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RING CLOSURE of $HSCH_2CH_2S^-$ AND $HSCH_2CH_2CH_2S^-$: A DENSITY FUNCTIONAL STUDY

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ABSTRACT
Density functional theory is used to study ring closure $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2S^-$. The transition state for ring closure of $HSCH_2CH_2S^-$ is predicted to be three-membered and for $HSCH_2CH_2CH_2S^-$ is four-membered. Geometries are optimized using a 3-21G basis set. Calculated charges using B3LYP density functional shows that TS1 has more ionic character than TS2. The reactions are found to be endothermic. The activation energy for $HSCH_2CH_2S^-$ is smaller than $HSCH_2CH_2CH_2S^-$.
Keywords: Density Functional Theory, B3LYP, B3PW91, Ring Closure, $HSCH_2CH_2S^-$, $HSCH_2CH_2CH_2S^-$.
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INTRODUCTION

Ring closure of $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2\ S^-$ reaction gives Thiirane and Thietan. Thiiranes and Thietanes are important intermediates in organic synthesis[1-3] just as their oxygen and nitrogen analogs (oxiranes and aziridines, and oxetanes and azetidines). Ring closure of $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2S^-$ reaction is predicted to take place via 3 and 4 membered ring formation. The calculated activation energies show three-membered ring formation is preferred over the four-membered ring. Density functional theory is the popular tool used here as its ability to include exchange and correlation functional at moderate cost in comparison to post SCF method for calculating the ground state properties of molecules.[4-16] In this paper, we present the results of our Density Functional study of the ring closure of $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2S^-$. Earlier theoretical studies[17] have also been made for $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2S^-$ using the post SCF method shows good agreement.

EXPERIMENTAL

Method of Calculations

In the present work B3LYP and B3PW91 density functional with 6-31 G(d) basis set used here for all calculations. The hybrid functional B3LYP used here has Becke's exchange functional correction.[18,19] The gradient corrected correlation functional of Lee, Yang, and Parr[20] and B3PW91 hybrid functional has Becke's exchange functional correction with Perdew and Wang's correlational functional.[21] Geometries optimization was made using analytical first derivatives. Gaussian 94 Quantum chemistry package[22] was used for all calculations presented here.

RESULTS AND DISCUSSION

Structures of Reactants, Transition States, and Products

The RHF/3-21G optimized geometries of $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2S^-$ reactants, TS1, TS2, and thiirane, and thietane are optimized and are listed in Tables-1 to 6.

Table-1: Calculated Optimized Geometries of the Reactant (I)[a] $HSCH_2CH_2S^-$

Bond length (in Å)		Bond Angles (in Degrees)		Dihedral Angles (in Degrees)	
C2-C1	1.517	H3-C1-C2	111.6	H4-C1-C2-H3	-124.2
H3-C1	1.076	H4-C1-C2	111.9	S5-C1-C2-H3	115.9
H4-C1	1.075	S5-C1-C2	113.4	S6-C2-C1-H3	63.6
S5-C1	1.959	S6-C2-C1	108.2	H7-C2-C1-S6	-120.7
S6-C2	1.901	H7-C2-C1	109.9	H8-C2-C1-S6	119.8
H7-C2	1.081	H8-C2-C1	110.0	H9-S5-C1-C2	31.3

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H8-C2	1.084	H9-S5-C1	97.3		
H9-S5	1.353				

a: See Fig.-1

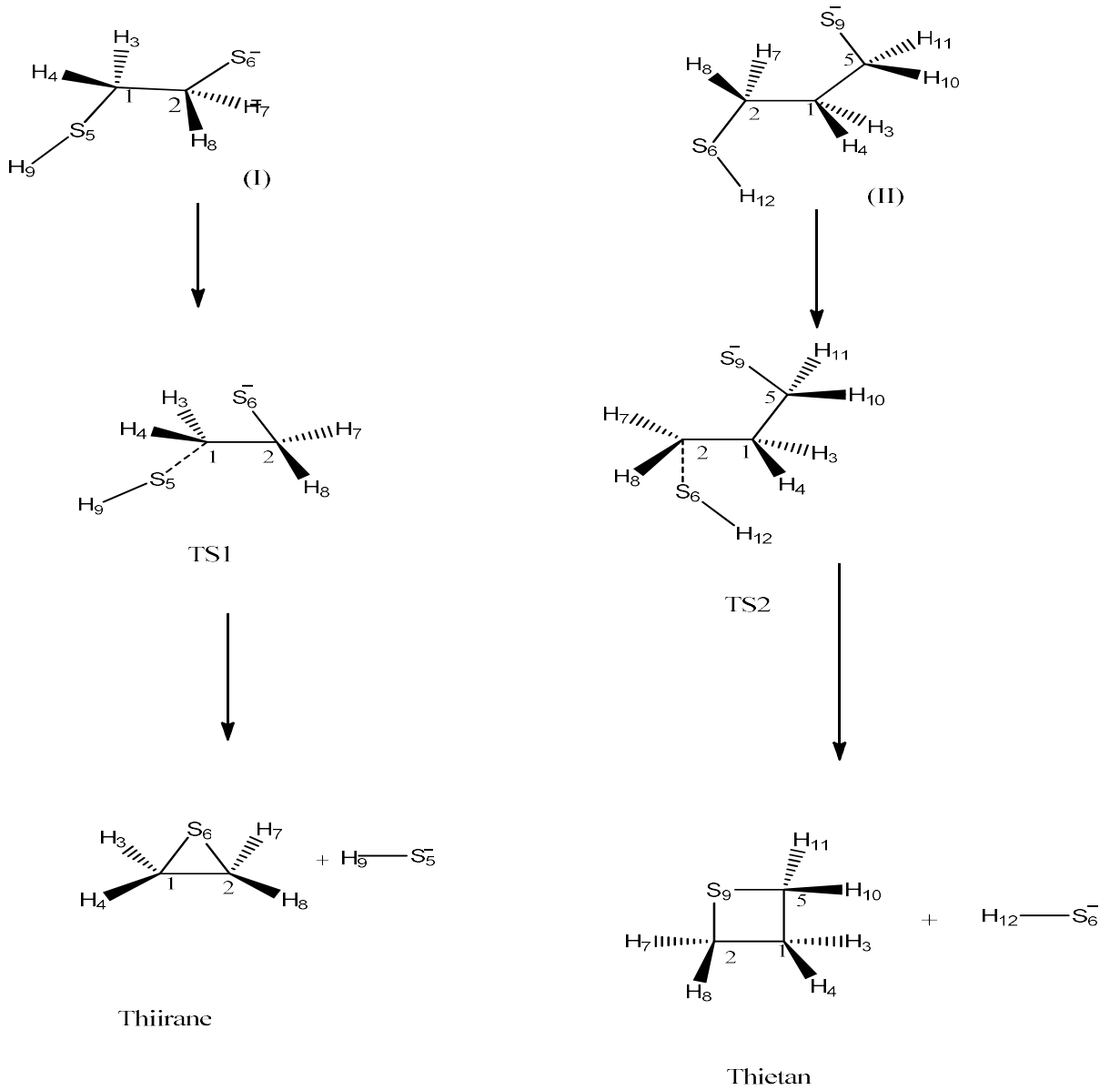

Fig.-1: Ring Closure of $HSCH_2CH_2S^-$ and $HSCH_2CH_2CH_2\ S^-$

Table -2: Calculated Optimized Geometries of the Transition State (TS1)[a]

Bond length (in Å)		Bond Angles (in Degrees)		Dihedral Angles (in Degrees)	
C2-C1	1.434	H3-C1-C2	120.4	H3-C1-C2-S5	87.5
H3-C1	1.062	H4-C1-C2	120.4	H4-C1-C2-S5	-87.5
H4-C1	1.062	S5-C1-C2	104.8	S6-C2-C1-S5	180.0
S5-C1	2.865	S6-C2-C1	78.8	H7-C2-C1-S5	-71.5
S6-C2	1.957	H7-C2-C1	117.1	H8-C2-C1-S5	71.5
H7-C2	1.070	H8-C2-C1	117.1	H9-S5-C1-C2	180.0
H8-C2	1.070	H9-S5-C1	100.5		
H9-S5	1.369				

a: See Fig.-1

Table-3: Calculated Optimized Geometries of Thiirane[a]

Bond length (in Å)		Bond Angles (in Degrees)		Dihedral Angles (in Degrees)	
C1-S6	1.934	C1-S6-C2	44.8	H3-C1-S6-C2	-113.1
H3-S6	1.070	H3-C1-S6	112.4	H4-C1-S6-C2	113.1
H4-S6	1.070	H4-C1-S6	112.4	H7-C2-S6-C1	113.1
S6-C2	1.934	H7-C2-S6	112.4	H8-C2-S6-C1	-113.1
H7-C2	1.070	H8-C2-S6	112.4		
H8-C2	1.070				

a: See Fig.-1

Table-4: Calculated Optimized Geometries of the Reactant (II)[a] $HSCH_2CH_2CH_2S^-$

Bond length (in Å)		Bond Angles (in Degrees)		Dihedral Angles (in Degrees)	
C2-C1	1.525	H3-C1-C2	109.4	H4-C1-C2-H3	-118.7
H3-C1	1.083	H4-C1-C2	109.4	C5-C1-C2-H3	118.7
H4-C1	1.088	C5-C1-C2	110.2	S6-C2-C1-H3	57.0
C5-C1	1.545	S6-C2-C1	112.7	H7-C2-C1-S6	-121.1
S6-C2	1.920	H7-C2-C1	110.1	H8-C2-C1-S6	116.1
H7-C2	1.075	H8-C2-C1	111.8	S9-C5-C1-C2	-63.3
H8-C2	1.080	S9-C5-C1	112.7	H10-C5-C1-S9	-120.8
S9-C5	1.901	H10-C5-C1	108.4	H11-C5-C1-S9	122.4
H10-C5	1.085	H11-C5-C1	109.1	H12-S6-C2-C1	-65.2
H11-C5	1.086	H12-S6-C2	97.5		
H12-S6	1.353				

a: See Fig.-1

Table-5: Calculated Optimized Geometries of the Transition State (TS2)[a]

Bond length (in Å)		Bond Angles (in Degrees)		Dihedral Angles (in Degrees)	
C2-C1	1.531	H3-C1-C2	110.6	H3-C1-C2-C5	-112.7
H3-C1	1.080	H4-C1-C2	108.5	H4-C1-C2-C5	118.0
H4-C1	1.080	C5-C1-C2	103.8	C5-C1-C2-H8	73.0
C5-C1	1.540	S6-C2-C1	94.5	S6-C2-C1-H8	88.8
S6-C2	2.580	H7-C2-C1	121.6	H7-C2-C1-H8	175.3
H7-C2	1.060	H8-C2-C1	119.5	H8-C1-C2-S6	88.8
H8-C2	1.063	S9-C5-C1	100.6	S9-C5-C1-C2	23.7
S9-C5	1.904	H10-C5-C1	111.4	H10-C5-C1-S9	-115.7
H10-C5	1.081	H11-C5-C1	113.5	H11-C5-C1-S9	120.1
H11-C5	1.080	H12-S6-C2	97.5	H12-S6-C2-C1	175.6
H12-S6	1.364				

a: See Fig.-1

Table-6: Calculated Optimized Geometries of Thietan[a]

Bond length (in Å)		Bond Angles (in Degrees)		Dihedral Angles (in Degrees)	
C2-C1	1.555	H3-C1-H4	109.5	C2-C1-H4-H3	124.4
H3-C1	1.080	H4-C1-C2	114.0	C5-C1-H4-H3	-124.4
H4-C1	1.080	C5-C1-H4	114.0	H7-C2-C1-H8	130.9
C5-C1	1.555	H7-C2-C1	113.8	H8-C2-C1-H4	-108.9
H7-C2	1.077	H8-C2-C1	115.9	S9-C5-C1-H4	134.6
H8-C2	1.076	S9-C5-C1	92.1	H10-C5-C1-S9	112.6
S9-C5	1.921	H10-C5-C1	113.8	H11-C5-C1-S9	-116.5
H10-C5	1.077	H11-C5-C1	115.9		
H11-C5	1.076				

a: See Fig.-1

It is observed that the transition state for the ring closure of $HSCH_2CH_2S^-$ (I) is a three-membered ring and the ring closure of $HSCH_2CH_2CH_2S^-$ (II) is four-membered one. For the ring closure of $HSCH_2CH_2S^-$, the

S6-C2, S5-C1, and S5-H9 bond lengths increases while going from reactant to the transition state. S6-C2-C1 bond angle is smaller for the transition state (TS1) as compared to that of the reactant. In-ring closure of $HSCH_2CH_2CH_2S^-$, S9-C5, and C2-S6 bond lengths increases while going from reactant to the transition state. S9-C5-C1 bond angle is smaller for the transition state (TS2) as compared to that of the reactant.

Charges on Various Atoms and Groups

Calculated charges for some atoms and groups are listed in table-7 and 8. In going to the transition from (I), the S fragment loses 0.31 electrons but the HS^- fragment gains 0.56(Table-7) electrons. Therefore, the CH_2CH_2 group loses 0.25 electrons with B3PW91 and 0.29 with B3LYP. Further $\nabla^2\rho_c$ values calculated also reconfirmed the ionic behavior of TS1. This development of positive charge on CH_2CH_2 group indicates increased contribution from ionic resonance form shown below:

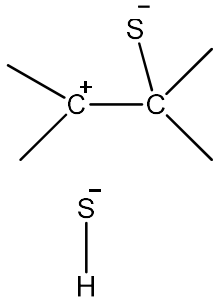

Table-7: Calculated Charges for Some Atoms and Groups for I and TS1[a]

Structure[b]	Group	Charge
I	S	-0.70(-0.71)
	SH	-0.19 (-0.20)
TS1	S	-0.39(-0.41)
	SH	-0.75(-0.79)

a: Obtained using B3PW91 density functional. The numbers in parentheses are those obtained from B3LYP calculations.
b: See Fig.-1

Table-8: Calculated Charges for some Atoms and Groups for II and TS2[a]

Structure[b]	Group	Charge
II	S	-0.73(-0.73)
	SH	-0.12 (-0.13)
TS2	S	-0.42(-0.43)
	SH	-0.65(-0.65)

a: Obtained using B3PW91 density functional. Numbers in parentheses are those obtained from B3LYP calculations.
b: See Fig.-1

A similar consideration will show that for the ring closure of reactant (II), the $CH_2CH_2CH_2$ group loses only 0.22 electron B3PW91, and with B3LYP charges (Table-8), the amount of electron transfer to the CH_2CH_2 group in TS1 is 0.29(B3LYP) electron while the amount of electron transfer to CH_2CH_2 CH_2.group in TS2 is 0.22(B3LYP) electron. Hence, TS1 will have more ionic interaction than TS2. This will lead to a lesser contribution of the ionic resonance form of TS2. The $\nabla^2\rho_c$ for the S6-C2 bond in TS1 is -0.080 for B3PW91 density functional. This suggests a smaller covalent interaction for the ring S and C in TS1 as compared to TS2. Therefore, the bending of the $S_{(ring)}$-C-C angle should be easier for TS1. The non-bonded C-S distance of II 3.28 Å or 0.50 Å longer than that in (I) leads to decreased proximity effect which in turn will suggest a more favorable three- membered ring formation (TS1).

Energetics of the Reactions

The calculated energy barrier (E_a) and ΔE results are listed in Tables-9 and 10. The calculated results of B3LYP and B3PW91 calculations are very close to each other. The energy of activation for the ring closure of $HSCH_2CH_2S^-$ is smaller than that for the ring closure of $HSCH_2CH_2CH_2S^-$ and this is in good agreement

with the result of high-quality quantum chemical studies.[17] Calculated values of ΔE are also in good agreement with others' estimate.[17].ΔE and activation energies are also calculated using B3LYP density functional with 6-31 G(d) basis set. E_a and ΔE values are found to be in good agreement with the results of single-point energy calculations (Table-9 and 10).

Table-9: Energetics[a] (kcalmol^{-1}) for the Reaction $HSCH_2CH_2\ S^-$ →Thiirane+ HS^-

	RB3LYP/6-31G(d)//RHF/3-21G	RB3PW91/6-31G(d)//RHF/3-21G	RB3LYP/6-31G(d)	Other[c]
E_a	13.3	14.9	14.8	19.2
ΔE	22.0	21.9	22.1	18.6

a: Activation Energy E_a and ΔE = E (Product) – E (Reactant). Values are after the zero–point vibrational energy correction.
b: See Fig.-1
c: Taken from Reference.[17]

Table-10: Energetics[a] (kcalmol^{-1}) for the Reaction $HSCH_2CH_2CH_2\ S$ → Thietan + HS^-

	RB3LYP/6-31G(d)//RHF/3-21G	RB3PW91/6-31G(d)//RHF/3-21G	RB3LYP/6-31G(d)	Other[c]
E_a	17.9	18.8	20.5	29.4
ΔE	19.3	18.8	23.6	21.7

a: Activation Energy E_a and ΔE = E (Product) – E (Reactant). Values are after the zero-point vibrational energy correction.
b: See Fig.-1
c: Taken from Reference.[17]

CONCLUSION

- Ring closure of $HSCH_2CH_2S^-$ is three-membered and for $HSCH_2CH_2CH_2S^-$ is four-membered.
- The energy of activation for the ring closure of $HSCH_2CH_2S^-$ is smaller than that for the ring closure of $HSCH_2CH_2CH_2S^-$.
- DFT method using B3LYP and B3PW91 using 6-31G (d) basis set give reliable results which are comparable to those obtained from high-quality quantum chemical calculations.

REFERENCES

1. Manfred Sander, Thiirenes, *Chemical Review,* **66(3)**, 297 (1966), https://doi.org/10.1021/cr60241a004
2. Warren Chew and David N. Harpp, *Sulphur Reports*, **15(1)**, 1(1993), https://doi.org/10.1080/01961779308050628
3. Vishnu Ji Ram, Arun Sethi, Mahendra Nath and Ramendra Pratap, *"The Chemistry of Heterocycles"*, Elsevier (2019)
4. Y. Quin and R. A. Wheeler, *Journal of Physical Chemistry*, **102**, 1689 (1995), https://doi.org/10.1063/1.468901
5. R. Kaushik, R.C. Rastogi and N.K. Ray, *Indian Journal of Chemistry*, **35A**, 629(1996)
6. R. Kaushik and N.K. Ray, *Indian Journal of Chemistry,* **36A**, 252(1997)
7. H.C. Tandon, R. Kaushik and N.K. Ray, *Proceedings of Indian National Science Academy*, **63A**, 345 (1997)
8. S. Rani, N.K. Ray, *Indian Journal of Chemistry*, **37A**,811(1998)
9. S. Rani, N. K. Ray *Indian Journal of Chemistry,***39A**,75 (2000)
10. E. Nazarparvar, M. Zahedi and E. Klein, *Journal of Organic Chemistry,* **77(22)**, 10093(2012), https://doi.org/10.1021/jo301612a
11. M. Miller, C Maichle- Mossmer and H.F. Bettinger, *Journal of Organic Chemistry,* **79**, 5478(2014), https://doi.org/10.1021/jo500549m
12. A. Heidari, *Journal of Applied and Computational Studies*, **5(1)**, (2016), https://doi.org/10.4172/2168-9679.1000e142
13. Renu Parashar, *Rasayan Journal of Chemistry,* **14(5),** 8 (2021), https://doi.org/10.31788/RJC.2021.1456610
14. Renu Parashar and Sunita Bansal, Research *Journal of Chemistry and Environment*, **25(12)**, 98 (2021), https://doi.org/10.25303/2512rjce98106

15. Sunita Bansal and Renu Parashar, *Journal of Emerging Technologies and Innovative Research,* **9(1)**, a500(2022)
16. Renu Parashar and Sunita Bansal, *Research Journal of Chemistry and Environment*, **26(2)**, 47(2022), https://doi.org/10.25303/2602rjce4751
17. S. Gronert and J. M. Lee, *Journal of Organic Chemistry,* **60**, 6731(1995), https://doi.org/10.1021/jo00126a023
18. A.D. Becke*, Journal of Chemical Physics*, **98**, 5648(1993), https://doi.org/10.1063/1.464913
19. A.D. Becke, *Physical Review A,* **38**, 3098(1988), https://doi.org/10.1103/PhysRevA.38.3098
20. C. Lee, W. Yang and R.G. Parr, *Physical Review B*, **37**, 785(1988), https://doi.org/10.1103/PhysRevB.37.785
21. J. P. Perdew and Y. Wang, *Physical Review B,* **45**, 13244(1992), https://doi.org/10.1103/PhysRevB.45.13244
22. *Gaussian* 94, Revision B2, M.J. Frisch, G.W. Trucks, H. B. Schlegel, P. M. W. Gill, B.G. Johnson, M.A. Robb, J.R. Montgomery, K. Raghavanchari, M.A. Al-Lahan, V.G. Zakrzewski, J. V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M.W. Wong, L. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. G. Fox, J. S. Binkley, D.J. Defrees, J. Baker, J. P. Stewart, M.Head-Gordon, C. Gonzalez and J. A. Pople (Gaussian, Inc., Pittsburgh, PA), 1995, https://gaussian.com/g03citation/

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