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Enolization of Cyclopropanone and Cyclopropanethione: A Theoretical Study

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Enolization of Cyclopropanone and Cyclopropanethione: A Theoretical Study[#]

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Abstract

Motivation. Cyclopropanones and cyclopropanethiones are highly reactive organic systems containing a number of labile sites on a small carbon skeleton. These are small unsaturated cyclic molecules with scarcely available experimental data making theoretical studies more relevant.

Method. The enolization reactions of cyclopropanone and its sulphur analog have been investigated by *ab initio* and DFT methods. Geometry optimizations for the structures were performed by means of analytical gradients using the standard 6–31G(d), 6–31+G(d), 6–31G(d,p), 6–31++G(d) and 6–31++G(d,p) basis sets with HF, MP2 and DFT with B3LYP hybrid functional SCF methods. The analysis of electron density distributions was carried out at MP2 and B3LYP levels using the AIM facility in the Gaussian 03W software package.

Results. Both the reactions are predicted to be endothermic. Inclusion of electron correlation through B3LYP hybrid functional in DFT and MP2 energy correction leads to significant decrease in activation enthalpies as compared to RHF results. Bader's topological analysis predicts all the bonds to be covalent except C=X (X = O, S). Our calculations also predict the syn-conformer of the enol/enethiol to be more stable than its anti form. The rotational barrier for the conversion of syn- to anti-conformer along the C–X bond lies in the range 3.3 to 5.0 kcal mol⁻¹.

Conclusions. The lower enolization and activation enthalpies for the thiocarbonyl compounds are attributed to the thiocarbonyl bond being weaker than the carbonyl bond. It has also been shown that the diffusibility and polarizability of sulphur play an important role in the determination of electronic distribution in small strained rings. NPA clearly predicts that enolization proceeds through H^{δ+} (proton) transfer for cyclopropanone, while H^{δ-} (hydride) like transfer is indicated for cyclopropanethione.

Keywords. Cyclopropanone; cyclopropanethione; enolization; DFT; MP2.

Abbreviations and notations

AIM, Atoms in Molecule	IRC, intrinsic reaction coordinates
B3LYP, Becke's three parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional	MP2, second order Møller–Plesset perturbation theory
BCP, bond critical point	NBO, natural bond orbital
CASSCF, complete active space self-consistent field method	NPA, natural population analysis
DFT, density functional theory	RCP, ring critical point
	RHF, restricted Hartree Fock

1 INTRODUCTION

Cyclopropanones and cyclopropanethiones are highly reactive organic systems containing a number of labile sites on a small carbon skeleton. Chemistry of the former with an unusual structure

[#] Dedicated to Professor Lemont B. Kier on the occasion of the 75th birthday.

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is of considerable interest because of the theoretical predictions about the properties of these compounds and their great potential as intermediates [1] in organic syntheses. Enols have been suggested as reactive intermediates in a wide variety of organic and biological reactions [2–4]. Most cyclopropanones are too unstable to permit isolation and purification. This is due to their unusual tendency towards adduct formation leading to polymerization, which releases some of the strain energy by $sp^2 \rightarrow sp^3$ rehybridization of a carbon atom constrained by a three-member ring [5]. While X-ray diffraction and routine elemental analysis cannot generally be employed for their structural elucidation [6], spectroscopic [7–12] and theoretical [13–31] studies have proved to be quite useful. The microwave studies [7] have shown C–C single bond facing the carbonyl carbon in cyclopropanone as one of the longest ever measured spectroscopically. The UV Photoelectron spectral studies [8] indicate that the nonbonding MO for cyclopropanone is highly delocalized. The C=O absorption in the vapour phase IR spectrum of cyclopropanone [11] occurs at 1906 cm^{-1} . Earlier studies assigned 1815 cm^{-1} as C=O absorption frequency of cyclopropanone [12] that was later proved to be C=O stretching frequency of cyclobutanone [11].

Numerous theoretical calculations have been made regarding structure [13–18], thermochemistry [19–24] and potential energy surfaces [25–31] of cyclopropanone and cyclopropanethione. Topological characteristics of electron density distributions for cyclopropanone in vacuo [MP2/6–31+G(d,p)] and in water [SCI-PCM/MP2/6–31+G(d,p)//HF/6–31+G(d,p)] have shown that the C=O bond is highly polar [14] as compared to oxirane, oxiranone and hydroxyoxiranone. *Ab initio* studies have predicted that thioxyallyl singlet state (A1) is 11 kcal mol^{-1} higher than the lowest singlet state (B2) and its methylene group undergoes disrotatory rotation to give cyclopropanethione [15] with no activation energy. Block *et al.* [16] predicted that it was impossible to isolate the thermodynamically unstable cyclopropanethione. Thermochemical calculations of cyclopropanone hydration energy [21] at MP2/6–311++G**//HF/6–31G*, reaction enthalpies [22] for hydride ion addition at G2(MP2), enthalpy of formation [23] at [QCISD(T)=full/6–311G(2df,p)//MP2=full/6–311G(d,p)] and enolization enthalpies of both acyclic and cyclic ketones (upto six-member ring systems) and their sulphur analogs at CBS–4 [24] levels have also been reported. Many studies on the reaction pathways involving cyclopropanone are available in the literature [25–31]. The rearrangement of allene oxide to cyclopropanone and racemization and isomerization of the substituted cyclopropanones have also been studied using DFT and CASSCF [28] methods. While HF and DFT studies predict thermal fragmentation of cyclopropanone to ethylene and CO to be a concerted single step reaction, the semi-empirical methods predict a multistep biradical reaction [29] with unrealistically low activation energy. Disrotatory ring opening of cyclopropanone to give oxyallyls has been studied by using semi-empirical [30], and *ab initio* (4/4) CASSCF and Monte Carlo [31] methods.

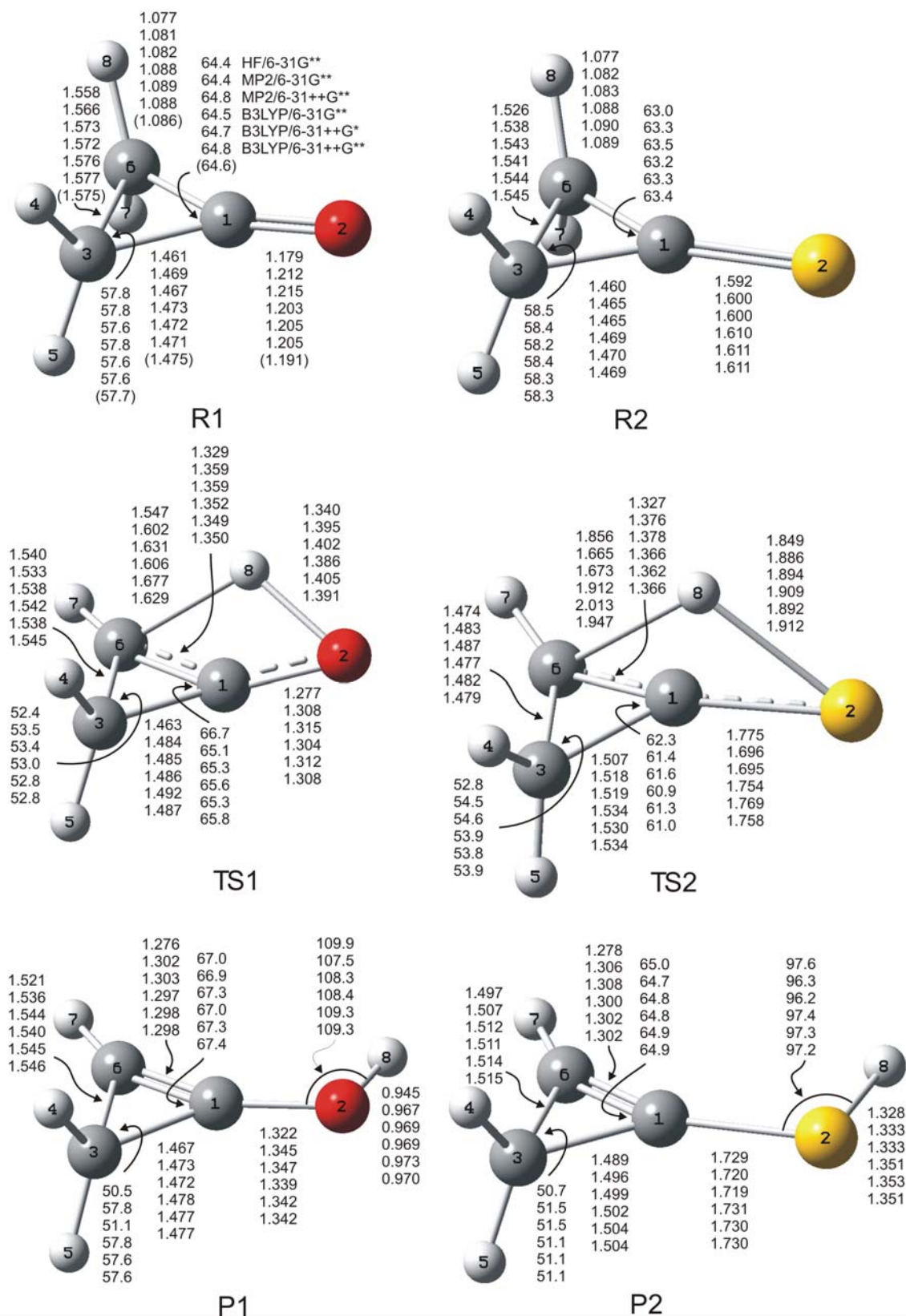


Figure 1. Optimized structures of cyclopropanone (R1), cyclopropanethione (R2), their tautomers and corresponding TS structures calculated at various levels of theory. All bond lengths and bond angles are in Å and degrees, respectively. The experimental data [7] are listed in parentheses.

The enolization of aldehydes and ketones is known to be negligible [2,3]. Notwithstanding many similarities between the properties of carbonyls and their sulphur analogs, thiocarbonyl derivatives having α -hydrogen have a greater tendency to tautomerize [32]. The enolization of cyclopropanone and its sulphur analog (Figure 1) is of considerable interest as enolisation enthalpy of the former is greater than that of the latter. Their enolization enthalpies are significantly larger than those of the corresponding higher cyclic and acyclic ketones and thiones [24]. This indicates considerable electronic redistribution in the three-member ring. In the present paper, we have studied the reaction pathways for the keto-enol tautomerization of cyclopropanone and cyclopropanethione using both *ab initio* (HF and MP2) and density functional theory (DFT) [33–38] based methods. To evaluate the effect of electron correlation on the equilibrium geometries and thermochemistry, a hybrid exchange-correlation functional, B3LYP [38,39], has been used with basis sets like 6-31G(d,p), 6-31++G(d), 6-31+G(d,p) and 6-31++G(d,p).

2 METHODS

Geometry optimizations for the structures in vacuo were performed by means of analytical gradients using the standard 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31++G(d) and 6-31++G(d,p) basis sets with HF, second-order Moller-Plesset (MP2) [40] and DFT [33–38] with B3LYP hybrid functional SCF methods. A B3LYP hybrid density functional is a combination of Becke's [38] three-parameter exchange and the correlation-functional of Lee, Yang and Parr [39].

Analysis of electron density distributions was carried out at MP2 and B3LYP levels using the AIM facility in the Gaussian 03W software package [41]. The line of maximal density joining two nuclei in the equilibrium geometry of a structure is a bond path; the minimum along this line is a bond critical point (BCP), a first-order saddle point in the electron density. A second-order saddle point defines a ring critical point (RCP). The values of electron density (ρ), Laplacian ($\nabla^2\rho$) and ellipticity (ε) at BCP are diagnostic of the type of bonding. The ellipticity is a measure of anisotropy of the electron density in direction perpendicular to the bond path at BCP and the Laplacian measures the local concentration ($\nabla^2\rho < 0$) or depletion ($\nabla^2\rho > 0$) of electronic charge. The bond path is often longer than the conventional straight-line drawn between the nuclei [42]. The angle between the tangents to the bond paths at a nucleus defines the bond-path angle; the difference between this and the geometrical bond angle, Δ_{ang} provides a useful indicator of ring strain.

Activation (ΔH^\ddagger) and reaction (ΔH) enthalpies for the rearrangement of cyclopropanone and its sulphur analog were calculated at 298.15K and 1.0 atm, and were corrected using zero-point vibrational energies. Calculations of intrinsic reaction coordinates (IRC) were performed to establish the connection of the transition structures and the corresponding local minima. The natural bond orbital (NBO) [43] technique was used for the natural population analysis (NPA). To examine the nature of the local charge flow ($H^{\delta+}$ or $H^{\delta-}$ transfer) within a species along the reaction path,

IRC calculations were performed to obtain the atomic charges from NPA of the B3LYP/6-31++G(d,p) structures. All the calculations were performed using the Gaussian 03W software [41] package and the stationary points were characterized by examining the number of imaginary frequencies and the eigenvalues of the Hessian matrix.

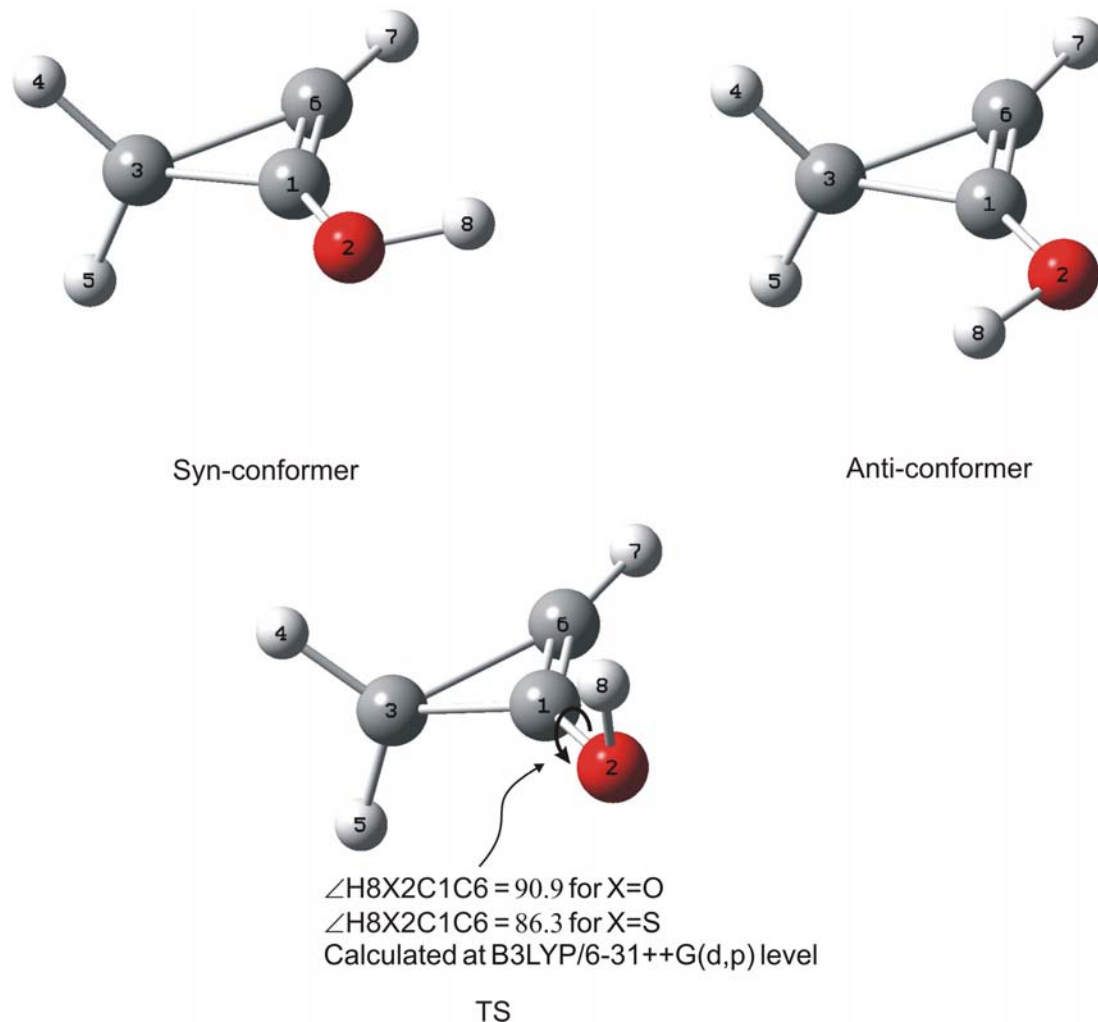


Figure 2. Schematic representation of rotational isomerization in cyclopropan-1-ol (X=O) / cyclopropan-1-thiol (X=S).

3 RESULTS AND DISCUSSION

Selected optimized geometrical parameters for cyclopropanone, cyclopropan-1-ol, transition state and their corresponding sulphur analogs at RHF, MP2 and RB3LYP levels of theory are depicted in Figure 1. Isomerization of syn- to anti-form of cyclopropan-1-ol/cyclopropan-1-thiol through rotation along C-X bond (X = O, S) is schematically represented in Figure 2. The energetics for the above reactions are presented in Tables 1 and 2. For cyclopropanone, optimized geometries at RB3LYP/6-31++G(d), RB3LYP/6-31G(d,p) and RB3LYP/6-31++G(d,p) levels are in good agreement with the results of microwave studies [7] and *ab initio* (4/4) CASSCF level calculations [31]. The *ab initio* gradient optimized geometries at SCF level [16] using double zeta

basis sets augmented with polarization functions for all valence electrons of cyclopropanethione are comparable with our results. The better agreement of RB3LYP optimized geometries with the experimental results [7] can be ascribed to inclusion of electron correlation. The C3–C6 bond is predicted to be conspicuously longer than the other two ring bonds corroborating the reactivity of substituted cyclopropanones in cycloaddition reactions along this bond. It has also been found that addition of diffuse function to hydrogen has little influence on geometrical parameters.

Table 1. Calculated total energies (E_{tot}), activation enthalpies (ΔH^\ddagger) and reaction enthalpies (ΔH) for the enolization of cyclopropanone ($X = O$) and cyclopropanethione ($X = S$)^a

Method	X = O			X = S		
	E_{tot} (R1)	E_{tot} (TS1)	E_{tot} (P1) ^b	E_{tot} (R2)	E_{tot} (TS2)	E_{tot} (P2) ^b
RHF/6–31G*	–190.655365	–190.475287	–190.613267	–513.301297	–513.174358	–513.277875
RHF/6–31G**	–190.669152	–190.495029	–190.625169	–513.314828	–513.184271	–513.287086
RHF/6–31+G*	–190.667065	–190.488484	–190.619363	–513.310262	–513.178183	–513.281270
MP2(full)/6–31G*	–191.236074	–191.090137	–191.191256	–513.837669	–513.723214	–513.807492
MP2(full)/6–31G**	–191.268026	–191.126343	–191.227150	–513.869689	–513.758853	–513.843246
MP2(full)/6–31++G**	–191.281068	–191.142922	–191.241891	–513.879384	–513.769613	–513.853620
RB3LYP/6–31G*// RHF/6–31G*	–191.812179	–191.669677	–191.767226	–514.781563	–514.675120	–514.752272
RB3LYP/6–31G**// RHF/6–31G**	–191.820860	–191.680100	–191.779977	–514.787939	–514.686485	–514.760395
RB3LYP/6–31G*	–191.816818	–191.670081	–191.771286	–514.783106	–514.680245	–514.751476
RB3LYP/6–31G**	–191.823113	–191.683328	–191.781709	–514.789380	–514.688840	–514.761479
RB3LYP/6–31+G*	–191.826782	–191.683588	–191.782454	–514.788854	–514.686694	–514.760121
RB3LYP/6–31++G*	–191.826832	–191.683726	–191.782607	–514.788907	–514.686896	–514.760240
RB3LYP/6–31++G**	–191.833067	–191.695166	–191.793099	–514.795139	–514.695341	–514.768209
RB3LYP/6–31++G**// MP2/6–31++G**	–191.832576	–191.694520	–191.792738	–514.794597	–514.692288	–514.768474
	X = O			X = S		
	Activation Enthalpy (ΔH^\ddagger) ^c	Reaction Enthalpy (ΔH^\ddagger) ^c		Activation Enthalpy (ΔH^\ddagger) ^c	Reaction Enthalpy (ΔH^\ddagger) ^c	
RHF/6–31G*	113.0	26.4		79.7	14.7	
RHF/6–31G**	109.3	27.6		81.9	17.4	
RHF/6–31+G*	112.1	29.9		82.9	18.2	
MP2(full)/6–31G*	91.6	28.1		71.8	18.9	
MP2(full)/6–31G**	88.9	25.6		69.6	16.6	
MP2(full)/6–31++G**	86.7	24.6		68.9	16.2	
RB3LYP/6–31G*// RHF/6–31G*	89.4	28.2		66.8	18.4	
RB3LYP/6–31G**// RHF/6–31G**	88.3	25.7		63.7	17.3	
RB3LYP/6–31G*	92.1	28.6		64.5	19.8	
RB3LYP/6–31G**	87.7	26.0		63.1	17.5	
RB3LYP/6–31+G*	89.9	27.8		64.1	18.0	
RB3LYP/6–31++G*	89.8	27.8		64.0	18.0	
RB3LYP/6–31++G**	86.5	25.1		62.6	16.9	
RB3LYP/6–31++G**// MP2/6–31++G**	86.6	25.0		64.2	16.4	
CBS–4 ^d	–	24.1		–	15.1	

^a See Figure 1.

^b Syn-conformer of the enol/enethiol form.

^c Total energy (E_{tot}) at 298K is in Hartree; ΔH^\ddagger and ΔH values are in kcal mol^{–1} after zero-point vibrational energy correction at 298K. 1 Hartree = 627.5095 kcal mol^{–1}.

^d Ref. [24].

Table 2. Calculated total energies (E_{tot}), activation enthalpies (ΔH^\ddagger) and reaction enthalpies (ΔH) for the rotational isomerization of cyclopropan-1-ol ($X = O$) and cyclopropan-1-thiol ($X = S$)^a

Method	X = O			X = S		
	$E_{\text{tot}}(\text{Syn})$	$E_{\text{tot}}(\text{TS})$	$E_{\text{tot}}(\text{Anti})$	$E_{\text{tot}}(\text{Syn})$	$E_{\text{tot}}(\text{TS})$	$E_{\text{tot}}(\text{Anti})$
RHF/6-31G*	-190.613268	-190.606464	-190.612767	-513.277876	-513.272604	-513.277595
RHF/6-31G**	-190.625169	-190.618560	-190.624676	-513.287086	-513.281859	-513.286807
MP2/6-31++G**	-191.241891	-191.234620	-191.241598	-513.853620	-513.847292	-513.853487
RB3LYP/6-31G*	-191.771286	-191.763286	-191.771118	-514.753552	-514.746671	-514.753282
RB3LYP/6-31+G*	-191.782454	-191.774874	-191.782397	-514.760121	-514.753170	-514.759952
RB3LYP/6-31G**	-191.781709	-191.773938	-191.781530	-514.761479	-514.754685	-514.761219
RB3LYP/6-31++G**	-191.793099	-191.785753	-191.793042	-514.768209	-514.761366	-514.768056

	X = O		X = S	
	ΔH^\ddagger ^b	ΔH ^b	ΔH^\ddagger ^b	ΔH ^b
RHF/6-31G*	4.27	0.31	3.31	0.18
RHF/6-31G**	4.15	0.31	3.28	0.18
MP2/6-31++G**	4.56	0.18	3.97	0.08
RB3LYP/6-31G*	5.02	0.11	4.32	0.17
RB3LYP/6-31+G*	4.76	0.04	4.36	0.11
RB3LYP/6-31G**	4.88	0.11	4.26	0.16
RB3LYP/6-31++G**	4.61	0.04	4.29	0.10

^a See Figure 2. ^b Total energy (E_{tot}) at 298K is in Hartree; activation enthalpy (ΔH^\ddagger) and reaction enthalpy (ΔH) values are in kcal mol⁻¹ after zero-point vibrational energy correction at 298K. 1 Hartree = 627.5095 kcal mol⁻¹.

Table 3. Calculated bond critical points (BCP)^a for cyclopropanone (R1), TS1, cyclopropan-1-ol (P1), cyclopropanethione (R2), TS2 and cyclopropan-1-thiol (P2) at B3LYP/6-31++G(d,p) and MP2/6-31++G(d,p)^b levels

Bond	BCP	X = O			X = S		
		R1	TS1	P1	R2	TS2	P2
C1-X2	ρ	0.409 (0.396)	0.339 (0.326)	0.297 (0.292)	0.232 (0.232)	0.179 (0.196)	0.205 (0.207)
	$\nabla^2\rho$	0.391 (0.342)	-0.635 (-0.518)	-0.242 (-0.218)	0.084 (0.153)	-0.278 (-0.247)	-0.420 (-0.452)
	ε	0.020 (0.048)	0.053 (0.041)	0.022 (0.006)	0.055 (0.018)	0.072 (0.114)	0.191 (0.228)
C1-C3	ρ	0.264 (0.265)	0.249 (0.249)	0.251 (0.252)	0.261 (0.261)	0.227 (0.233)	0.234 (0.235)
	$\nabla^2\rho$	-0.572 (-0.586)	-0.452 (-0.459)	-0.450 (-0.461)	-0.536 (-0.542)	-0.309 (-0.353)	-0.331 (-0.343)
	ε	0.210 (0.224)	0.331 (0.336)	0.344 (0.340)	0.295 (0.303)	0.717 (0.618)	0.640 (0.614)
C1-C6	ρ	0.264 (0.265)	0.313 (0.301)	0.346 (0.338)	0.261 (0.261)	0.308 (0.290)	0.343 (0.335)
	$\nabla^2\rho$	-0.572 (-0.586)	-0.701 (-0.624)	-0.890 (-0.836)	-0.536 (-0.542)	-0.710 (-0.572)	-0.871 (-0.813)
	ε	0.210 (0.224)	0.185 (0.181)	0.314 (0.307)	0.295 (0.303)	0.026 (0.033)	0.228 (0.219)
C3-C6	ρ	0.209 (0.210)	0.219 (0.222)	0.218 (0.218)	0.222 (0.222)	0.250 (0.245)	0.230 (0.231)
	$\nabla^2\rho$	-0.292 (-0.295)	-0.264 (-0.281)	-0.214 (-0.217)	-0.340 (-0.341)	-0.449 (-0.419)	-0.302 (-0.308)
	ε	0.599 (0.629)	0.700 (0.660)	1.001 (1.032)	0.589 (0.622)	0.381 (0.403)	0.678 (0.688)
Line 8 ^c	ρ	0.278 (0.281)	- (0.178)	0.360 (0.358)	0.279 (0.282)	0.226 (0.214)	0.213 (0.220)
	$\nabla^2\rho$	-0.971 (-1.011)	- (-0.277)	-2.075 (-2.065)	-0.977 (-1.014)	-0.616 (-0.526)	-0.575 (-0.632)
	ε	0.029 (0.029)	- (0.868)	0.021 (0.022)	0.026 (0.028)	0.143 (0.307)	0.121 (0.148)

^a See Figures 1 and 3. ρ : electron densities in e au⁻³, $\nabla^2\rho$: laplacians in e a₀⁻³ and ε : ellipticities (1 e au⁻³ = 1.081×10¹² C m⁻³, 1 e a₀⁻³ = 3.8611×10³² cm⁻³). ^b MP2/6-31++G(d,p) values are in parentheses.

^c Line 8: C6-H8 for reactants (R1 and R2), X2-H8 for products (P1 and P2), C1-H8 for transition states (TS1 and TS2).

Table 4. Calculated bond lengths and bond–path lengths and bond angles and bond–path angles of reactant (R), transition state (TS), product (P) in the enolisation of cyclopropanone (X = O) and cyclopropanethione (X = S) at the B3LYP/6–31++G(d,p) level ^a

	Bond	X = O		X = S	
		Bond length/Å	Bond–Path length/Å	Bond length /Å	Bond–Path length/Å
R	C1–X2	1.205	1.205	1.611	1.611
	C1–C3	1.471	1.485	1.469	1.480
	C3–C6	1.577	1.582	1.545	1.550
TS	C1–X2	1.308	1.309	1.758	1.769
	C1–C3	1.487	1.500	1.534	1.540
	C1–C6	1.350	1.368	1.366	1.382
	C3–C6	1.545	1.547	1.479	1.488
P	C1–X2	1.342	1.342	1.730	1.730
	C1–C3	1.477	1.491	1.504	1.511
	C1–C6	1.298	1.390	1.302	1.316
	C3–C6	1.546	1.548	1.515	1.520
	X2–H8	0.970	0.970	1.351	1.351

	Angle	X = O			X = S		
		Bond angle/°	Bond–Path angle/°	$\Delta_{\text{ang}}/^\circ$	Bond angle/°	Bond–Path angle/°	$\Delta_{\text{ang}}/^\circ$
R	C1C3C6	57.6	77.0	19.4	58.3	76.5	18.2
	C3C1C6	64.8	85.7	20.9	63.4	84.1	20.7
TS	C1C3C6	52.8	69.6	16.8	53.9	72.4	18.5
	C3C1C6	65.8	90.2	24.4	61.0	78.7	17.7
	C3C6C1	61.4	76.3	14.9	65.1	87.1	22.0
P	C1C3C6	50.8	67.7	16.9	51.1	69.1	18.0
	C3C1C6	67.4	94.6	27.2	64.9	85.9	21.0
	C3C6C1	61.8	73.4	11.6	64.0	77.2	13.2
	C1X2H8	109.3	103.3	–6.0	97.2	98.1	0.9

^a See Figures 1 and 3

Bader's topological parameters [44] for the optimized geometries at RB3LYP/6–31++G(d,p) level are represented in Figure 3. The diagnostic charge density (ρ), Laplacian ($\nabla^2\rho$) and ellipticity (ϵ) values at BCPs calculated at MP2/6–31++G(d,p) and B3LYP/6–31++G(d,p) levels are given in Table 3. Also, the bond–path length and path–angle data along with the corresponding bond lengths and bond angles are presented in Table 4. The large Δ_{ang} values indicate noticeable strain in the three–member rings.

The values of Laplacian show that C=O bond is more ionic than C=S and all other interactions are predicted to be covalent in nature. It is pertinent to mention here that, during enolization of cyclopropanone, BCP gradually moves towards oxygen along the >C=O bond from reactant to product signifying gradual increase in the potential of carbonyl carbon to attract electrons while an opposite trend is observed in the case of cyclopropanethione (see Figure 3). Unlike the anisotropy normally observed in carbonyl/thiocarbonyl bonds, the ellipticity (ϵ) values in the present study indicate the electronic distribution along the >C=X (X = O, S) bonds to be isotropic.

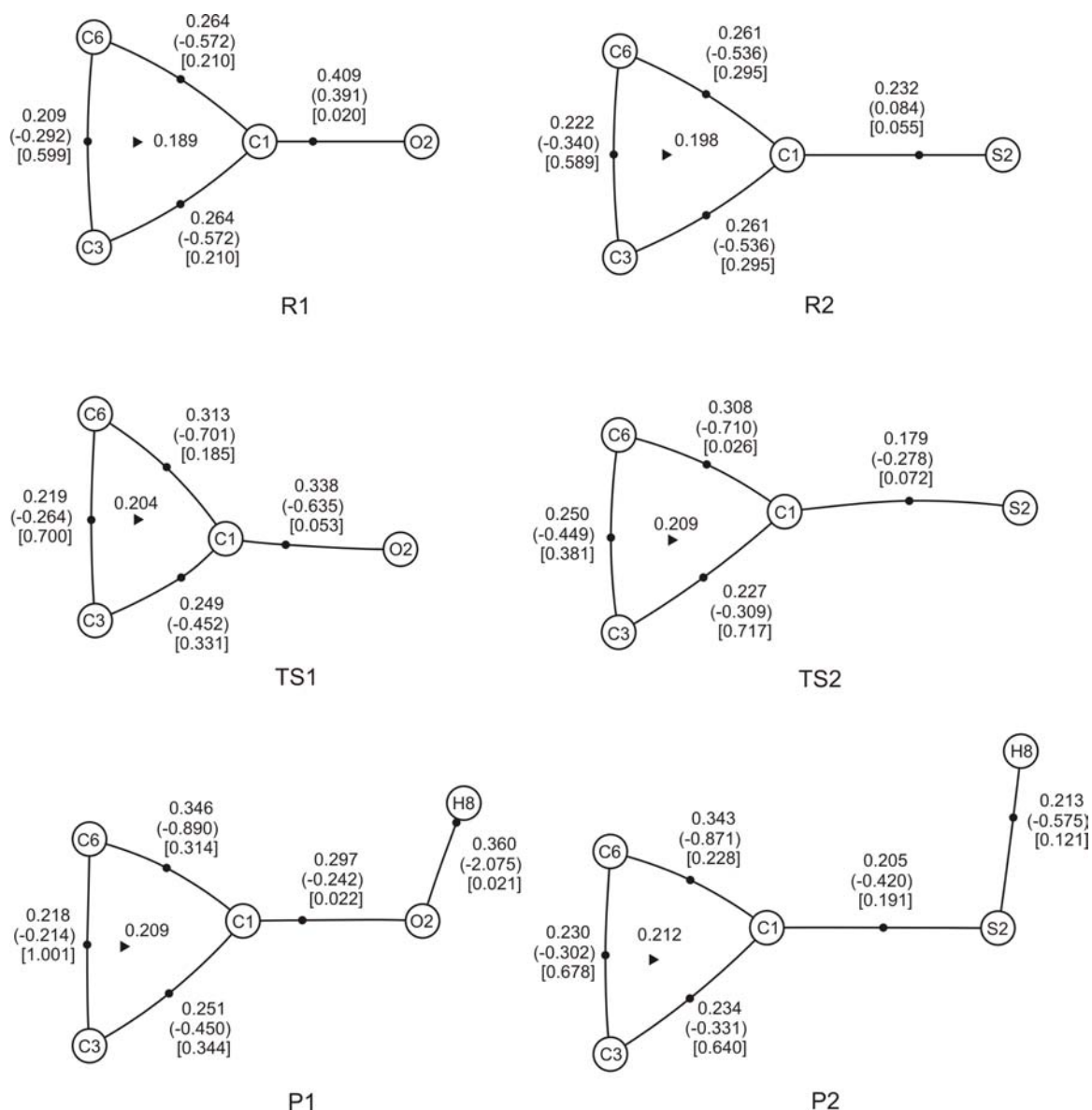
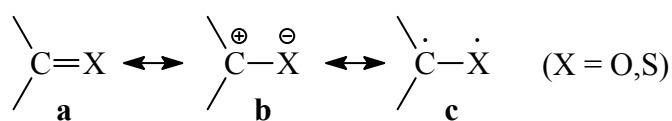


Figure 3. Bond critical points (•) and ring critical points (▲) for cyclopropanone (R1), transition state (TS1), cyclopropan-1-ol (P1), cyclopropanethione (R2), transition state (TS2) and cyclopropan-1-thiol (P2) from B3LYP/6–31++G(d,p) calculations along with electron densities ($\rho/e \text{ au}^{-3}$), laplacians ($\nabla^2\rho/e \text{ a}_0^{-5}$, in parentheses) and ellipticities (ϵ , in square brackets). ($1 \text{ e au}^{-3} = 1.081 \times 10^{12} \text{ Cm}^{-3}$; $1 \text{ e a}_0^{-5} = 3.8611 \times 10^{32} \text{ Cm}^{-5}$).

Also, the proximity of the IR carbonyl stretching frequency of cyclopropanone (1906 cm^{-1} , [11]) to that of carbon monoxide (2143 cm^{-1}) suggests that the carbonyl bond has some carbon monoxide like characteristics. The opposite displacement of BCP in cyclopropanethione can be explained in terms of the diffuse and polarizable nature of lone-pair electrons on sulphur, which manifests itself in terms of the following canonical forms:



It is reasonable to expect that the canonical form 'b' will be more relevant when X is oxygen and resonance energy of carbonyl group will be higher than that of thiocarbonyl. However, all physical (dipole moment, pK_T , etc.) and chemical (nucleophilic reactions, etc.) evidences [45] indicate that 'b' and 'c' contribute more to thiocarbonyl than to carbonyl group. The π -bond energy of carbonyl is greater than that of the thiocarbonyl due to greater contribution of 'a' to the former. It is also known that the bond energy difference between carbon-carbon single and double bonds ($60\text{--}65\text{ kcal mol}^{-1}$) is comparable to corresponding carbon-sulfur single and double bonds. This explains that the resonance energy of thiocarbonyl bond (contributions from 'b' and 'c' forms) is good enough to compensate for the unfavorable $2p\text{--}3p$ π -overlap.

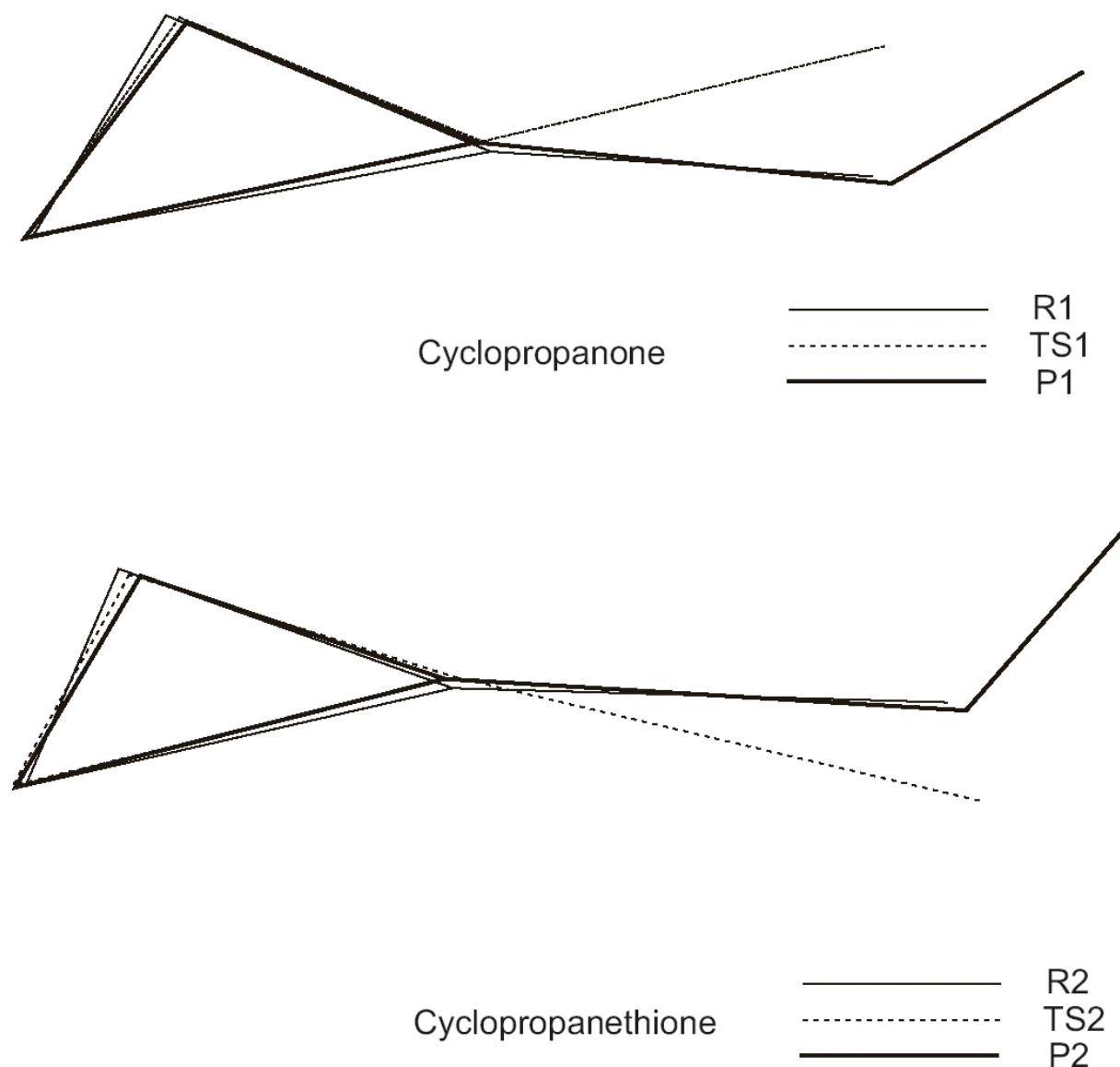


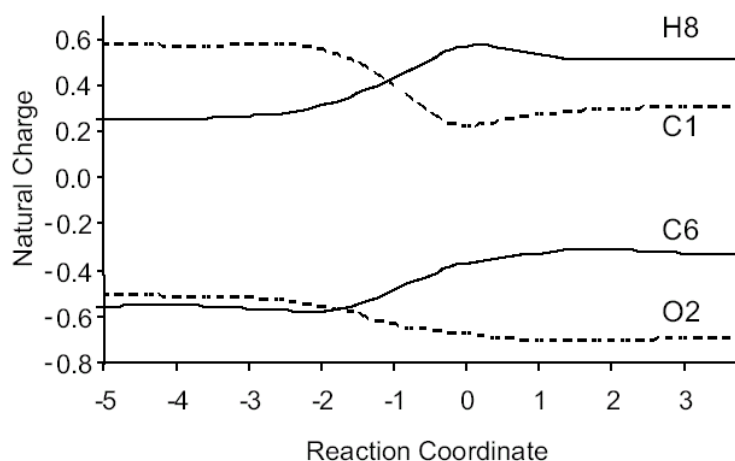
Figure 4. Schematic representation of the RMS fit and overlay for reactant(R), transition state(TS) and product (P) involved in the tautomerization.

Examination of optimized geometries and Bader's topological parameters (Figures 1 and 3, and Table 3) shows that both reactions differ considerably in terms of geometrical parameters of transition states and products. RMS fit and overlay (Figure 4), using HyperChem 5.1 Pro. (Hypercube Inc., USA), show the movement of oxygen above the ring plane in TS1 leading to increase in C1–C3 and decrease in C3–C6 bond-lengths. In spite of increase in π -character of the former, the increase in bond length may be due to the bonding orbital on C1 moving out of the ring-plane along the C1–C3 bond (Figure 1). While going from TS1 \rightarrow product, the C1–C3 bond length decreases as oxygen returns to the ring plane thereby facilitating the bonding between C1 and C3. Unlike cyclopropanone, the variation in geometrical parameters of enolization of cyclopropanethione is not gradual. In TS2, the sulphur atom moves below the ring plane which leads to lengthening of C1–C3 bond and shortening of C3–C6 bond. Regardless of decrease in π -character along C3–C6 bond, the decrease in bond length may be mainly due to increase in σ -type interaction. It is worth mentioning here that the decrease in C1–C6 bond length in cyclopropen-1-thiol is due to increase in σ bonding along the bond. C1–S2 bond of TS2 is observed to be larger than that of the product. This may be due to increase in conjugation in cyclopropen-1-thiol caused by the return of sulphur atom to the ring plane and availability of its p-orbital, as the lone-pair electrons prefer to have more s-character.

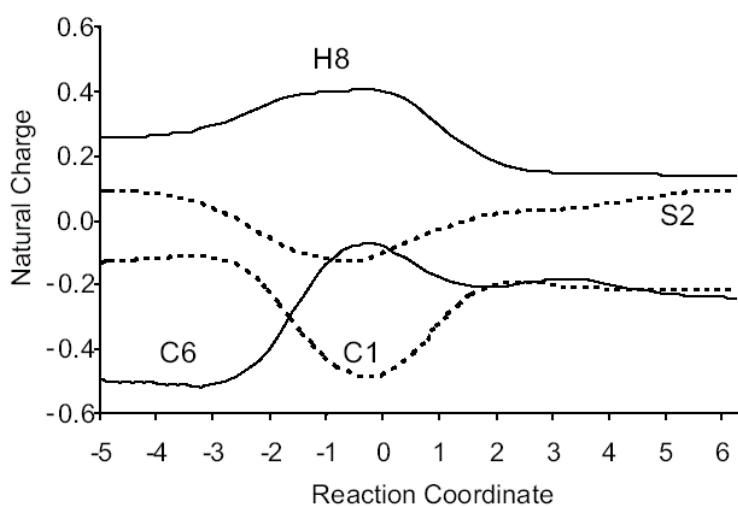
Though the three-member ring in cyclopropen-1-thiol is nearly symmetrical about the double bond (as in cyclopropene), yet the symmetry of the ring is lost in the cyclopropen-1-ol. This may be attributed to the influence of sulphur through extended conjugation of the electronic distribution of the ring by its p-orbital. This is further evident from the fact that the ellipticity values along C1–S2, C1–C3 and C3–C6 bonds are higher in the enolized product than those of reactant (Table 3). It is noteworthy that ellipticity value decreases from cyclopropanethione to its enethiol form along C1–C6 bond that signifies the increase in σ -interaction along the bond. The increase in ϵ values along the C1–C6 bond in cyclopropanone points to increase in π -interaction. The maximum difference between the bond-path length (1.390Å) and bond length (1.298Å) along the C1–C6 bond in cyclopropen-1-ol, as compared to other bonds in all the stationary points, indicates the maximum strain (Table 4). The lower bond angle, $\angle C1S2H8$ ($\sim 97^\circ$), in cyclopropen-1-thiol may be attributed to the extensive participation of p-orbital of sulphur in bonding with hydrogen [45].

The rate of 1,3 shift of the hydrogen (H8) during tautomerization depends on the energy of the C6–H8 bond and the pushing and pulling ability of C1=X2 (X = O, S) functional group. Furthermore, the “push and pull” effect of the C1=X2 bond depends on the electronegativity of the atom, X (its σ -withdrawing ability) and the π -donating ability of the C=X bond. Figure 5 illustrates profiles of the charges on relevant atoms by NPA in IRC calculations. As can be seen in Figure 5a, the electronic charge of O2 is negative while that of C1 is positive. The greater increase in the electronic charge of O2 relative to that of C1 leads to the delocalization of π -electron in C=O to give $C^{\delta+}=O^{\delta-}$; meanwhile the migrating hydrogen becomes gradually more positive. This migration

of the hydrogen with partial build up of positive charge is denoted as $H^{\delta+}$ (proton) transfer. On the other hand, for $X=S$ (Figure 5b), though the electronic charge of S2 is negative near the transition state, yet it is positive relative to that of C1. The decrease in the electronic charge of S2 leads to delocalisation of π -electron in $C=S$ to give $C^{\delta-}=S^{\delta+}$; meanwhile the positive charge of migrating hydrogen gradually decreases indicating an $H^{\delta-}$ (hydride) like transfer. A similar trend has also been predicted by Chuang *et al.* [46,47] in their *ab initio* studies on the tautomerization of $H_3CC(X)=Y$ and $H_2C(X)CH=Y$ ($Y = SiH_3, PH, S; X = H, CH_3, NH_2, OH, F$) and their second period analogs of Y ($Y = CH_2, NH, O$).



(a)



(b)

Figure 5. Charge profiles of the main atoms at the B3LYP/6–31++G(d,p) level for cyclopropanone (a) and cyclopropanethione (b). The keto form, transition state (TS) and enol form are on the left–hand side, in the center and on the right–hand side of the reaction coordinate, respectively.

The calculated activation (ΔH^\ddagger) and reaction enthalpies (ΔH) for the tautomerization and rotational isomerization of enol/enethiol forms are presented in Tables 1 and 2, respectively. It has been found that the second order Moller–Plesset (MP2) correction to energy and inclusion of electron correlation by using B3LYP functional leads to significant lowering of energies as well as activation enthalpies. At the RHF level, addition of diffuse and/or polarization functions to hydrogen does not give a well-defined trend in activation and reaction enthalpies, which may be due to different extents of cancellation of correlation effects. Addition of polarization function to hydrogen in cyclopropanethione at B3LYP level leads to significant lowering of activation and reaction enthalpies whereas the effect of diffuse function to hydrogen is negligible. This supports our earlier suggestion about the predominant p-character of sulphur bonding–electrons. It has been shown that B3LYP calculated single point results using MP2 optimized geometries are comparable to B3LYP full optimizations. The fact that the activation energy for the enolization of cyclopropanone is higher than that for cyclopropanethione confirms that thiones have greater tendency to tautomerize than ketones.

The calculated ΔH values (Table 1) for the reactions are comparable to higher-level *ab initio* (CBS–4) calculations [24] and predict the carbonyl/thiocarbonyl isomer to be significantly more stable than corresponding enol/enethiol form as observed in most of the carbonyls and thiocarbonyls. Though it appears that RHF/6–31G* reaction enthalpy of cyclopropanone is close to CBS–4 results (as compared to MP2 and B3LYP), it is largely due to partial cancellation of correlation effects in reactants and products. It is worth noting that the addition of diffuse function to hydrogen contributes more to cyclopropanone than its transition state and the product leading to an increase in both activation and reaction enthalpies. The endothermicity of the reaction is consistent with the fact that introduction of double bond (either endocyclic or exocyclic) into the cyclopropane ring increases the strain [5] which is maximum when two sp^2 hybridized carbon atoms are introduced in the three-member ring. This fact is supported by the isomerization of methylcyclopropene to methylenecyclopropane, which is exothermic by 10.3 kcal mol⁻¹ [48]. RB3LYP/6–31++G(d,p) results yield the lowest activation barrier and the calculated reaction enthalpies are in good agreement with *ab initio* CBS–4 results.

Cyclopropen–1–ol and its sulphur analog may exist in at least two distinct conformers with the dihedral angle (θ), $\angle H8X2C1C6$; *i.e.*, *syn* ($\theta = 0^\circ$) or *anti* ($\theta = 180^\circ$) (Figure 2). The enol/enethiol form prefers *syn*– to the *anti*–conformer. In the transition state, –XH (X = O, S) group is nearly perpendicular to the three-member ring (dihedral angle, θ , in the range of 85.0–94.0 degrees). The rotational barriers for the above transformations lie in the range, 3.3 – 5.0 kcal mol⁻¹ (Table 2) and electron correlation has no definite effect on the trend of activation enthalpies, which is again due to difference in magnitude of cancellation of correlation energy. It is important to mention that at higher levels of theory both rotamers move to same energy.

4 CONCLUSIONS

Cyclopropanone and cyclopropanethione are small–unsaturated cyclic molecules with scarcely available experimental data making theoretical studies more relevant. Bader’s topological analysis suggests isotropic electronic distribution along the carbonyl/thiocarbonyl bond. This supports the observed proximity of cyclopropanone carbonyl stretching frequency to that of carbon monoxide. In the present study, it has been shown that the diffusability and polarizability of sulphur play an important role in the determination of electronic distribution in small strained rings. NPA clearly predicts that enolization proceeds through $H^{\delta+}$ (proton) transfer for cyclopropanone, while $H^{\delta-}$ (hydride) like transfer is indicated for cyclopropanethione. Conformational analysis reveals the syn–conformer of the enol/enethiol to be more stable than its corresponding anti–form. Thermochemical calculations reflect that the incorporation of electronic correlation plays an important role for these strained systems.

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