



# Ab initio and density functional theory studies on selected thioaldehydes and thioketones

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## ABSTRACT

*Ab initio* and Density functional theory with three basis sets have been used to study seventeen isomers comprising of six thioaldehydes and eleven thioketones, relative stabilities of the isomers and electronic properties of the molecules are reported. The results revealed that there is an increase in C=S bond length as the number of carbon atoms increases, although C=S bond lengths for thioaldehydes are shorter than that of the corresponding thioketones analogues. Generally, thioketone isomers are more thermodynamically stable than that of the corresponding thioaldehydes. The rearrangement of thioaldehydes to thioketones would be feasible and exothermic since both  $\Delta G^\circ$  and  $\Delta H^\circ$  have negative values.  $^{13}\text{C}$  NMR of thiocarbonyl carbon atoms and UV-visible absorption ( $\lambda_{\text{max}}$ ) showed similar trend when plotted against C=S bond length, thus the electronic properties and chemical reactivities of the molecules would be predominantly governed by C=S group.

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## Introduction

Thials are generally more reactive than the thioketones, unhindered thioaldehydes are generally unstable. For instance, methanethial ( $\text{H}_2\text{C}=\text{S}$ ) condensed to the cyclic trimer 1,3,5-trithione [1], however stable thials like thiobenzaldehydes have been isolated [2]. The photoelectron studies of thioaldehydes and thioacetone revealed that their vertical ionization potentials are  $8.98 \pm 0.02$  and  $8.60 \pm 0.05$  eV respectively. The microwave rotational spectra showed hindered internal rotation of  $1545 \pm 20$  cal/mol and  $1300 \pm 50$  cal/mol for the thioaldehydes and thioacetone respectively [1]. Also, the nature of methyl internal rotational barrier in thioacetone has been investigated by relaxation effects, natural bond orbitals (NBO) analysis and Pauli exchange interactions and compared with its parent acetone [3]. The enolization enthalpies at 0 and 298K for nine aliphatic carbonyl and nine aliphatic thiocarbonyl compounds have been theoretically studied with *ab initio*. The results revealed that enolization enthalpies of thiocarbonyls were much lower than corresponding carbonyls, this was attributed to weaker C=S bond than C=O. The enolization of cyclothioketones was significantly dependent on the size of the cyclic rings [4]. The structures and energies of conformations of thioacetones and thiopronaldehyde have been studied by *ab initio* STO-3G and HF/3-21G basis sets. The results were compared with available data on acetone and propanaldehyde to assess the effects of oxygen-by-sulphur substitution on the molecular properties [5]. In this work, we present the results of our unmitigation on simple thiocarbonyls and thioketones and due to scanty experimental data available in the literatures for these simple compounds, The structural and electronic properties of these two series of thioaldehydes and thioketones (Figure 1) and possible geometrical relationship with electronics properties are compared experimental values where available.

## Computational methods

All calculations to study the n-thials, n-thiones and cyclothiones were performed with Spartan 06 program [6] implemented on an Intel Pentium M 2.0 GHz Computer.

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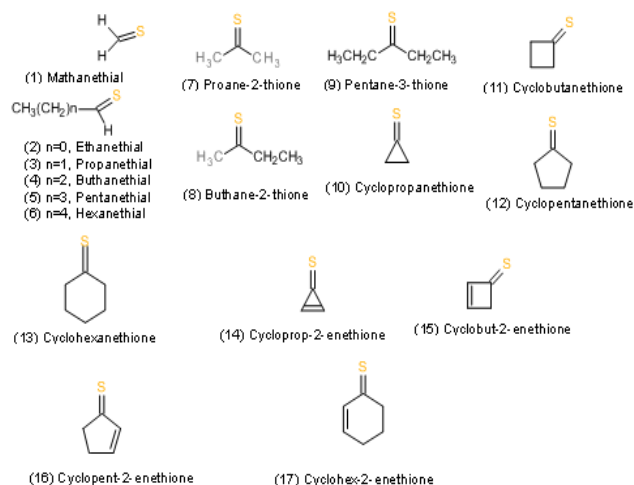


Figure 1: The studied molecules

The initial geometry of the studied molecules were optimized at Semi-empirical method PM3 and further geometry optimization using *ab initio* methods (HF/6-31G\*, HF/6-31+G\* and HF/6-311G\*) and B3LYP hybrid exchange-correction functional [7,8] together with the 6-31G\*, 6-31+G\* and 6-311G\* basis sets as implemented on Spartan 06 package. The harmonic vibrational frequencies and isotropic chemical shifts for hydrogen atoms were calculated from the optimized geometry in the ground  $S_0$  state at both *ab initio* and DFT levels. The harmonic vibrational frequencies and isotropic chemical shifts at B3LYP/6-31+G\* and B3LYP/6-311G\* were obtained using the geometry already obtained at B3LYP/6-31G\* level. The UV-absorptions were calculated using Configuration interaction (CIS) for both DFT and *ab initio* methods.

## Results and discussion

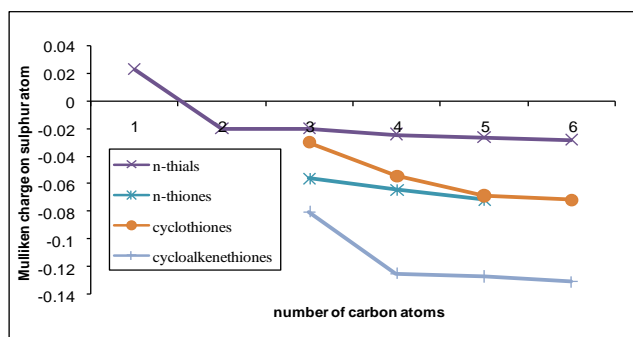
The total energies and C=S bond lengths for the two series using *ab initio* methods and DFT with three basis sets are presented in Tables 1 and 2. The results reveal that the C=S bond lengths predicted at *ab initio* levels are shortened than those calculated at DFT.

The C=S bond lengths calculated at HF/6-31+G and DFT/6-31+G are longer than other methods. In each series, there is an increase in C=S bond length as the number of carbon atoms increases and also the bond lengths for thioaldehydes are shorter than that of the corresponding thioketones analogues. Considering the cyclothioketones especially cyclopropanethione (**10**) and cycloprop-2-enethione (**14**) and cyclopentanethione (**12**) and cyclopent-2,4-dienethione (**15**), the C=S bond lengths calculated at DFT levels are increased in molecules **14** and **15**, this indicates that the presence of double bond increased strain in the molecules compared to **10** and **11** respectively. However, the C=S bond of propane-2-thione (**7**) calculated at PM2/6-31+G is shorter than that of DFT/6-31+G by 0.007Å [3].

The stabilities and thermodynamics properties of thioaldehyde and thioketone isomers are compared in Table 3. Generally, thioketone isomers are more thermodynamically stable than that of the corresponding thioaldehydes. The orientation of the electric dipole moment vector of any molecule with respect to the direction, size of the electric dipole moment vector and orientations determines interactions with the solvent and electrochemical characteristics of such molecule. Therefore, we expect thioketone isomers to be more interactive with solvents especially polar solvents. The inter-conversion or rearrangement of thioaldehydes to thioketones would be feasible and exothermic since both  $\Delta G^\circ$  and  $\Delta H^\circ$  have negative values (Table 3).

#### Electronic properties

The HOMO, LUMO, band gap and Mulliken charges on thiocarbonyl carbon and sulphur are displaced in Table 4. The results show that the band gap calculated at DFT with three basis sets is inversely proportion to the stability, although the band gap calculated at DFT/6-31+G\* are higher. Figure 2 show the relationship between calculated mulliken charges on sulphur atom and number of carbon atoms, the graph reveals that the charges on sulphur decreases while the charges on thiocarbonyl carbon atoms increases with increase in carbon atoms (Table 4). This indicates that the ability of Sulphur atom to donate electrons increases and that of thiocarbonyl carbon decreases with increasing number of carbon atoms. Thus the probability of sulphur atom reaction towards electrophilic reagents would increase for both thioaldehydes and thioketones with the increase in number of carbon atoms.

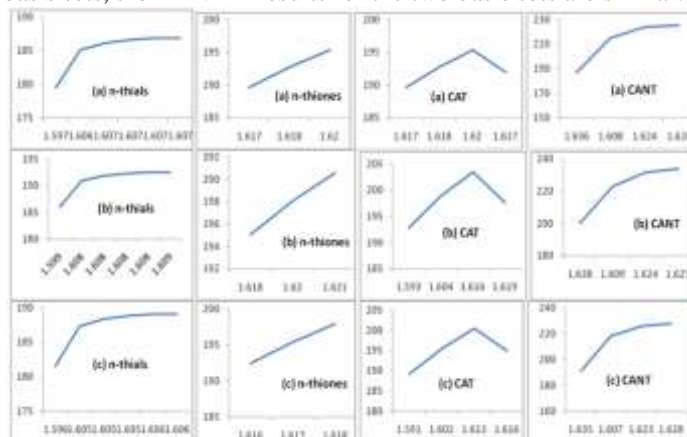


**Figure 2: Relationship between number of carbon atoms and Mulliken charges on sulphur**

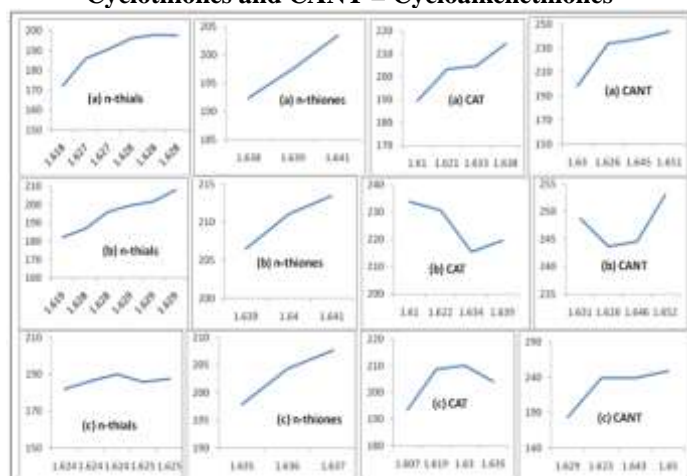
Attempt is made to establish any correlation between C=S bond length and UV-visible absorption ( $\lambda_{\max}$ ) of the molecules as depicted in figures 3 and 4. The *ab initio* calculations show that the curves for n-thioaldehydes (n-thials) and cycloalkenethiones (CANT) are quite similar; there are sharp increase in wavelengths then gradually flattens up (Figure 3). For n-thiones, both *ab initio* and DFT calculations show linear relationships between the C=S and  $\lambda_{\max}$  with  $R^2 > 0.997$  and  $0.967$  for *ab initio* and DFT calculations respectively.

Generally, the graph plotted from *ab initio* methods show the same trend for each series of molecules, however DFT curves do not follow similar trend (i.e. there is no distinct relationship between C=S bond length and  $\lambda_{\max}$  especially for CAT and CANT (figure 4).

The molecular structure of the studied molecules using *ab initio* methods and B3LYP method with 6-31G\*, 6-31+G\* and 6-311G\* basis sets were used to calculate  $^{13}\text{C}$  and  $^1\text{H}$  chemical shift calculations as shown in Tables 4 and 5. The result in Table 4 shows that the range  $^{13}\text{C}$  NMR chemical shift of the molecules are greater than 100 ppm which is the typical  $^{13}\text{C}$  NMR chemical shift for organic molecule [31,32]. A critical look at Table 4 also reveals that  $^{13}\text{C}$  NMR of thiocarbonyl carbon atoms have similar relationship identified in Figures 3 and 4 when values of  $^{13}\text{C}$  NMR of thiocarbonyl carbons are compared with C=S bond lengths, thus the electronic properties and chemical reactivities of the molecules would be predominantly governed by C=S group. The values of  $^{13}\text{C}$  NMR chemical shifts for thiocarbonyl carbon for n-thiones are higher than that of the corresponding n-thials, this is the indication that thiocarbonyl carbons for n-thiones experienced more de-shielding as compared to n-thials. For instance, the chemical shift for molecules 3 and 5 are 183.59 and 268.85 ppm as compared to 288.41 and 292.03 ppm for molecules 7 and 9 respectively. Presence of double bonds in cyclothiones shielded thiocarbonyl carbons which resulted in lower chemical shift. Table 5 shows the  $^1\text{H}$  NMR calculated at DFT with 6-31+G\* and 6-311G\* basis sets, the  $^1\text{H}$  NMR results for the two basis sets are similar.



**Figure 3: The graph of  $\lambda_{\max}$ (nm) against C=S bond length; (a) HF/36-1G\*, (b) HF/631+G\*, (c) HF/6311G\*, CAT = Cyclothiones and CANT = Cycloalkenethiones**



**Figure 4: The graph of  $\lambda_{\max}$ (nm) against C=S bond length; (a) DFT/36-1G\*, (b) DFT/631+G\*, (c) DFT/6311G\*, CAT = Cyclothiones and CANT = Cycloalkenethiones**

**Table 1. Total energies in kCal/mol**

Mol	HF			B3LYP		
	6-31G*	6-31+G*	6-311G*	6-31G*	6-31+G*	6-311G*
1	-273912.17	-273913.16	-273931.38	-274512.01	-273912.56	-274534.85
2	-298413.48	-298414.67	-298436.87	-299189.31	-298413.86	-299217.85
3	-322908.24	-322909.69	-322935.91	-323859.03	-322908.73	-323892.03
4	-347403.05	-347404.71	-347434.94	-348528.92	-347402.72	-348566.99
5	-371896.83	-347188.67	-371932.90	-373197.96	-371896.39	-373241.09
6	-396391.47	-396393.50	-396431.73	-397867.71	-396390.96	-397915.89
7	-322912.87	-322914.26	-322940.47	-323864.36	-322913.24	-323897.15
8	-347406.81	-347408.40	-347438.60	-348533.41	-347407.20	-348571.22
9	-371909.94	-371902.68	-371936.90	-373202.80	-371900.30	-373245.61
10	-322144.93	-322146.50	-322171.24	-323070.71	-322145.48	-323102.43
11	-346655.65	-346657.60	-346686.76	-347755.50	-346656.44	-347792.30
12	-371171.79	-371173.71	-371207.04	-372444.84	-371171.36	-372486.94
13	-395669.71	-395671.75	-395709.31	-397118.11	-395669.11	-397165.25
14	-321400.11	-321401.90	-321426.50	-322293.87	-321400.41	-322326.50
15	-345907.97	-345910.36	-345939.14	-346980.96	-345909.02	-347017.54
16	-370432.89	-370451.36	-370477.14	-371680.04	-347199.02	-372417.54
17	-394929.16	-394948.65	-395001.67	-396315.65	-396621.23	-397226.11

**Table 2: Calculated C=S bond lengths (Å) for the studied molecules**

Mol	HF			B3LYP		
	6-31G*	6-31+G*	6-311G*	6-31G*	6-31+G*	6-311G*
1	1.597	1.599	1.596	1.618	1.619	1.614
2	1.606	1.608	1.605	1.627	1.628	1.624
3	1.607	1.608	1.605	1.627	1.628	1.624
4	1.607	1.608	1.605	1.628	1.629	1.624
5	1.607	1.608	1.606	1.628	1.629	1.625
6	1.607	1.609	1.606	1.628	1.629	1.625
7	1.617	1.618	1.616	1.638	1.639	1.635
8	1.618	1.620	1.617	1.639	1.640	1.636
9	1.620	1.621	1.618	1.641	1.641	1.637
10	1.592	1.593	1.591	1.610	1.610	1.607
11	1.603	1.604	1.602	1.621	1.622	1.619
12	1.614	1.616	1.613	1.633	1.634	1.630
13	1.617	1.619	1.616	1.638	1.639	1.635
14	1.636	1.638	1.635	1.630	1.631	1.629
15	1.608	1.609	1.607	1.626	1.626	1.623
16	1.624	1.624	1.623	1.645	1.646	1.643
17	1.626	1.627	1.628	1.651	1.652	1.650

**Table 3: Energy (E), change in thermodynamics properties and Dipole moment (D.M) calculated for the isomers at B3LYP/6-311G\* level.**

Mol	Relative. E (Kcal/mol)	D.M (debye)	* $\Delta H^\circ$ (Kcal/mol)	* $\Delta S^\circ$ (J/mol)	* $\Delta G^\circ$ (Kcal/mol)
Isomers 3	5.10	2.73	-5.3	-0.26	-5.5
7	0.00	3.02	-	-	-
Isomers 4	4.22	2.84	-4.36	6.93	-4.85
8	0.00	3.05	-	-	-
Isomers 5	3.62	2.92	-3.48	-9.63	-2.79
9	0.00	3.06	-	-	-

\* $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  are differences in thermodynamics properties of thioaldehyde and thioketone isomers.

**Table 4: Calculated HOMO, LUMO, Band gap and Mulliken charges on thiocarbonyl carbon and sulphur atoms at B3LYP with different basic sets.**

mol	B3LYP									Mulliken Charges	
	6-31G*			6-31+G*			6-311G*			B3LYP/6-311G*	
	HOMO	LUMO	Band gap	HOMO	LUMO	Band gap	HOMO	LUMO	Band gap	C	S
1	-6.35	-2.57	3.78	-6.52	-2.85	3.67	-6.55	-2.77	3.78	-0.512	0.023
2	-6.09	-2.15	3.94	-6.28	-2.40	3.88	-6.31	-2.37	3.94	-0.315	-0.020
3	-6.04	-2.13	3.91	-6.23	-2.39	3.84	-6.26	-2.35	3.91	-0.308	-0.020
4	-6.01	-2.11	3.90	-6.21	-2.36	3.85	-6.23	-2.32	3.91	-0.308	-0.024
5	-6.00	-2.09	3.91	-6.19	-2.35	3.84	-6.22	-2.31	3.91	-0.307	-0.026
6	-5.99	-2.08	3.91	-6.18	-2.33	3.85	-6.20	-2.29	3.91	-0.306	-0.028
7	-5.88	-1.92	3.96	-6.08	-2.17	3.91	-6.11	-2.15	3.96	-0.143	-0.056
8	-5.84	-1.90	3.94	-6.04	-2.15	3.89	-6.07	-2.13	3.94	-0.127	-0.064
9	-5.83	-1.97	3.86	-6.01	-2.15	3.86	-6.03	-2.13	3.90	-0.115	-0.071
10	-5.85	-2.18	3.67	-6.05	-2.43	3.62	-6.06	-2.40	3.66	-0.110	-0.030
11	-5.90	-1.97	3.93	-6.10	-2.22	3.88	-6.12	-2.20	3.92	-0.110	-0.054
12	-5.76	-1.89	3.89	-5.96	-2.13	3.83	-5.99	-2.12	3.87	-0.119	-0.068
13	-5.75	-1.84	3.91	-5.95	-2.09	3.86	-5.98	-2.07	3.91	-0.126	-0.071
14	-5.57	-1.29	4.28	-5.79	-1.69	4.10	-5.81	-1.56	4.25	-0.149	-0.080
15	-5.94	-2.32	3.62	-9.14	0.99	9.23	-6.17	-2.55	3.62	-0.062	-0.125
16	-5.70	-2.22	3.48	-5.73	-2.26	3.47	-5.72	-2.23	3.49	-0.044	-0.127
17	-5.73	-2.31	3.42	-5.73	-2.32	3.41	-5.74	-2.30	3.43	-0.007	-0.129

Table 4:  $^{13}\text{C}$  NMR of the thiocarbonyl carbon atom in ppm

Mol	HF			B3LYP		
	6-31G*	6-31+G*	6-311G*	6-31G*	6-31+G*	6-311G*
1	248.86	247.34	255.67	237.56	240.06	256.98
2	258.49	259.43	267.79	243.94	246.24	263.89
3	263.92	264.66	273.07	250.38	252.86	269.86
4	263.60	264.25	272.62	249.36	251.68	268.56
5	263.48	264.67	272.87	249.62	252.14	268.85
6	263.97	264.63	272.98	249.59	252.16	268.82
7	271.76	272.55	281.03	255.28	257.36	274.27
8	280.23	280.46	289.51	264.01	266.15	283.37
9	287.81	288.18	297.24	272.14	274.26	292.03
10	281.68	281.50	291.79	270.04	270.90	289.29
11	284.33	284.30	293.25	268.76	270.45	288.41
12	288.02	288.31	297.07	270.64	272.21	290.17
13	279.76	280.25	288.74	265.29	267.37	284.22
14	184.85	185.20	191.59	169.87	172.67	183.59
15	251.62	252.11	258.72	233.28	235.99	249.81
16	267.89	269.01	274.50	246.48	249.89	254.46
17	259.42	263.44	269.21	239.70	241.42	245.03

Table 5:  $^1\text{H}$  NMR of the thiocarbonyls and thioketones in PPM

Mol	B3LYP/6-31+G			B3LYP/6-311G		
	CH	CH <sub>2</sub>	CH <sub>3</sub>	CH	CH <sub>2</sub>	CH <sub>3</sub>
1	11.584 (2)*	-	-	11.555 (2)	-	-
2	11.566 (1)	-	2.883-2.772 (3)	11.536 (1)	-	2.893-2.759 (3)
3	11.530 (1)	3.085-2.932 (2)	1.581-1.032 (3)	11.536 (1)	3.133-2.932 (2)	1.570-1.010 (3)
4	11.549 (1)	3.093-1.441 (4)	1.269-1.018 (3)	11.550 (1)	3.115-1.443 (4)	1.345-1.059 (3)
5	11.539 (1)	3.095-1.387 (6)	1.202-0.998 (3)	11.552 (1)	3.129-1.358 (6)	1.313-1.044 (3)
6	11.528 (1)	3.313-1.328 (8)	1.212-0.912 (3)	11.552 (1)	3.358-1.324 (8)	1.315-0.974 (3)
7	-	-	2.828-2.821 (6)	-	-	2.896-2.826 (6)
8	-	3.173-2.926 (2)	3.115-1.259 (6)	-	3.208-3.005 (2)	3.132-1.253 (6)
9	-	3.303-2.839 (4)	1.286-1.188 (6)	-	3.342-2.893 (4)	1.377-1.230 (6)
10	-	1.634 (2)	-	-	1.658 (2)	-
11	-	3.220-2.235(3)	-	-	3.380-2.304 (3)	-
12	-	2.954-1.828 (4)	-	-	3.101-2.069 (4)	-
13	-	3.129-1.490 (5)	-	-	3.225-2.828 (5)	-
14	8.810 (2)	-	-	8.747 (2)	-	-
15	8.959-6.337 (2)	3.184 (2)	-	-	-	-
16	7.541-6.438 (2)	2.888-2.646 (4)	-	7.553-6.448 (2)	2.897-2.665 (4)	-
17	6.613-6.501 (2)	3.155-1.757 (6)	-	6.642-6.561 (2)	3.237-1.852 (6)	-

(\*) number of hydrogen atoms

## Conclusion

Seventeen molecules comprising of six thioaldehydes and eleven thioketones are studied at both *ab initio* and DFT levels.  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR and UV-absorptions are calculated at both DFT and *ab initio* methods. The thioketone isomers are more thermodynamically stable, have higher dipole moment, longer C=S bond lengths, longer wave lengths and larger  $^{13}\text{C}$  NMR values than that of the corresponding thioaldehydes.

The ability of sulphur atom to donate electrons increases with increase in C atoms while carbon that of thiocarbonyl carbon decreases with increasing number of carbon atoms. The plot of C=S bond length and UV-visible absorption ( $\lambda_{\text{max}}$ ) of the molecules show similar trend for *ab initio* calculations.

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