganicheskikh soedinenii* [*Molecular Constants of Inorganic Compounds*], Ed. K. S. Krasnov, Khimiya, Leningrad, 1979, 448 pp. (in Russian).
16. Y.-J. Zheng and K. M. Merz, *J. Comput. Chem.*, 1992, **13**, 1151.
17. S. Wolf, C.-K. Kim, K. Yang, N. Weinberg, and Z. Shi, *Can. J. Chem.*, 1998, **76**, 359.
18. K. Raghavachari, J. Chandrasekhar, and R. C. Burnier, *J. Am. Chem. Soc.*, 1984, **106**, 3124.
19. G. A. Olah, A. Burrichter, G. Rasul, R. Gnann, K. O. Christe, and G. K. S. Pracash, *J. Am. Chem. Soc.*, 1997, **119**, 8035.
20. D. H. Aue and M. T. Bowers, in *Gas Phase Ion Chemistry*, Ed. M. T. Bowers, Academic Press, New York, 1979, **2**, 18.
21. T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, 1986, **108**, 6502.
22. G. A. Olah, N. Hartz, G. Rasul, O. Wang G. K. S. Pracash, J. Casanova, and K. O. Christe, *J. Am. Chem. Soc.*, 1994, **116**, 5671.
23. G. D. Andreetti, G. Bocelli, L. Cavalca, and P. Sgarabotta, *Gazz. Chim. Ital.*, 1972, **102**, 355.
24. N. M. Pozdeev, O. B. Anulinin, A. A. Shakshin, and N. N. Magdesieva, *Zh. Strukt. Khim.*, 1970, **11**, 869 [*J. Struct. Chem. (USSR)*, 1970, **11** (Engl. Transl.)].
25. Y. Yamamoto and K.-Y. Akiba, *J. Am. Chem. Soc.*, 1984, **106**, 2713.

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