Ab Initio Molecular Orbital and Density Functional Studies on The Sigmatropic Rearrangement of Cycloprop-2-En-1-Thiol And Its Fluorine Derivative

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Abstract: Theoretical study of sigmatropic rearrangement reaction of cycloprop-2-en-1-thiol and its fluorine derivative was carried out in gas phase. To understand the nature of the reaction, whether it undergoes pericyclic/pseudopericyclic mechanism NICS calculation is performed. It shows sigmatropic reaction of cycloprop-2-en-1-thiol is pericyclic in nature. When fluorine is substituted in three member ring of cycloprop-2-en-1-thiol its shows pseudopericyclic nature. To know involvement of the lone pair of electrons during the reaction, lone pair electron present on the sulphur atom is locked by hydrogen bonding. CR-CCSD(T)/6-311+G** levels are used to study the reactions more accurately.

Key word: Pseudopericyclic reaction; Aromaticity; Density functional calculations; Ab initio calculations; sigmatropic rearrangement reaction.

1. Introduction

Not all reactions in organic chemistry involve intermediates. Absence of intermediates indicates that the reactions in which bond making and breaking takes place by single step process called concerted reaction and that particular class of concerted reactions called pericyclic reaction[1]. Pericyclic reactions involve cyclic transition states. Woodward and Hoffmann[2] showed that symmetry of the orbitals that are involved in a reaction decide the mechanism of that particular reaction. In pericyclic reaction the lone pair electron on hetero atom which take part in the cyclic transition state known as pseudopericyclic reactions[3-18]. Since there is no clear cut criteria exist to differentiate a pericyclic reaction from a pseudopericyclic one, some reactions have difficulty in being classified[19-23]. The magnetic property study is helpful to assess the extent of aromatization along the reaction path[24-36] and also helps in quantifying reactions as pericyclic or pseudopericyclic.

In this manuscript we have presented a comprehensive theoretical study of the sigmatropic rearrangement (SR) reaction of cycloprop-2-en-1-thiol. Effect of fluorine substitution in the place of ring hydrogen atoms has been studied. To differentiate the pericyclic/pseudopericyclic nature of a reaction and to know involvement of the lone pair of electrons during the reaction, locking of lone pair of electrons[37,38] (LLPE) method is used in addition to Nucleus-independent chemical shift (NICS).

2. Computational method

SR reaction of cycloprop-2-en-1-thiol and its fluorine derivative was studied using *ab initio* molecular orbital and density functional theory at various level of calculations. The computations were performed at B3LYP/6-311+G** and CR-CCSD(T)/6-311+G**[39-41] (RUNTYPE=ENERGY) levels of calculation. Firefly[42] and the GAMESS (US)[43] program were used for the computations. In all cases, the structures of reactant, transition state and the product were completely optimized. From the transition state structure, intrinsic reaction coordinates (IRC) calculations were carried out. Hessian calculations were done and the frequencies for reactants and products were found to be real values and the transition states have one imaginary frequency. NICS calculation were performed at B3LYP/6-311+G** basis using the gauge including atomic orbital method[44] (GIAO) in GAUSSIAN-03[45] package. The magnetic shielding tensor calculations were carried out by placing the ghost atom at the ring critical points (RCP) at the lowest electron density in the ring plane[46-49]. NICS calculations were carried out to measure the value of aromaticity due to π-system and sometimes obscured by the σ-current. MacMolplt[50] software is used to visualize the graphical outputs.

3. Result and discussion

In the SR reaction of cycloprop-2-en-1-thiol, 1,2,3-trifluorocycloprop-2-en-1-thiol was studied using B3LYP/ 6-311+G** and CR-CCSD(T)/6-311+G** levels of calculation, the energy of the reactant, transition state, and the product were calculated and are given in table.1. Structure of SR reaction of cycloprop-2-en-1-

thiol and its fluorine derivative are given in figure.1 & 2. IRC computations show that the transition state connects the reactant and the product smoothly. The transition state of the SR reaction of cycloprop-2-en-1-thiol and its fluorine derivative has one imaginary frequency and it shows first order saddle points and its value for transition state of cycloprop-2-en-1-thiol is 462.05i cm^{-1} and 1,2,3-trifluorocycloprop-2-en-1-thiol is 754.77 i cm^{-1} calculated at B3LYP/ 6-311+G** level of calculation. Selected geometrical parameters of the transition state for the SR reaction of cycloprop-2-en-1-thiol and its fluorine derivate are given in table 2 & 3.
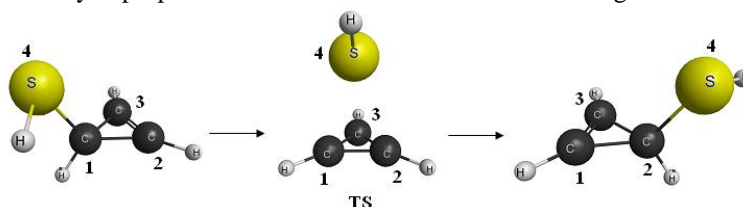

Figure 1. Structure of the reactant, transition state and product of the SR reaction of
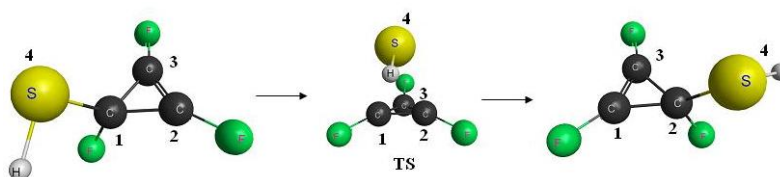Cycloprop-2-en-1-thiol

Figure 2. Structure of the reactant, transition state and product of the SR reaction of
1,2,3-trifluorocycloprop-2-en-1-thiol

Figure 3. Structure of the reactant, transition state and product of the SR reaction of
3-methylcyclopropene

Table 1. Energies for the sigmatropic rearrangement of 3-methylcyclopropene, cycloprop-2-en-1-thiol and its fluorine derivative

Levels of calculations	1,3 Sigmatropic shift	Reactant (hartrees)	Transition State (hartrees)	Product (hartrees)	Energy Barrier (kcal mol^{-1})
CR-CCSD(T)/ 6-311+G**	-SH in C_3H_3SH	-514.0085	-513.9284	-514.0085	50.3
B3LYP/6-311+G**	-SH in C_3H_3SH	-514.8748	-514.8135	-514.8748	38.5
B3LYP/6-311+G**	-SH in C_3F_3SH	-812.6634	-812.5866	-812.6634	48.2
B3LYP/6-311+G**	-SH in C_3H_3SH, with LLPE	-889.1272	-889.0517	-889.1272	47.4
B3LYP/6-311+G**	-CH_3 in C_4H_6 PARENT	-155.9842	-155.8447	-155.9843	87.5

TABLE 2. Selected geometrical parameters of the transition state for the [1, 3]-Sigmatropic shift of cycloprop-2-en-1-thiol, distances are in Å

Selected geometrical parameter between	TS (cycloprop-2-ene-1-thiol)	
	Bond length	**Bond order**

C_1-C_2	1.383	1.321
C_2-C_3	1.371	1.396
C_3-C_1	1.372	1.395
C_1-S_4/ C_2-S_4	2.569	0.382

TABLE 3. Selected geometrical parameters of the transition state for the [1, 3]-Sigmatropic shift of 1,2,3-trifluorocycloprop-2-en-1-thiol, distances are in Å

Selected geometrical parameter between	TS (1,2,3-trifluorocycloprop-2-en-1-thiol)	
	Bond length	Bond order
C_1-C_2	1.385	1.205
C_2-C_3	1.387	1.415
C_3-C_1	1.387	1.415
C_1-S_4/ C_2-S_4	2.389	0.262

Pericyclic / Pseudopericyclic reactions

For a better understanding of the SR reaction of cycloprop-2-en-1-thiol, 1,2,3-trifluorocycloprop-2-en-1-thiol first we analyzed [1, 3] sigmatropic shift of methyl in 3-methylcyclopropene, it was considered as the parent SR reaction as shown in figure 3. From the point of Birney *et al*[4-8] pseudopericyclic reaction have low activation energy and disconnection in orbital overlap in the TS which leads to lower aromaticity. The barrier for the methyl group migration in cyclopropene ring has been computed to be 87.5 kcal mol^{-1} and is given in table 1. At the B3LYP/6-311+G** level calculation the transition state has one imaginary frequency (1021.64 i cm^{-1}) and IRC computation connects the transition state into its particular reactant and product. Comparing the energy barrier of [1, 3] sigmatropic shift of methyl with [1, 3] sigmatropic shift of thiol group it is seen that the methyl migration in the parent hydrocarbon has a much higher barrier for the SR than for the substituted compounds. The lower activation energy barrier of SR shifts of thiol group shows pseudopericyclic nature. But the low activation energy may be due to presence of reactive sulphur atom. NICS and LLPE methods are used to study pericyclic/pseudopericyclic character more accurately.

3.2. Nucleus-Independent Chemical Shift (NICS)

In this SR studies, NICS calculations were carried out by placing ghost atom in the geometrical center of the three-member ring to a set of point 1 Å below the ring to avoid the effects of σ bonds[51] and also the spurious effect associated with lone pair of electrons present in sulphur atom above the ring as shown in Figure 1&2. NICS calculation was carried out for both transition states (TS) and reactants to study the differences between them. The results are plot in figure 4. From the reference point 0.3 to 1.0 NICS computations shows enhanced in aromaticity which shows that the SR reaction of cycloprop-2-en-1-thiol is pericyclic in nature. If the reaction was pseudopericyclic, the involvement of the lone pair of electrons on the sulphur atom during the transition state would reduce the aromaticity of the ring. To understand the involvement of lone pair present on the sulpur atom, NICS calculations were carried out for the fluorine derivatives of cycloprop-2-en-1-thiol. In the SR reaction of 1,2,3-trifluorocycloprop-2-en-1-thiol, NICS values shows lower value for aromaticity, Plotted in figure 4. The substitution of three fluorine atoms in ring causes the withdrawal of the pi electrons present on three member ring. Due to the lower availability of pi electrons for migration, the lone pair of electrons present on the sulpur atom gets more involved in reaction. Hence the SR reaction of 1,2,3-trifluorocycloprop-2-en-1-thio is pseudopericyclic in nature.

When hydrogen bonding is used to lock the lone pair of electrons present on the sulphur atom, the involvement of lone pair electron in the cyclic transition is blocked and hence the aromaticity is increased. On comparing the NICS values calculated on TS during with and without LLPE of 1,2,3-trifluorocycloprop-2-en-1-thiol, using the points 0.0 to 1.0 Å below the ring has given in figure 5. The NICS values, when LLPE shows slightly increase in aromaticity compared to NICS calculated during without LLPE. This show on hydrogen bonding the lone pair of electrons is not completely available to take part in the cyclic transition and causes the increase in aromaticity, which indicates SR reaction of 1,2,3-trifluorocycloprop-2-en-1-thio during LLPE is

pericyclic in nature. Thus LLPE and NICS method conforms the lone pair of electron present on sulphur atom involves in SR reaction of 1,2,3-trifluorocycloprop-2-en-1-thiol and not involved in cycloprop-2-en-1-thiol.
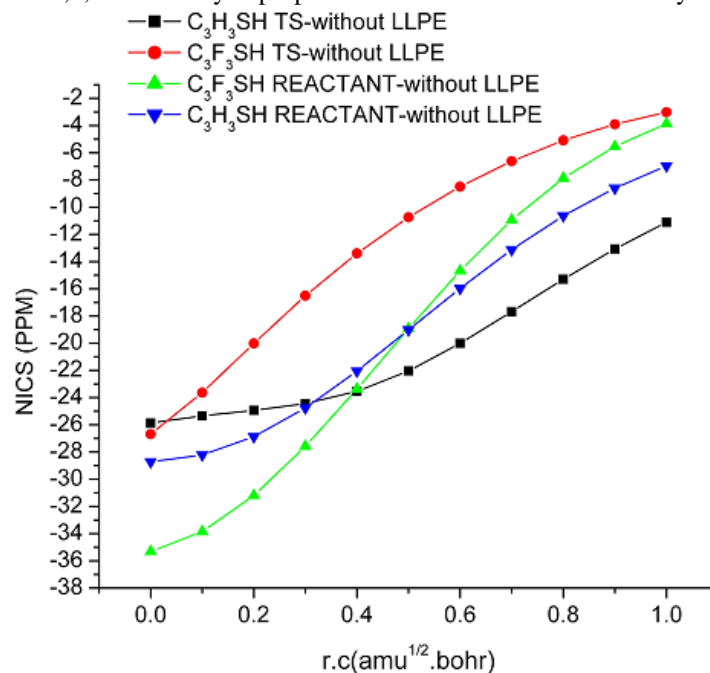

Figure 4. NICS values for SR reaction of cycloprop-2-en-1-thiol and 1,2,3,trifluorocycloprop-2-en-1-thiol without LLPE calculated at B3LYP/6-311+G** level of calculation
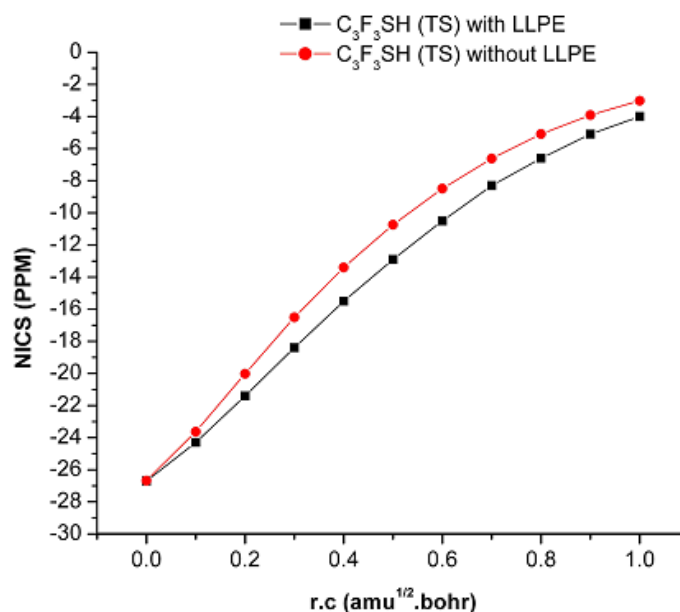

Figure 5. NICS values for transition state of SR reaction of cycloprop-2-en-1-thiol, 1,2,3- trifluorocycloprop-2-en-1-thiol with and without LLPE calculated at B3LYP/6-311+G** level of calculation.

4.   Conclusion

SR reaction of cycloprop-2-en-1-thiol and its fluorine derivative was studied using *ab initio* molecular orbital and density functional theory. Transition state and energy barrier were calculated at different levels of calculation. The SR reaction of cycloprop-2-en-1-thiol and its fluorine derivative are comparing with 1-methyl cyclopropene, the lower activation energy is due to presence of sulphur atom. To investigate the behavior of aromaticity, the NICS profiles have been computed. On the basis of NICS profile the SR reaction of cycloprop-2-en-1-thiol is pericyclic in nature and 1,2,3-trifluorocycloprop-2-en-1-thiol was found to be pseudopericyclic in

nature. Substitution of fluorine atoms on the ring results in withdrawal of pi electrons causing the migrating sulphur atom to donate more of its electrons to the sigmatropic migration. This results in increasing pseudopericyclic nature.

Acknowledgments

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