Chapter 2

Conformational and structural stability of ethanethiol

2.1 Introduction

Ethanethiol is analogous to ethanol where the sulfur atom in ethanethiol replaces the oxygen atom in ethanol. Ethanethiol is one of the thiols that are found in the interstellar medium and hence understanding its property in totality is of utmost importance. Even though it shares structural aspects with ethanol, due to the presence of sulfur atom, it significantly differs in various physical properties [81]. Ethanethiol undergoes rotational isomerism due to rotation along the C-S bond resulting in gauche and anti-conformations with C_1 and C_s symmetries respectively. With the rotation of the certain bonds, a huge number of the conformers result and quantum mechanical methods help in conformational analysis as seen by various reports [82-86]. It has been found that ethanethiol exists in anti and gauche conformer in liquid and gaseous state at room temperature in the ratio of 1:3 [82]. Szydlowski et al. have shown through deuterium isotope labelling that the gauche conformer is more stable than the anti-conformer. In the solid crystalline phase too it is the gauche conformer that gets predominated over the anti-conformer whereas the anti-conformer dominates the gauche in the solid amorphous state as investigated by Don Smith et al. with the help of low temperature infrared spectroscopy [83].

Conformational study of ethanethiol was done by vacuum ultraviolet mass-analysed threshold ionization (VUV-MATI) spectroscopy which confirmed the existence of two conformers of this molecule [87]. Non-resonant two-photon pulsed-field ionization-photoelectron spectroscopy [88] and vacuum ultraviolet laser pulsed field ionization-photoelectron studies [89] showed that the gauche form of ethanethiol is stable in its ionized form as well. Works on molecules similar to ethanethiol like ethanol [90], ethane [91], and dimethyl sulfide [92] predict the anti-form to be more stable due to hyper-conjugation and

steric hindrance. Puzzarini et al. employed computational tools for analysis of spectroscopic parameters (mainly rotational and torsional parameters) and also illustrate isotopic effect on spectroscopic parameters of ethanethiol and dimethyl sulphide (DMS). According to Puzzarini et al., the calculated energy of gauche conformer (162.2 cm^{-1}) farther from the experimental results and PES diagram of ethanethiol (correspond to SH group rotation) reports 176.2 cm^{-1}. Herein the authors calculated two energy values for gauche conformer whose difference is 14 cm^{-1} and both were calculated at the CCSD(T)/aug-cc-pVTZ level of theory which is ambiguous as explicit clarity on the stable conformer is lacking [93,94]. Computational studies of ethanethiol conformers have also shown that the gauche conformer is lower in energy than the anti by 0.48 kcal/mol [89] and 0.46 kcal/mol which is farther from the experimentally determined value [95–97]. DFT calculations using B3LYP functional with different basis sets predicted the energy difference to be about 0.5 to 0.72 kcal/mol. Another study done by Allinger et al. carried out molecular mechanics calculations on ethanethiol and reported the gauche conformer to be the most stable one [98].

Literature reveals initial contradictions in identifying the most stable conformer although once it was shown by experiment that the gauche conformer is most stable, subsequent research works followed suit. Even though there are reports based on quantum chemical calculations which have been used to support the experimental findings, to the best of our knowledge there exists no report hitherto where the rotational barrier for ethanethiol is computed and which matches well with experimental results. Smith et al. proposed a two cosine term potential for the thiol rotation barrier, nevertheless, a precise computation of the

barrier value has not been reported yet. Even though there are reports on the experimentally measured geometrical parameters of ethanethiol there exists no computational reports to support them accurately. Besides, with the advancement in the computational tools like the availability of larger basis sets, it is pertinent to see how these improved basis sets contribute to the accuracy in the predictions.

In this work we revisited the conformational studies of ethanethiol molecule and rationalise the stability of one of the conformers compared with the other. We report the values for the rotational barriers in ethanethiol which is hitherto not reported in the literature using computational methods. We evaluated the performance of larger basis sets and higher levels of theory (CCSD(T)/CBS limit) in predicting the stabilization energies of the two conformers of ethanethiol. Through NBO calculations we highlight the reasons for gauche being the most stable conformer. Our FMO, Mullikan charges and conformer's population corroborates well with other predictions.

2.2 Computational methods

Gaussian 16 was used to perform all calculations [68]. All conformers of ethanethiol were optimized at CCSD level of theory using both cc-pVDZ and cc-pVTZ basis sets. Single point energy was calculated at HF, MP2, MP3, MP4, CCSD, and CCSD(T) with basis set cc-pVNZ, N=D, T, Q, 5. For extrapolation of the correlation energy, the Helganker et al. method [67] was adopted and prediction at cc-pVNZ (where N= Q, 5) was chosen to fit the energies.

The rotational barriers for the both conformers were calculated by taking difference of the stabilization energies of both the conformers at CCSD/cc-pVTZ level of theory. The

potential energy scans were done at the CCSD/cc-pVDZ level of theory with a step size of 5° (containing 73 points) corresponding to the C-C and C-S bonds, separately. A 2-dimensional potential energy surface was generated for the molecule by simultaneously varying the dihedral angles HCCS and CCSH which correspond to the simultaneous rotation of C-C bond and C-S bond rotation with a step size of 30º at CCSD/cc-pVDZ level of theory (containing 144 points). Mulliken charge analysis, FMO analysis, and NBO calculations were also done at the CCSD/cc-pVTZ level of theory for explaining orbital interaction in between the conformers. Normal modes of vibrations were computed for the gauche and anti-conformer of the ethanethiol at CCSD/cc-pVTZ level of theory.

2.3 Results and discussion

The optimized geometries of ethanethiol conformers are shown in Fig. 2.1 (a) and (b) and their corresponding geometrical parameters are given in Table 2.1 and 2.2.

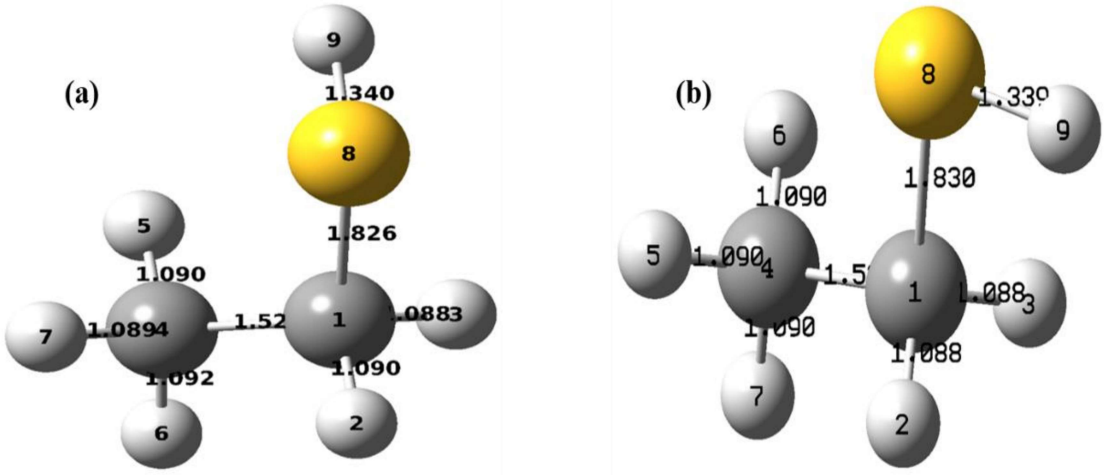

Figure 2.1 Optimized geometries (at CCSD/cc-pVTZ level of theory) of (a) anti, (b) gauche conformers of ethanethiol (Atoms are numbered for describing their properties elsewhere in the text).

Literature show contradictory information about the most stable conformer of the ethanethiol. Smith et al. reported the anti to be the most stable conformer with low temperature infrared spectroscopy whereas Allinger et al. reported the contrary, identifying the gauche to be the most stable conformer by using molecular mechanics method [83,98]. The latest study on ethanethiol by Sunyoung et al. reports the ionization potential determined with vacuum ultraviolet mass-analyzed threshold ionization (MATI) spectroscopy and confirmed that gauche conformer was the most stable one [89]. In the same work, the researchers performed quantum chemical computation at B3LYP/6-311++G(2dp, 2pd) level of theory and demonstrated a close agreement between their experimentally measured energy of this molecule and computational prediction of its gauche conformer. Although, it is to be noted that this paper does not carry any report about the geometrical parameters that were experimentally reported earlier by Hayashi et al in the 70's in two different reports for the two conformers separately [96,97]. Taking cue from this we computed the geometrical parameters at different levels of theory with different basis sets as reported in Table 2.1.

Table 2.1 Geometrical parameters of gauche and anti- conformer at different levels of theory with different basis sets [Bond distances (R) in Å, Bond angle (A) in degree and Dihedral angle (D) in degree]

	Geom. Parameter *	B3LYP/6-311++G(2dp, 2pd)		B3LYP/cc-pVTZ		CCSD/cc-pVTZ		Experimental [95,96]	
		Gauche	Anti	Gauche	Anti	Gauche	Anti	Gauche	Anti
R1	R(1,2)	1.09	1.09	1.10	1.10	1.09	1.09	1.09	1.09
R2	R(1,3)	1.09	1.09	1.10	1.10	1.09	1.09	1.09	1.09
R3	R(1,4)	1.52	1.52	1.53	1.53	1.52	1.52	1.53	1.53
R4	R(1,8)	1.84	1.84	1.84	1.84	1.83	1.83	1.81	1.82

R5	R(4,5)	1.09	1.09	1.11	1.10	1.09	1.09	1.09	1.09
R6	R(4,6)	1.09	1.09	1.11	1.10	1.09	1.09	1.09	1.09
R7	R(4,7)	1.09	1.09	1.10	1.10	1.09	1.09	1.09	1.09
R8	R(8,9)	1.34	1.34	1.35	1.35	1.34	1.34	1.34	1.32
A1	A(2,1,3)	107.1°	108.6°	107.1°	108.4°	107.3°	108.7°	106.6°	108.9°
A2	A(2,1,4)	110.9°	110.7°	110.7°	110.4°	110.8°	110.6°	110.7°	110.2°
A3	A(2,1,8)	103.8°	108.7°	104.5°	109.3°	104.4°	109.1°	104.9°	109.4°
A4	A(3,1,4)	111.4°	110.7°	111.9°	110.4°	111.3°	110.6°	111.3°	-
A5	A(3,1,8)	108.7°	108.7°	109.2°	109.3°	109.0°	109.1°	109.3°	109.4°
A6	A(4,1,8)	114.5°	109.4°	113.8°	109.2°	113.6°	108.8°	111.9°	111.9°
A7	A(1,4,5)	111.2°	111.3°	110.9°	110.9°	110.8°	110.9°	110.6°	110.6°
A8	A(1,4,6)	110.3°	111.3°	110.8°	110.9°	110.8°	110.9°	110.5°	-
A9	A(1,4,7)	111.1°	110.1°	110.4°	110.2°	110.5°	110.3°	106.9	109.7°
A10	A(5,4,6)	107.8°	108.1°	108.0°	108.2°	108.0°	108.2°	-	108.1°
A12	A(6,4,7)	108.4°	108.0°	108.7°	108.3°	108.6°	108.2°	109.0°	108.6°
A13	A(1,8,9)	97.1°	97.3°	96.0°	96.5°	96.5°	97.1°	96.0°	96.2°
D12	D(4,1,8,9)	-62.9°	-180.0°	-63.1°	-180.0°	-61.8°	-180.0°	61.8°	180.0°
*Note: Numbers in parenthesis corresponds to atoms in Fig. 2.1									

As it is apparent, the level of theory adopted in the work of Sunyoung et al i.e., DFT/6-311++G(2dp, 2pd), does not have good agreement with the experimentally measured geometrical parameters [87, 96-97]. Interestingly, the predictions at B3LYP/cc-pVDZ,

B3LYP/cc-pVTZ and CCSD/cc-pVDZ too does not match significantly with the experimental results (Refer Table 2.2).

Table 2.2 Geometrical parameters of gauche and anti-conformer at different levels of theory with different basis sets [Bond distances (R) in Å]

	Geom. Parameters**	**CCSD/cc-pVDZ**		**B3LYP/cc-pVDZ**		**Gauche**	**Anti**
		Gauche	Anti	Gauche	Anti	(Exp.)	(Exp.)
R1	R(1,2)	1.09	1.09	1.10	1.10	1.09	1.09
R2	R(1,3)	1.09	1.09	1.10	1.10	1.09	1.09
R3	R(1,4)	1.52	1.52	1.53	1.53	1.53	1.53
R4	R(1,8)	1.84	1.84	1.84	1.84	1.81	1.82
R5	R(4,5)	1.09	1.09	1.11	1.10	1.09	1.09
R6	R(4,6)	1.09	1.09	1.11	1.10	1.09	1.09
R7	R(4,7)	1.09	1.09	1.10	1.10	1.09	1.09
R8	R(8,9)	1.35	1.35	1.35	1.35	1.34	1.32
A1	A(2,1,3)	107.2°	108.7°	107.1°	108.4°	106.6°	108.9°
A2	A(2,1,4)	110.9°	110.7°	110.7°	110.4°	110.7°	110.2°
A3	A(2,1,8)	103.8°	108.7°	104.5°	109.3°	104.9°	109.4°
A4	A(3,1,4)	111.5°	110.7°	111.9°	110.4°	111.3°	-
A5	A(3,1,8)	108.6°	108.7°	109.2°	109.3°	109.3°	109.4°
A6	A(4,1,8)	114.4°	109.3°	113.8°	109.2°	111.9°	111.9°
A7	A(1,4,5)	111.2°	111.2°	110.9°	110.9°	110.6°	110.6°
A8	A(1,4,6)	110.3°	111.2°	110.8°	110.9°	110.5°	-
A9	A(1,4,7)	111.1°	110.1°	110.4°	110.2°	106.9°	109.7°
A10	A(5,4,6)	107.8°	108.1°	108.0°	108.2°	-	108.1°
A12	A(6,4,7)	108.4°	108.0°	108.7°	108.3°	109.0°	108.6°
A13	A(1,8,9)	97.0°	97.2°	96.0°	96.5°	96.0°	96.2°
D12	D(4,1,8,9)	-63.5°	-180.0°	-63.1°	-180.0°	61.8°	180.0°
**Note: Numbers in parenthesis corresponds to atoms in Fig. 2.1							

Our calculations at the CCSD/cc-pVTZ level of theory are in good agreement with the experimentally obtained geometrical parameters [96,97]. As far as the energy of ethanethiol is concerned, the earlier reported methods give a range from 0.50 to 0.70 kcal/mol [89]. Our

calculations, using incremental basis sets are well in agreement with the values reported previously in literature on computational results. One of the major disadvantages of these larger basis sets is that they overestimate the energy. This is mitigated by resorting to complete basis set limit. The energy computed at CCSD(T)/CBS limit and CCSD(T)/cc-pVDZ unambiguously predict 0.50 kcal/mol and 0.70 kcal/mol as the difference in energy between the two conformers of ethanethiol and the intermediate basis sets predict the values in between these two values, which is shown in Fig. 2.2.

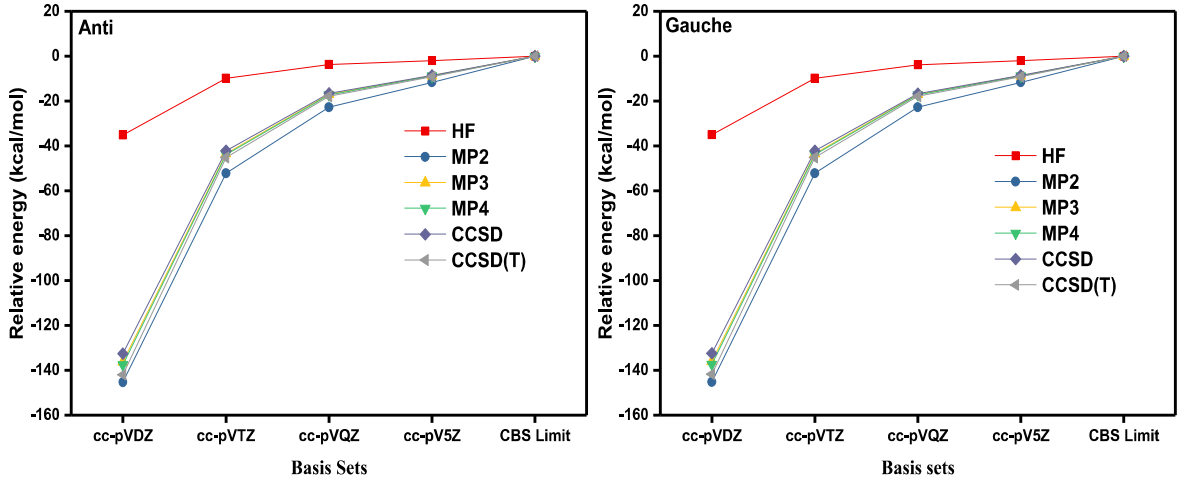

Figure 2.2 Relative energy with respect to CBS limit at various level of theories corresponding to the gauche and anti-conformer of the ethanethiol.

Fig. 2.2 depicts how the energy values monotonously converge at the CBS limit. Smith et al. have used calorimetric methods and determined two rotational barriers corresponding to the C-S and C-C bonds of ethanethiol as 1.42 and 3.75 kcal/mol [83]. We computed the two rotational barriers by step scan as discussed in the methods section. Fig. 2.3 shows the potential energy curves generated by rotating C-C bond of ethanethiol in steps of 5° in the HCCS

dihedral angle with the optimized geometry of the gauche conformer as the starting point. In Fig. 2.3 we obtain two degenerate global minima (gauche-conformers) and one local minimum (anti-conformer). For better accuracy in calculating the rotational barrier, the calculations were repeated for the structures at all the points of extrema at the CCSD/cc-pVTZ level of theory. The energy for converting the gauche to anti is 3.62 kcal/mol (3.71 kcal/mol at the CCSD/cc-pVDZ level of theory). This value is in very close agreement with 3.75 kcal/mol, the experimental value referred above.

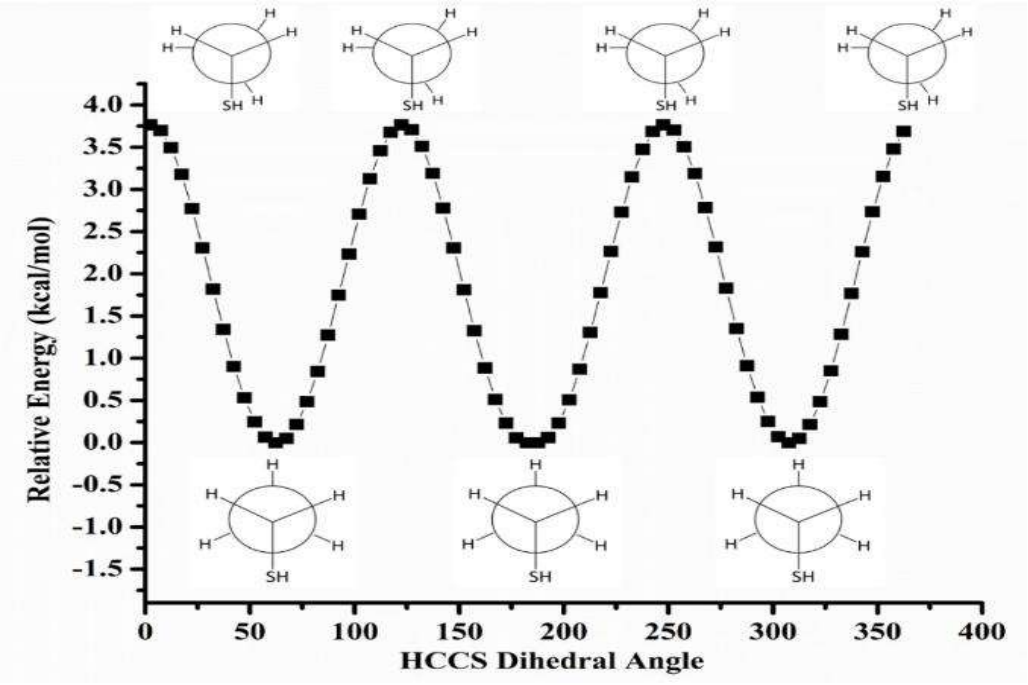

Figure 2.3 Potential energy curve generated at the CCSD/cc-pVDZ level of theory, by step-wise rotation of the C-C bond (anti clockwise).

Fig. 2.4 corresponds to another potential energy curve generated at the CCSD/cc-pVDZ level of theory by rotating the C-S bond of ethanethiol in steps of 5° in the CCSH dihedral angle once again starting with the optimized geometry of the gauche conformer. The threefold

symmetry of the methyl group is reflected in the potential energy curve. In this case we cannot use the labels gauche/anti to label the extrema in the curve. Nevertheless, the barrier to overcome while transforming one minimum to the other minimum is 1.47 kcal/mol at CCSD/cc-pVTZ level of theory (1.65 kcal/mol at CCSD/cc-pVDZ level of theory) and this value is also in very good agreement with the experimentally determined value by Smith et al.[83]. The close proximity of the computed values with the experimentally determined values may be looked upon as empirical or accidental because in the computational approach it is only a single parameter that is varied vis-a-vis in experiment where all variables get varied simultaneously.

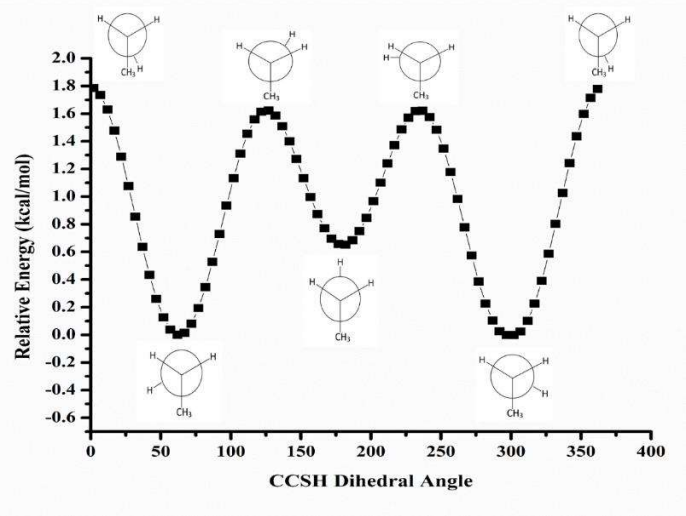

Figure 2.4 Potential energy curve generated at the CCSD/cc-pVDZ level of theory, by step-wise rotation of the C-S bond (anti-clockwise).

In order to be closer to the experimental condition we generated the potential energy surface by simultaneously varying both the C-S and the C-C bonds in ethanethiol and the same is shown in Fig. 2.5. Rotational barriers calculated from this surface are 1.44 and 3.61 kcal/mol

which are indeed very close to the values computed from the curves in Fig. 2.3 and 2.4 and also to the experimentally measured values. Hence we have conclusively demonstrated that the predictions at CCSD/cc-pVT(or D)Z level of theory about the rotational barriers of ethanethiol supports the experimentally determined values satisfactorily.

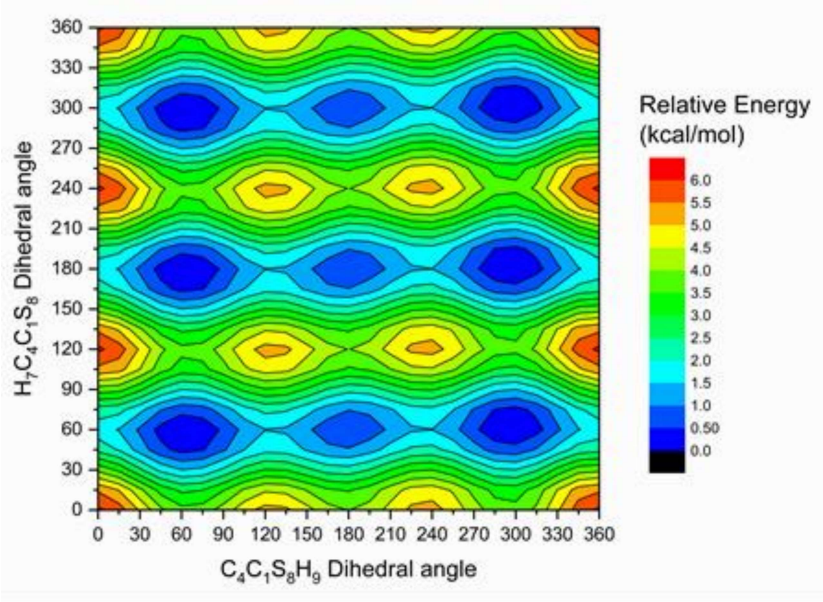

Figure 2.5 Potential energy surface generated at the CCSD/cc-pVDZ level of theory, by simultaneous rotation of the C-C and C-S bonds. [Atom numbers here used as Fig. 2.1]

Due to rotation, the ethanethiol molecular structure gets distorted and attains some unfavorable geometries which results in significant change of a few geometrical parameters (Refer Table 2.3). The C-S bond rotation apparently causes more distortion in geometric parameters compared to the C-C bond rotation. During the C-S rotation the sulfur atom comes in close proximity to the CH_3 moiety and owing to the size of the sulfur atom, this proximity results in an increased electronic distortion occur. We see that the lone pair electrons of the sulfur atom interact with the anti-bonding molecular orbital of the C-C bond which results in

a decrease in the bond order that manifests as bond elongation of C-C bond. No such interaction and subsequent bond elongation is observed with the rotation of C-S bond.

Table 2.3 Impact on select geometrical parameters due to the rotation of C-S and C-C bonds (Bond distances in Å) at CCSD/cc-pVTZ level of theory

C-S Bond Rotation			
	C-S bond	Angle CCS	Angle CSH
Longest	1.84	113.7°	97.3
Shortest	1.83	108.8°	96.3
Diff	0.0108	4.91°	0.94
% Diff.	0.59	4.52	0.98
C-C Bond Rotation			
	C-C bond	Angle CCS	Angle CSH
Longest	1.54	115.0°	97.0
Shortest	1.52139	113.6°	96.1
Diff	0.02	1.32°	0.96
% Diff.	1.06	1.16	1.00

This reasoning is amply supported by the NBO calculations that is summarized in Table 2.5. NBO analysis make an understanding about the interactions of the molecule, extent of charge transfers and stability regarding to the molecular system. Generally, NBO analysis assign stability of the molecular system and strength of the interactions in terms of the second order perturbation energy (E(2)) correspond to each donor-acceptor interactions.

2.3.1 Natural bond orbital (NBO)

The NBO calculations reveal the presence of more number of interactions in the gauche conformer than the anti-conformer. Hence the presence of more interactions in the gauche conformer is responsible for it to attain extra stability. Steve et al. reported a strong correlation (correlation coefficient = 0.863) between the second order perturbation stabilization energy

(E(2)) and the C-O bond length in the ethanol molecule [99]. They reported that for every 1 kcal/mol increase in the E(2) was correlated with a milli-angstrom increase in the C-O bond length. No such positive correlation is predicted for the ethanethiol molecule by our calculations where the correlation coefficient between E(2) and the C-S bond length is -0.1976 between. Here we clearly see the vast variation in the properties of ethanol and ethanethiol molecules through NBO calculations.

Table 2.4 Relative change in energy (ΔE in kcal/mol) of the anti-conformer with respect to the gauche conformer at different levels of theory

Basis set	HF	MP2	MP3	MP4	CCSD	CCSD(T)
cc-pVDZ	0.45	0.70	0.69	0.68	0.65	0.70
cc-pVTZ	0.33	0.51	0.50	0.49	0.47	0.51
cc-pVQZ	0.32	0.49	0.48	0.47	0.45	0.49
cc-pV5Z	0.32	0.50	0.49	0.48	0.46	0.50
CBS limit	0.33	0.50	0.50	0.49	0.46	0.50
Note: $\Delta E = E_{\text{local minimum}} - E_{\text{global minimum}}$						

Owing to the incompleteness of finite basis sets we carried out Helgaker's two-point complete basis set (CBS) limit extrapolation (at CCSD/cc-pVNZ where N = D, T, Q, 5 level of theory) for both gauche and anti-conformers [67]. Calculations at CBS limits are reported to be more accurate in capturing the electronic interactions. The difference of energy between the two conformers as measured experimentally by previous researchers is 0.49 kcal/mol whereas the previous computational studies have reported this difference to be from 0.5 to 0.7 kcal/mol. Our calculations at the CBS limits also predict the difference in the energy of the two conformers to be 0.7 kcal/mol which is indeed an overestimate when compared to the experimental value whereas the predictions at CCSD(T) level are promising.

Table 2.5 Natural orbital interaction (second order perturbation) energies (E(2) (kcal/mol)) for conformers (at CCSD/cc-pVTZ level of theory)

Orbital Interactions	Gauche	Anti
$\sigma_{C-H} \rightarrow \sigma^*_{C-H}$	3.57	3.53
$\sigma_{C-H} \rightarrow \sigma^*_{S-H}$	2.09	-
$\sigma_{C-C} \rightarrow \sigma^*_{S-H}$	-	0.90
$\sigma_{C-S} \rightarrow \sigma^*_{C-H}$	2.87	3.28
$\sigma_{C-S} \rightarrow \sigma^*_{S-H}$	0.88	0.79
$\sigma_{C-H} \rightarrow \sigma^*_{C-S}$	6.13	5.38
$\sigma_{S-H} \rightarrow \sigma^*_{C-C}$	-	2.88
$\sigma_{S-H} \rightarrow \sigma^*_{C-H}$	2.44	-
$\sigma_{S-H} \rightarrow \sigma^*_{C-S}$	1.68	1.48
$LP_S \rightarrow \sigma^*_{C-H}$	5.43	5.74
$LP_S \rightarrow \sigma^*_{C-C}$	5.48	-

Table 2.4 depicts the effect of various levels of theory as well basis sets has on the calculation of the energies of the two conformers of ethanethiol. At all level, the gauche conformer turns out to be of lower energy, hence stable. Therefore, in Table 2.4, only the difference is reported. The basis set cc-pVDZ consistently predicts the highest values at all levels of theory and higher basis sets reduce this value by approximately 30% across all levels of theory. The basis set cc-pVQZ consistently predicts the lowest values at all levels of theory. The ratio between the values predicted with the cc-pVDZ basis set and the values at the CBS limit remains nearly the same in all levels of theory.

2.3.2 Mullikan charge analysis

Mullikan charge (MC) are a good indicator in conformational studies because it is inter dependent on vibrations of the molecules. It affects the dipole moment, electronic structure,

polarizability and extent of hydrogen bonding etc. of a molecule [78,100]. We computed MC for the anti and gauche conformers of ethanethiol molecule at the CCSD/cc-pVTZ level of theory. Negative MC on sulfur atom in the gauche conformer is slightly lower than in the anti-conformer and the positive MC on H_3 and H_7 are larger in the anti-conformer (Refer Table 2.6). This indicates delocalization of charges into anti bonding molecular orbital of the C-H bond in the gauche conformer. These results clearly indicate the stability of the gauche conformer is because of the intra molecular hydrogen bonding which is also supported by the NBO results very well.

Table 2.6 Mullikan charge (MC) for anti and gauche conformer of the ethanethiol at CCSD/cc-pVTZ level of theory (All MC charges in a.u.)

Atoms[&]	Anti	Gauche
C_1	-0.200	-0.209
H_2	0.128	0.127
H_3	0.128	0.134
C_4	-0.349	-0.332
H_5	0.123	0.111
H_6	0.123	0.118
H_7	0.121	0.125
S_8	-0.168	-0.164
H_9	0.093	0.090
& Note: Atom labels used as per the Fig 1.		

2.3.3 Population analysis

The abundance/population analysis of the ethanethiol conformers was computed using the well-known Boltzmann distribution equation [101]. PES was generated corresponding to

dihedral angles HCCS and CCSH at CCSD/cc-pVTZ level of theory. With the generated potential energy surface the relative abundances of ethanethiol conformers i.e. gauche and anti was computed. It was found that relative abundance is 49.82% and 0.1% for gauche and anti-conformers respectively, corresponding to the scan in the dihedral angle HCCS. However, when the dihedral angle CCSH was scanned, the abundance values were 64.07% and 14.94 % for the gauche and anti-conformers, respectively (Refer Table 2.7).

Table 2.7 Conformational analysis of ethanethiol at CCSD/cc-pVTZ

HCCS			CCSH		
Dihedral angle	ΔE(kcal/mol)	N_f (%)	Dihedral angle	ΔE(kcal/mol)	N_f (%)
2.36°	3.76	0.06	1.92	1.79	1.95
62.36°	0	**49.82**	61.92	0	**64.07**
122.36°	3.76	0.06	121.92	1.62	**2.59**
187.36°	0	**49.82**	181.92	0.65	14.94
247.36°	3.70	0.06	241.92	1.62	**2.60**
307.36°	0	**49.82**	301.92	0	**64.07**
362.36°	3.70	0.13	361.92	1.78	3.30

Note: Population of different conformers was calculated using the Boltzmann distribution equation, $N = \frac{e^{-\Delta E/RT}}{\sum_n e^{-\Delta E_n/RT}}$; where ΔE represents the difference in energy of conformer with respect to the global minima conformer and summation applied over all n possible conformers, $R = 1.987 \times 10^{-3}$ kcal/K *mol and $T = 298$ K).

Furthermore, we performed frontier molecular orbital (i.e. highest occupied molecular orbital (HOMO) & lowest unoccupied molecular orbital (LUMO)) analysis to corroborate the stability of the conformer and look into their kinetic stability [78,100].

2.3.4 Frontier molecular orbital (FMO)

Frontier molecular orbital (FMO) play a vital role into description of the chemical behavior of the molecules. So for the description of the chemical properties like reactivity and kinetics highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are two dominating molecular orbitals that are referred as FMO [102–105]. These orbitals are also vitally necessary for describing phenomena such as charge transfer, photo excitation, and molecular electronics etc. According to Janak and Perdew et al. [106,107], FMO indexing HOMO eigen value (E_{HOMO}) as ionization potential (IP) and LUMO eigen value (E_{LUMO}) as electron affinity (EA) helps to calculate reactivity indices i.e. hardness (η), chemical potential (μ), electronegativity (χ), and electronegative index (ω) [108–110].

According to Manolopoulos et al. [111], higher the HOMO–LUMO (H-L) gap higher will be the kinetic stability. Thus, the energy required for the addition of electrons into a high-lying LUMO or for releasing electrons from a low-lying HOMO and for the formation of an activated complex is not possible with lower energy gap. In reference [110,112–115] the authors calculated IP and EA for organic molecules and through which they predicted chemical stability, kinetic stability and its electronic properties.

From Table 2.8 and Fig. 2.6, the calculated HOMO and LUMO for conformers of ethanethiol shows H-L gap (E_g) to be 138.1 kcal/mol for gauche and 135.4 kcal/mol for anti-

conformer which indicates that the gauche conformer is kinetically more stable. The higher hardness (η) value (-106 kcal/mol) for the gauche conformer shows its low polarizability, once again indicating that it is more stable with respect to the anti-conformer. The electronegativity (χ) and electrophilicity index (ω) values too are consistent with other indications that the gauche conformer has more stability.

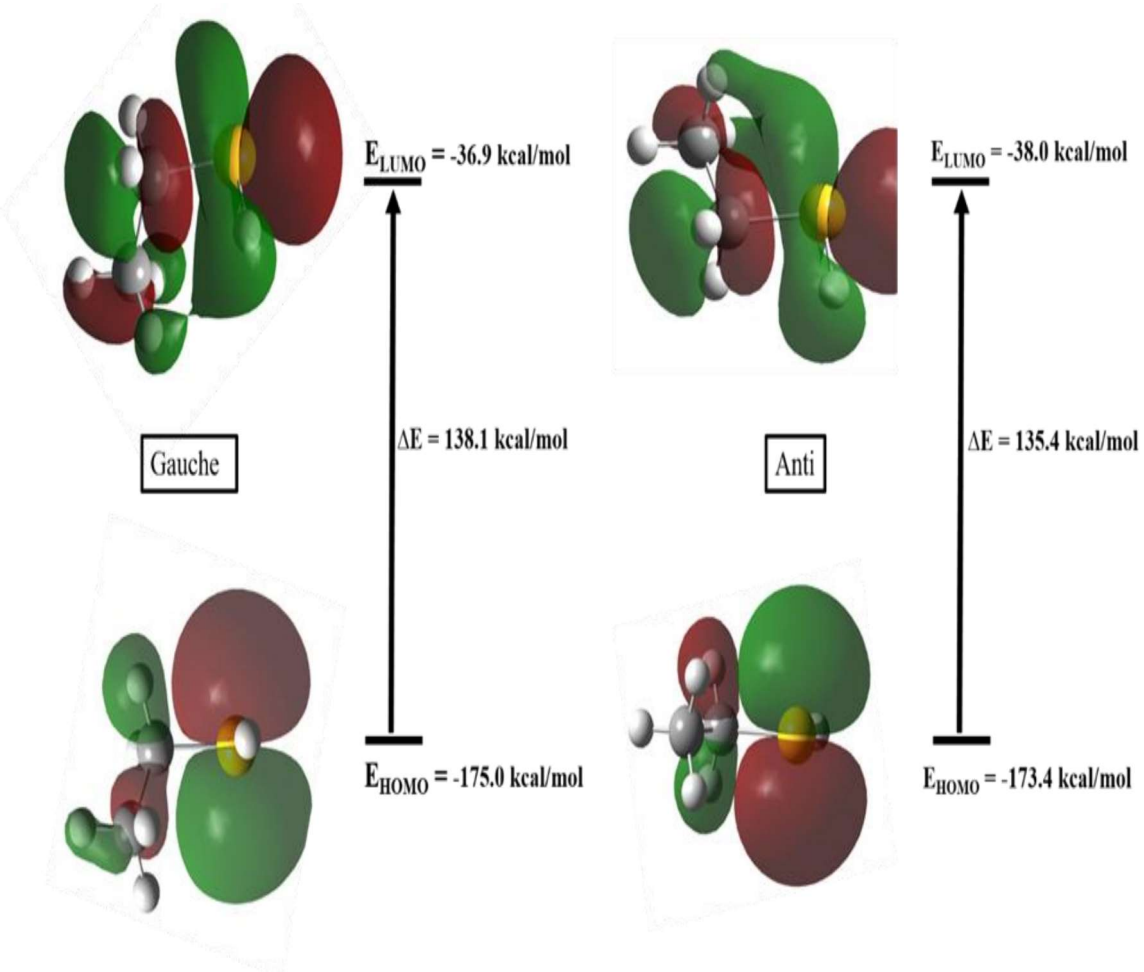

Figure 2.6 HOMO-LUMO gap for gauche and anti-conformers of ethanethiol at CCSD/cc-pVTZ level of theory.

Table 2.8 Calculated energy parameter for ethanethiol conformers at CCSD/cc-pVTZ level of theory

Energy Parameters	Gauche	Anti
E_{HOMO} (IP) (kcal/mol)	-175.0	-173.4
E_{LUMO} (EA) (kcal/mol)	-36.9	-38.0
H-L gap (E_g)	138.1	135.4
Dipole moment (D)	1.60	1.61
Hardness (η)	-106.0	-105.7
Chemical Potential (μ)	106.0	105.7
Electronegativity (χ)	-106.0	-105.7
Elecrophilicity Index (ω)	-53	-52.9

The decrease in the H-L gaps of gauche and anti-conformer of ethanethiol molecule happens because of the intra molecular charge transfer. All this calculation was done at CCSD/cc-pVTZ level of theory and they support the NBO and Mullikan charge analysis significantly.

2.3.5 Normal mode analysis

Vibrational analysis for these conformers were also done with CCSD/cc-pVTZ level of theory that have good experimental validation with an appropriate scaling factor (Refer Table 2.9). Computed normal modes of vibration (with a scaling factor of 0.959) [117] are tabulated above and they appear to be in reasonably good agreement with the experimental values. In this calculation, no any imaginary frequency was found which confirms the optimized geometry is in the minimum.

Table 2.9 Normal modes of vibrations of gauche and anti-conformers at CCSD/cc-pVTZ level of theory scaled by a factor of 0.959. (All frequencies in cm^{-1})

Predicted IR Frequency		Exp. IR Frequency [82]	Tentative Assignment [116]
Gauche	Anti		
198	171	-	-
250	244	-	--
318	293	*317*	*δ(C-C-S)*
654	667	*663*	*υ(C-S)*
715	765	*735*	*ρ(CH_2)*
849	839	*879*	*δ(S-H)*
965	972	*969*	*υ(C-C)*
1041	1017	-	-
1091	1083	*1101*	*ρ(CH_3)*
1246	1234	*1255*	*τ(CH_2)*
1275	1268	*1277*	*ω(CH_2)*
1372	1373	*1382*	*δ(CH_3), δ(CH_2)*
1437	1451	-	*δ(CH_3), δ(CH_2)*
1450	1452	*1457*	*δ(CH_3), δ(CH_2)*
1456	1461	-	*δ(CH_3), δ(CH_2)*
2609	2616	*2600*	*υ(S-H)*
2929	2936	*2887*	*υ(CH_3), υ(CH_2)*
2962	2965	*2942*	*υ(CH_3), υ(CH_2)*
2993	3000	*2972*	*υ(CH_3), υ(CH_2)*
3002	3008	*2989*	*υ(CH_3), υ(CH_2)*
3021	3022	-	-

2.4 Conclusion

Rotational barriers of ethanethiol molecule calculated at the CCSD/cc-pVTZ are in good agreement with the experimentally reported values. Rotation barriers for the C-S and C-C bond rotation are 1.42 kcal/mol and 3.75 kcal/mol respectively as obtained from the one dimensional potential energy curve and 1.44 kcal/mol & 3.61 kcal/mol obtained from the two dimensional potential energy surface. Gauche conformer was found to be more stable compared to the anti-conformer by 0.5 kcal/mol and 0.70 kcal/mol at the CCSD(T)/CBS limit and CCSD(T)/cc-pVDZ level of theory, respectively. NBO results provided a clear evidence for the stability of the gauche conformer in comparison of anti-conformer by highlighting the presence of strong charge transfers in the gauche conformer and the absence of the same in the anti-conformer. These predictions are very well validated with Mullikan charge analysis and frontier molecular analysis.