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INDO STUDY OF 1,2-FLUORINE ATOM MIGRATION IN 1,1,2,2-TETRAFLUOROETHYL RADICAL, CATION AND ANION

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SUMMARY

INDO molecular orbital calculations have been carried out to estimate the energy barrier heights of the 1,2-migration of a fluorine atom in 1,1,2,2-tetrafluoroethyl radical, cation, and anion. In addition, the 1,2-hydrogen atom migration in these chemical species has been studied.

The results suggest that (1) the 1,2-fluorine atom migration through a fluorine atom bridging intermediate will occur more readily than the 1,2-hydrogen atom migration through a hydrogen atom bridging intermediate in the 1,1,2,2-tetrafluoroethyl radical, (2) on the contrary, the 1,1,2,2-tetrafluoroethyl cation will undergo the 1,2-migration of a hydrogen atom more readily than that of a fluorine atom, and (3) it will be difficult for the 1,1,2,2-tetrafluoroethyl anion to undergo the 1,2-migration of a fluorine and a hydrogen atom. The enthalpy change associated with the 1,2-fluorine atom migration in the radical was estimated to be 2.5 kcal/mol, which was 1.5 times larger than the corresponding change in the trifluoroethyl radical.

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INTRODUCTION

Recently, the intramolecular 1,2-migration of a fluorine atom has experimentally been found to occur in some radicals and carbenes[1-5]. Siefert et al. investigated the reactions of recoil tritium atoms with 1,2-difluoroethylene[1]. Since tritiated 1,1-difluoroethylene was one of the main products, they suggested that the 1,2-migration of a fluorine atom occurred in the reaction intermediate, 1,2-difluoroethyl radical.

Holmes has studied the unimolecular decomposition of chemically activated CF_3CH_2Cl, which was prepared by gas phase combination of $\dot{C}F_3$ and $\dot{C}H_2Cl$ radicals[2]. It was found that the decomposition pathways for CF_3CH_2Cl included 1,2-elimination of HF giving $CF_2{=}CHCl$ and 1,1-elimination of HCl giving 2,2,2-trifluoromethyl carbene CF_3-CH:, and that the carbene underwent 1,2-fluorine migration to give $CF_2{=}CHF$ as final decomposition product.

Our laboratory has studied the reactions of trifluoroethylene with both hydrogen and recoil tritium atoms[3-5]. The analysis of reaction products was made by means of gas chromatography, mass spectrometry, and ^1H and ^{19}F-NMR spectroscopy. Some of main products observed were 1,1,1-trifluoroethane, 1,1,1,4,4,4-, 1,1,1,3,3,4-, and 1,1,1,3,4,4-hexafluorobutane which contained CF_3- group. These products cannot be expected to be formed until 2,2,2-trifluoroethyl radical is produced by the 1,2-migration of a fluorine atom in the reaction intermediate, 1,1,2-trifluoroethyl radical.

Moreover, we have determined the energy barrier heights of the 1,2-migration of a fluorine and a hydrogen atom in 1,1,2-trifluoroethyl and 1,2-difluoroethyl radical by the INDO molecular orbital calculations[6]. The calculated results suggested that the 1,2-fluorine atom migration through a fluorine atom bridging intermediate would occur more readily than the 1,2-hydrogen atom migration in both radicals. The enthalpy change associated with the 1,2-fluorine atom migration in 1,1,2-trifluoroethyl radical was estimated to be 1.7 kcal/mol, which was in good agreement with the value (1.6 kcal/mol) obtained experimentally[4].

The molecular orbital calculations on the 1,2-migration of a fluorine atom in fluorinated ethyl radical have been carried out only on the monofluoroethyl radical except our calculation described above. The calculated energy barrier heights of the migration ranged from 28.6 to 107 kcal/mol depending on the method employed[7-9].

There are a number of theoretical studies on the 1,2-fluorine atom migration in monofluoroethyl cation[10-13]. Hopkinson et al. obtained the energy profiles for the open and fluorine atom bridging monofluoroethyl cations by ab initio molecular orbital calculations at three different basis sets [12]. The calculated energy barrier between the open and bridging cation was sufficiently low for a rapid migration of fluorine atom at room temperature. Lischka and Kohler also carried out MINDO/3 calculations and ab initio ones both at the SCF level and with inclusion of electron correlation(IEPA-PNO, PNO-CI, and CEPA-PNO) for the cation[13]. They concluded that the bridging cation was only slightly more stable than the open one(1.4 kcal/mol).

There are no experimental studies on 1,2-fluorine atom migration in the monofluoroethyl cation. Olah and Bollinger, however, studied the ionization of 1,1,2,2-tetramethyl-1,2-difluoroethane in SO_2/SbF_5 solvent by means of ^1H-NMR spectroscopy[14]. It was found that a fluorine atom rapidly exchanged between the two carbons in the 1,1,2,2-tetramethylfluoroethyl cation produced in the solvent.

The substantial previous theoretical studies on fluorinated ethyl anions have focused only on hyperconjugation at the open structures[15-22]. To date, total energies of the bridged anions and the 1,2-migration of a fluorine and a hydrogen atom in the anions have not been estimated, as far as we are aware.

In view of the present situation, the theoretical approach to the 1,2-fluorine atom migration in some fluorinated ethyl radicals, cations, and anions has aroused our interest. The objective of the present work is to theoretically estimate the energy barrier heights of the 1,2-fluorine atom migration through a fluorine atom bridging intermediate in 1,1,2,2-tetrafluoroethyl radical, cation, and anion. For comparison, the 1,2-hydrogen atom migration in these chemical species has also been studied.

CALCULATIONS

Total energies and geometries of open and bridged structures of tetrafluoroethyl radical, cation, and anion were determined by the INDO molecular orbital calculations. For open structures, all parameters of geometry were optimized. For bridged structures, a bridging atom was assumed to occupy the position at the top of the isosceles triangle made of the C-C bond as one side. The INDO calculations were performed with the same parametrization as the Pople original version. The INDO program was incorporated with the automatic geometry optimization based on the Davidon-Fletcher-Powell(DFP) algorithm. The descent direction in each cycle of optimization was determined by Broyden-Fletcher-Goldfarb-Sanno(BFGS) modification, which provided good stability and rapid convergence around the optimum point.

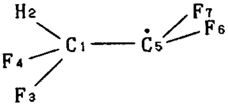
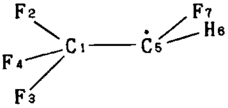
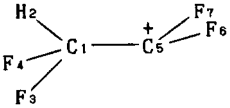
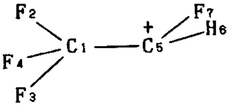
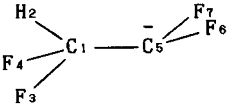
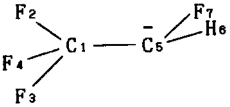
RESULTS AND DISCUSSION

The optimized geometry parameters of open tetrafluoroethyl radicals, cations, and anions are given in Table 1. For the bridging structures, the parameters are given in Table 2. Total energies calculated for these chemical species are summarized in Table 3. On a basis of the total energies, we can draw the energy profiles(kcal/mol) for 1,2-migration processes of a fluorine and a hydrogen atom through the bridged intermediates in 1,1,2,2-tetrafluoroethyl radical, cation, and anion. These profiles are shown in Figs. 1, 2, and 3, respectively.

It is obvious from Fig. 1 that the energy difference between the open 1,1,2,2-tetrafluoroethyl and the fluorine bridging radical is 25.9 kcal/mol, while the difference between the open and the hydrogen bridging radical 56.1

TABLE 1

Optimized Geometries for Open-Structures of Tetrafluoroethyl Radicals, Cations and Anions

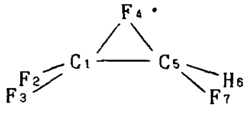
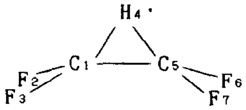
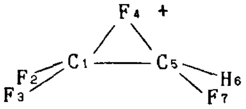
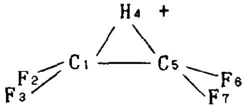
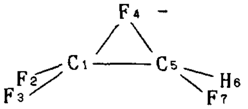
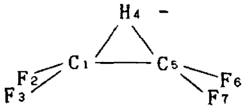
Chemical Species	Geometry		
	r(C1H2)=1.135 r(C1F3)=1.352 r(C1F4)=1.355 r(C1C5)=1.447 r(C5F6)=1.330 r(C5F7)=1.331	∠ H2C1F3=107.1 ∠ F3C1F4=106.1 ∠ F4C1H2=107.0 ∠ C5C1H2=112.6 ∠ C5C1F3=112.0 ∠ C5C1F4=111.8	∠ F6C5F7=110.5 ∠ C1C5F6=125.0 ∠ C1C5F7=124.6
	r(C1F2)=1.355 r(C1F3)=1.352 r(C1F4)=1.352 r(C1C5)=1.456 r(C5H6)=1.110 r(C5F7)=1.328	∠ F2C1F3=104.7 ∠ F3C1F4=105.9 ∠ F4C1F2=104.6 ∠ C5C1F2=113.6 ∠ C5C1F3=113.5 ∠ C5C1F4=113.7	∠ H6C5F7=114.4 ∠ C1C5H6=128.2 ∠ C1C5F7=117.4
	r(C1H2)=1.139 r(C1F3)=1.349 r(C1F4)=1.350 r(C1C5)=1.449 r(C5F6)=1.301 r(C5F7)=1.301	∠ H2C1F3=108.8 ∠ F3C1F4=107.5 ∠ F4C1H2=108.7 ∠ C5C1H2=109.9 ∠ C5C1F3=110.9 ∠ C5C1F4=110.9	∠ F6C5F7=109.7 ∠ C1C5F6=125.4 ∠ C1C5F7=124.9
	r(C1F2)=1.349 r(C1F3)=1.345 r(C1F4)=1.346 r(C1C5)=1.471 r(C5H6)=1.123 r(C5F7)=1.287	∠ F2C1F3=107.0 ∠ F3C1F4=107.1 ∠ F4C1F2=107.0 ∠ C5C1F2=111.8 ∠ C5C1F3=111.8 ∠ C5C1F4=111.8	∠ H6C5F7=113.5 ∠ C1C5H6=128.3 ∠ C1C5F7=118.3
	r(C1H2)=1.166 r(C1F3)=1.369 r(C1F4)=1.366 r(C1C5)=1.420 r(C5F6)=1.364 r(C5F7)=1.365	∠ H2C1F3=100.4 ∠ F3C1F4=106.6 ∠ F4C1H2=100.3 ∠ C5C1H2=120.0 ∠ C5C1F3=114.0 ∠ C5C1F4=113.7	∠ F6C5F7=109.6 ∠ C1C5F6=125.3 ∠ C1C5F7=125.0
	r(C1F2)=1.381 r(C1F3)=1.364 r(C1F4)=1.366 r(C1C5)=1.420 r(C5H6)=1.112 r(C5F7)=1.370	∠ F2C1F3=98.1 ∠ F3C1F4=105.0 ∠ F4C1F2=98.4 ∠ C5C1F2=119.8 ∠ C5C1F3=116.0 ∠ C5C1F4=116.6	∠ H6C5F7=114.0 ∠ C1C5H6=127.8 ∠ C1C5F7=118.2

r: Bond lengths in angstroms, ∠ : bond angles in degrees.

kcal/mol. The former difference is somewhat larger than the corresponding energy differences in the 1,1,2-trifluoroethyl and the 1,2-difluoroethyl radical obtained previously by the INDO calculations[6]. There is now experimental evidence that the 1,1,2-trifluoroethyl and the 1,2-difluoroethyl radicals undergo the intramolecular 1,2-migration of a fluorine atom through the fluorine bridging intermediates[1, 3-5].

TABLE 2

Optimized Geometries for Bridged-Structures of Tetrafluoroethyl Radicals, Cations and Anions

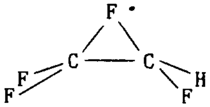
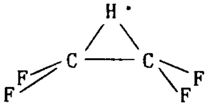
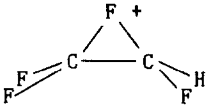
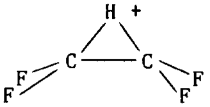
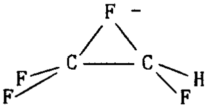
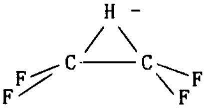
Chemical Species	Geometry		
	r(C1F2)=1.334 r(C1F3)=1.335 r(C1F4)=1.484 r(C1C5)=1.430 r(C5H6)=1.126 r(C5F7)=1.350	∠ F2C1F3=107.8 ∠ C5C1F2=125.9 ∠ C5C1F3=126.1 ∠ C5C1F4=61.2 ∠ H6C5F7=111.4 ∠ C1C5H6=120.8	∠ C1C5F7=114.7 ∠ F4C1F2=108.4 ∠ F4C1F3=108.1 ∠ F4C5H6=125.8 ∠ F4C5F7=114.4
	r(C1F2)=1.338 r(C1F3)=1.338 r(C1H4)=1.485 r(C1C5)=1.350 r(C5F6)=1.337 r(C5F7)=1.338	∠ F2C1F3=109.1 ∠ C5C1F2=125.5 ∠ C5C1F3=125.2 ∠ C5C1H4=63.0 ∠ F6C5F7=109.4 ∠ C1C5F6=125.3	∠ C1C5F7=125.0 ∠ H4C1F2=107.9 ∠ H4C1F3=107.7 ∠ H4C5F6=107.8 ∠ H4C5F7=107.7
	r(C1F2)=1.325 r(C1F3)=1.326 r(C1F4)=1.434 r(C1C5)=1.450 r(C5H6)=1.122 r(C5F7)=1.330	∠ F2C1F3=110.8 ∠ C5C1F2=124.4 ∠ C5C1F3=124.7 ∠ C5C1F4=59.6 ∠ H6C5F7=114.3 ∠ C1C5H6=127.2	∠ C1C5F7=118.1 ∠ F4C1F2=108.1 ∠ F4C1F3=107.6 ∠ F4C5H6=111.1 ∠ F4C5F7=106.2
	r(C1F2)=1.327 r(C1F3)=1.328 r(C1H4)=1.306 r(C1C5)=1.410 r(C5F6)=1.327 r(C5F7)=1.328	∠ F2C1F3=110.5 ∠ C5C1F2=124.7 ∠ C5C1F3=124.4 ∠ C5C1H4=57.3 ∠ F6C5F7=110.8 ∠ C1C5F6=124.6	∠ C1C5F7=124.3 ∠ H4C1F2=110.5 ∠ H4C1F3=110.3 ∠ H4C5F6=110.4 ∠ H4C5F7=110.3
	r(C1F2)=1.360 r(C1F3)=1.360 r(C1F4)=1.585 r(C1C5)=1.380 r(C5H6)=1.126 r(C5F7)=1.360	∠ F2C1F3=103.7 ∠ C5C1F2=122.8 ∠ C5C1F3=123.5 ∠ C5C1F4=64.2 ∠ H6C5F7=109.4 ∠ C1C5H6=121.6	∠ C1C5F7=119.6 ∠ F4C1F2=119.6 ∠ F4C1F3=120.0 ∠ F4C5H6=118.9 ∠ F4C5F7=116.8
	r(C1F2)=1.343 r(C1F3)=1.344 r(C1H4)=1.864 r(C1C5)=1.330 r(C5F6)=1.342 r(C5F7)=1.343	∠ F2C1F3=108.6 ∠ C5C1F2=125.8 ∠ C5C1F3=125.5 ∠ C5C1H4=69.1 ∠ F6C5F7=108.9 ∠ C1C5F6=125.7	∠ C1C5F7=125.4 ∠ H4C1F2=103.3 ∠ H4C1F3=103.2 ∠ H4C5F6=103.2 ∠ H4C5F7=103.1

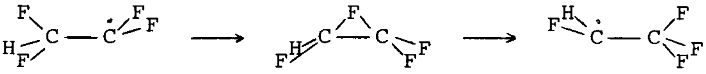
r: Bond lengths in angstroms, ∠ : bond angles in degrees.

Therefore, if 1,1,2,2-tetrafluoroethyl radicals are produced by the addition reaction of hydrogen atom with tetrafluoroethylene, it should be possible for them to change 1,2,2,2-tetrafluoroethyl radicals(CF_3-CHF) by 1,2-migration process of a fluorine atom through a fluorine atom bridging intermediate as follows,

TABLE 3

Total Energies(hartree) Calculated for Open- and Bridged-Tetrafluoroethyl Radicals, Cations and Anions

Chemical Species	Total Energy	Chemical Species	Total Energy
$CHF_2\text{-}\dot{C}F_2$	-120.08666	$CF_3\text{-}\dot{C}HF$	-120.09631
$CHF_2\text{-}CF_2^+$	-119.69164	$CF_3\text{-}CHF^+$	-119.64101
$CHF_2\text{-}CF_2^-$	-120.07484	$CF_3\text{-}CHF^-$	-120.12527
	-120.04535		-119.99715
	-119.77521		-119.71375
	-119.91977		-119.84860



and then the final reaction products including some CF_3-groups, for example, $CF_3\text{-}CH_2F$, $CF_3\text{-}CHF\text{-}CHF\text{-}CF_3$ etc., should be formed.

From Fig. 2, it is obvious that the fluorine and the hydrogen atom bridging tetrafluoroethyl cation are 52.4 and 13.9 kcal/mol more stable than the open cation $CHF_2\text{-}CF_2^+$, respectively, while the open cation $CF_3\text{-}CHF^+$ is 31.7 kcal/mol less stable. These results suggest that (1) the 1,1,2,2-tetrafluoroethyl cation will undergo the 1,2-hydrogen atom migration through the hydrogen atom bridging intermediate more readily

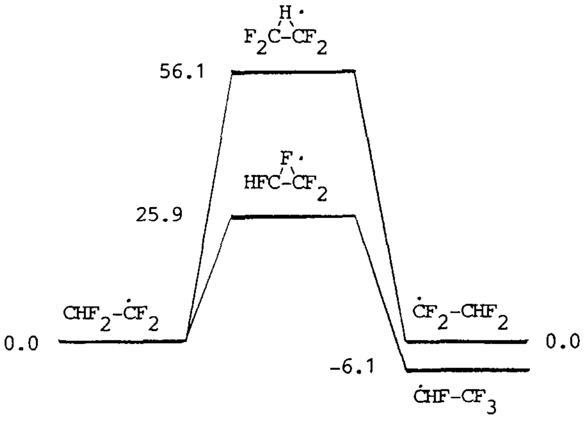


Fig. 1. Energy Profile(kcal/mol) for 1,2-Migration Processes of Fluorine and Hydrogen Atom in Tetrafluoroethyl Radicals

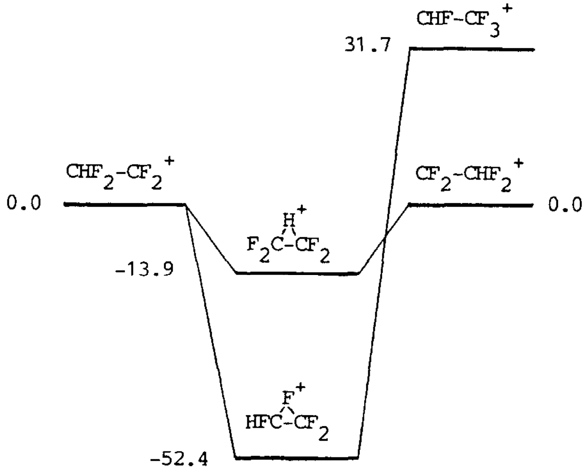


Fig. 2. Energy Profile(kcal/mol) for 1,2-Migration Processes of Fluorine and Hydrogen Atom in Tetrafluoroethyl Cations

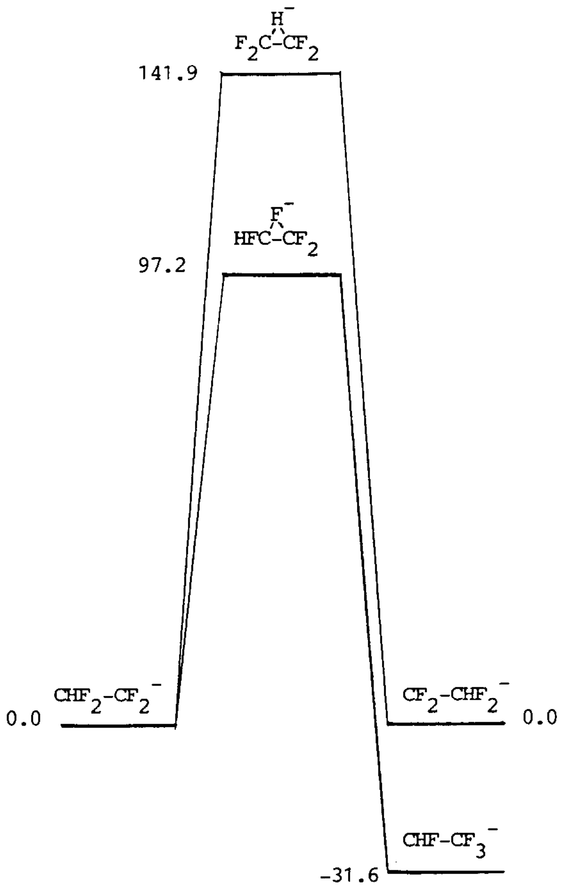


Fig. 3. Energy Profile(kcal/mol) for 1,2-Migration Processes of Fluorine and Hydrogen Atom in Tetrafluoroethyl Anions

than the 1,2-fluorine atom migration, in contrast with the corresponding radical, and (2) the tetrafluoroethyl cation has a preference for the bridging structure, particularly the fluorine atom bridging one, over the open structure.

There is substantial theoretical and experimental evidence that chloroethyl and ethyl cations have a preference for the bridged structures over the open structures[10,11,13,23-31].

It has already been described in the Introduction that the fluorine bridging monofluoroethyl cation is more stable than the open one. Thus, our calculated results for the tetrafluoroethyl cation should be reasonable.

It is obvious from Fig. 3 that (1) the energy barrier heights for 1,2-migration of a fluorine and a hydrogen atom through the bridged intermediate in the $CHF_2\text{-}CF_2^-$ anion are 97.2 and 141.9 kcal/mol, respectively, and (2) the open anion $CF_3\text{-}CHF^-$ is 31.6 kcal/mol more stable than the open anion $CHF_2\text{-}CF_2^-$. To date, there has been no theoretical and experimental evidence for 1,2-migration of a fluorine and a hydrogen atom in fluorinated ethyl anions except our present work, as far as we are aware. Therefore, we can compare only our results of the tetrafluoroethyl anion and radical. Since the energy barriers for 1,2-migration of a fluorine and a hydrogen atom in the $CHF_2\text{-}CF_2^-$ anion are 3.8 and 2.5 times higher than those in the radical, it will be difficult for the anion to undergo the 1,2-migrations.

In the previous work, it was recognized that the open fluorinated ethyl radical in which fluorine atoms were set aside to one carbon atom was energetically more stable than those in which fluorine atoms were distributed over two carbon atoms[6]. It can be also applied to the open tetrafluoroethyl radicals and anions, but not applied to the open cations, since the $CF_3\text{-}\dot{C}HF$ and $CF_3\text{-}CHF^-$ are 6.1 and 31.6 kcal/mol more stable than the $CHF_2\text{-}\dot{C}F_2$ and $CHF_2\text{-}CF_2^-$, respectively, while the $CF_3\text{-}CHF^+$ is 31.7 kcal/mol less stable than the $CHF_2\text{-}CF_2^+$.

The absolute value obtained by the INDO calculation is not reliable. In the case of tetrafluoroethyl radicals, the calculated values can be normalized by the process described in the previous work[6]. Consequently, the calculated values in Figure 1 should be read by multiplying 0.41, when quantitative argument has to be made. For example, the enthalpy change between $CF_3\text{-}\dot{C}HF$ and $CHF_2\text{-}\dot{C}F_2$ can be estimated to be 2.5 kcal/mol(= 6.1 x 0.41). Therefore, the ratio(k_b/k_f) of forward and reverse rate constants for reaction 1 is estimated

$$CHF_2\text{-}\dot{C}F_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CF_3\text{-}\dot{C}HF \qquad (1)$$

to be 0.02 at 298 K, if E_b-E_f= 2.5 kcal/mol, and the Arrhenius equation can be applied as follows: k_f=2Aexp(-E_f/RT) and k_b=3Aexp(-E_b/RT).

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