Gazi University Journal of Science
GU J Sci
25(2):343-354 (2012)

ORIGINAL ARTICLE

Theoretical Conformational Studies of Thiol and Thione Forms of Thioacetic Acid

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Received: 09.08.2011 Accepted: 03.02.2012

ABSTRACT

The theoretical conformational structure analyses were performed using density functional theory for thiol and thione tautomeric forms of thioacetic acid (TAA). At the B3LYP/6-311++G(d,p) level, thiol [CH3(C=O)SH] and thione [CH3(C=S)OH] were found more stable than anti forms and the energy differences between these two forms were computed to be ca. 6.7 kJ mol−1 and ca. 27 kJ mol−1, respectively. Barrier energies for thiol and thione forms of thioacetic acid were calculated by using the density functional theory [DFT(B3LYP)/6-311++G(d,p)] method contributing to more than 90% of the population in gas phase at room temperature and also reported a theoretical study on vibrational spectra of thiol and thione tautomeric forms of thioacetic acid obtained by the density functional theory.

Key Words: *thioacetic acid, DFT calculations, tautomerisation, PES, IR spectroscopy.*

1. INTRODUCTION

Thioacetic acid has been used as a thiol group in the synthesis of organic compounds such as rubber chemicals, curing agents, cross linking agents, metallurgical agent, pesticides, pharmaceuticals. Thiols are stronger acids than the relevant alcohols and phenols. Organosulfur compounds are being widely used in refineries, steam crackers, aromatic extraction and petrochemical manufacturing as they acts as hydro treating catalysts, initial catalyst improvers, sulfur source and catalyst presulfiding.

Thioacetic acid has been the subject of many theoretical and experimental investigations. The understanding of conformational preferences of the molecules containing the -C (=O) S- or -C (=S) O- fragments is related to interpret some biologically important macromolecules, especially to coenzyme A. It is a major interest to improve our knowledge about some proteolytic reactions like those catalyzed by serine or cysteine proteinases (e.g., quimotripsin and papain), which involve the generation of a -C (=O) S- enzyme antigen complex within the enzyme's active site [1,2].

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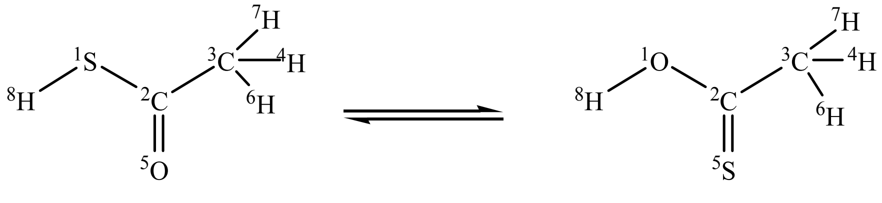
Thioacetic acids exist as a tautomeric mixture of thiol and thione forms (Scheme 1). In general, thiol forms predominate over the thione forms. Previously Rui Fausto and coworkers were reported a quantum chemical calculation about TAA conformers using 3-21G and 4-31G basis sets with Monster-Gauss 80 program package. They found ***syn*** thiol conformer was the most stable conformer [3,4].



Scheme 1. Tautomeric forms of thioacetic acids.

In the last two decades both experimental and theoretical studies on some of these systems have reached a highly sophisticated level and it is however essential to obtain a better description of changes produced in molecular properties by O→S exchange [5-13]. Following different levels of calculation reported in the previous studies [3], in the present study the DFT/B3LYP/6-311++g(d,p) level of theoretical calculations were performed. Previously Romano and coworkers were reported matrix isolation spectroscopy of several molecules in an argon matrix at 15K which contains -C(O)S- moiety. They also investigated photoproducts of molecule in the argon matrix and irradiated with UV visible light [14-24].

In this study, we revised ground state equilibrium geometries of thioacetic acid (TAA) at the DFT/B3LYP level of theory with the standard 6-311++G(d,p) basis set which also allowed characterization of the nature of the stationary point through inspection of the corresponding Hessian matrix. Compared to the previously reported values of the energies and vibrational frequencies of TAA, we obtained better results with DFT/B3LYP 6-311++G(d,p) basis set. In this paper, we present the theoretical calculations by using density functional theory (DFT) method to elucidate the structures, conformational properties and infrared spectra of thioacetic acid.

2. COMPUTATIONAL SECTION

Molecular geometries of tautomeric forms of thioacetic acid were optimized at the Gaussian 03 [25]. Programs at the DFT level of theory, using the 6-31+G(d,p), 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets [26,27]. The three-parameter hybrid density functional abbreviated as B3LYP, which includes Becke's gradient exchange correction [28] and the Lee, Yang and Parr [29] and Vosko,Wilk and Nusair correlation functionals [30] was selected for the calculations. Also, the relative energies and dipole moments were computed by the MP2 with different basis sets using the 6-31+G(d,p) and 6-31++G(d,p). Structures were optimized using the Geometry Direct Inversion of the Invariant Subspace (GDIIS) method [31,32], with the transition state structures for conformational interconversion located using the Synchronous Transit-Guided Quasi-Newton (STQN) approach [33]. The 2D potential energy surface maps were built by varying the H_8-S_1-C_2-O_5 and H_8-O_1-C_2-C_3 dihedral angles from 0 to 360^o in increments of 30^o and optimizing all other structural parameters at the selected level of theory. Harmonic vibrational frequencies and IR intensities were then calculated at the optimized geometries. In order to correct for systematic shortcomings of the applied methodology, the predicted vibrational wave numbers were scaled down with a single factor of 0.978.

3. RESULTS AND DISCUSSION

The calculations predicted the ***syn***-thiolacetic tautomer as the most stable form, in agreement with the spectroscopic observations [14], also provided a general overview of the change in properties like atomic charges, dipole moments, barriers to methyl group internal rotation (Figure 1 and 2). In the present study, we performed a detailed conformational search on the DFT/B3LYP/6-311++G(d,p) potential energy surface of TAA. Two different conformers identified conformers shown at Figure 1, 2 and 3. Geometrical parameters for two forms given in Table 4 where they are compared with that of obtained by Romano et al [14].

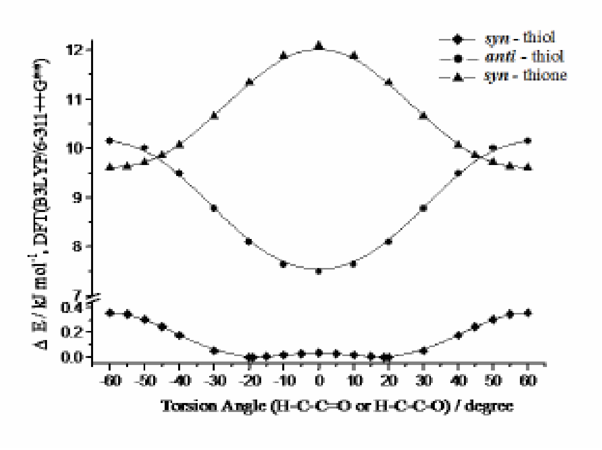


Figure 1. ΔE energies calculated by DFT/B3LYP/6-311++G(d,p) as a function of the methyl group rotation for ***syn***-thiol, ***anti***-thiol and ***syn***-thione tautomers of thioacetic acid.

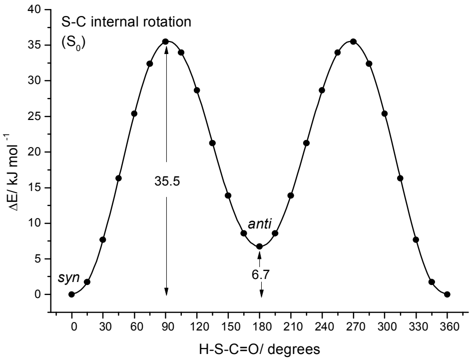


Figure 2. The DFT/B3LYP/6-311++G(d,p) potential energy profiles for interconversion between two low energy forms of HSC=O thiol tautomer of thioacetic acid.

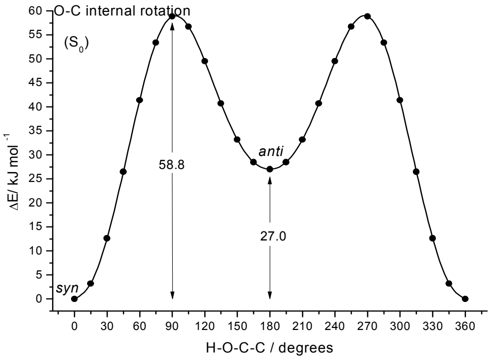
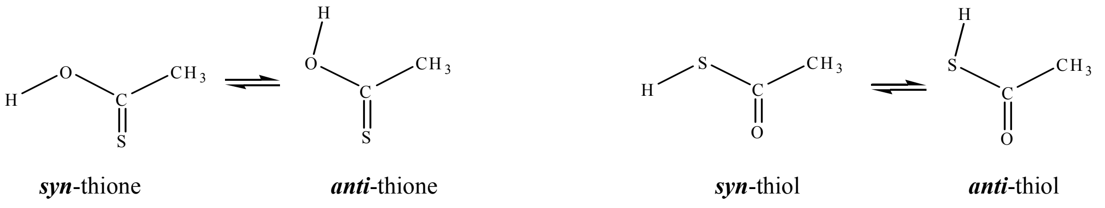


Figure 3. The DFT/B3LYP/6-311++G(d,p) potential energy profiles for interconversion between two low energy forms of HOC=S thione tautomer of thioacetic acid.



Scheme 2. The possible geometrical isomers for tautomeric acid molecules.

Table 1. Theoretically calculated relative energies for ***syn***-thiol, ***anti***-thiol, ***syn***-thione, ***anti***-thione conformers of thioacetic acid ($CH_3C(=O)SH$ and $CH_3C(=S)OH$), their dipole moments and equilibrium in Boltzmann populations calculated at different levels of theory.

Conformers	***syn***-thiol	***anti***-thiol	***syn***-thione	***anti***-thione	ΔE^a	
Calculation method	*Relative energies (kJ mol^{-1})*				thiol *(anti-syn)*	thione *(anti-syn)*
B3LYP/6-31+g(d,p)	0.000	10.29	19.51	49.66	10.29	30.16
B3LYP/6-31++g(d,p)	0.000	10.18	19.36	49.61	10.18	39.43
B3LYP/6-311+g(d)	0.000	10.86	27.91	60.05	10.86	32.14
B3LYP/6-311++g(d,p)	0.000	6.689	21.87	48.59	6.689	26.72
MP2/6-31+g(d,p)	0.000	10.13	17.96	48.85	10.13	30.89
MP2/6-31++g(d,p)	0.000	9.956	17.67	48.80	9.956	31.13
	Dipole Moments (debye)					
B3LYP/6-31+g(d,p)	1.84	3.70	1.93	4.55		
B3LYP/6-31++g(d,p)	1.84	3.68	1.92	4.53		
B3LYP/6-311+g(d)	1.80	3.65	1.82	4.54		
B3LYP/6-311++g(d,p)	1.82	3.62	1.85	4.45		
MP2/6-31+g(d,p)	1.93	3.93	2.08	4.98		
MP2/6-31++g(d,p)	1.92	3.92	2.07	4.97		
Temperature	*Equilibrium Boltzmann populations (%)*					
297 K	93.75	6.25				

[a]ΔE ***syn → anti*** B3LYP/6-311++g(d,p) calculated for thiol form as 35.50 kJ mol^{-1} and thione form as 58.8 kJ mol^{-1} (4-31G* calculated for thiol form as 39.43 kJ mol^{-1} and thione form as 55.89 kJ mol^{-1} in the previous studies [3].)

DFT 6-311++g(d,p) basis set is required in order to calculate correctly the relative energies of the four relevant thioacetic acid conformers and the energy trend was found as (***syn***-(thiol) < ***anti***-(thiol) < ***syn***-(thione) < ***anti***-(thione) (Table 1). In particular, the ***syn***-thiol conformer was proved to be the most stable form [3,5,9,11-12,34-38].

Table 1 summarizes the energetic data resulting from the calculations, including the barriers for conformational tautomer between the different forms. The calculated optimized geometries for the two minima found on the potential energy surface of TAA were shown at Figure 4.In the 60/0o valley at H8-S1-C2-C3 and S1-C2-C3-H4, two minima were located, which differ mainly in the geometry of the SH group (see Figure 4). So, the energy levels of all the forms at vibrationally excited state were calculated and between all the forms, anti forms seemed as the conformers of the highest energy. The relative energy of the syn and anti thiol conformers was computed to be 6.7kJ mol-1 and syn conformer was found more stable than anti conformer. By using the Boltzmann statistics, the equilibrium populations of the conformers could be estimated as 93.75% and 6.25% for syn and anti thiol forms respectively at room temperature.

Calculated energy barrier for ***syn → anti*** isomerization of thiol tautomers of thioacetic acid, by internal rotation of methyl group around S-C bond was found to be 35.5 kJ mol^{-1} (28.8 kJ mol^{-1} in the reverse direction- if zero point vibrational energy correction is taken into account). This value for thione tautomers of thioacetic acid, by internal rotation of methyl group around O-C bond was found to be 58.8 kJ mol^{-1} (31.8 kJ mol^{-1} in the reverse direction- if zero point vibrational energycorrection is taken into account). The analysis of the results of barrier energies compared with literature [3].

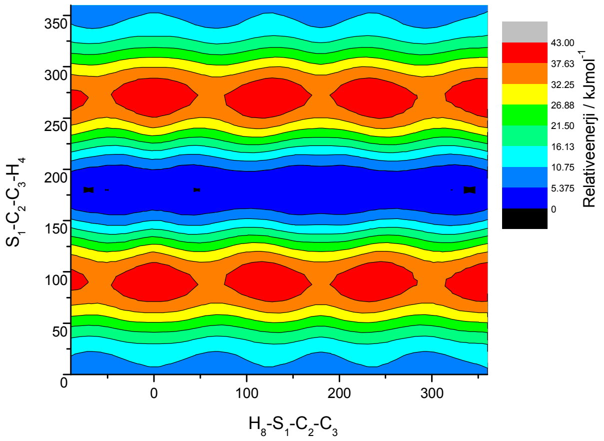


Figure 4. Potential energy map for *syn*-thiol isomer of thioacetic acid. The map resulted from a relaxed potential energy scan where the D1 frozen (H_8-S_1-C_2-C_3) and D3 change (S_1-C_2-C_3-H_4) dihedral angles varied from 0° to 360° in increments of 30° and all other structural parameters optimized at the B3LYP/6-311++g(d,p) level of theory. The plot shows two valleys which were then fully explored for identification of the conformers of the molecule.

The general intramolecular effects which make ***syn*** conformer more stable than ***anti*** forms have already analyzed in detail, the most important ones being an extended ***syn*** form π electronic delocalization and the subsequent formation of hydrogen bonding. Thus, the lower energy differences and barriers of internal rotation in $CH_3C(=O)SH$, as compared with those of $CH_3C(=S)OH$, are ascribed both to poor conjugation properties of the sulphur 3p orbitals as compared with oxygen 2p orbitals as well as the weakness of S-H•••X hydrogen bond as compared with an O-H•••X hydrogen bond [3,38].

The results of the Mulliken population analyses were shown in Table 2. The presence of sulphur *d* polarization functions does not affect the trends exhibited by the ***syn→anti*** geometric variations [3, 35, 38]. Changes in the sulphur and oxygen atomic charges during internal rotation around the C-O(S) bond are obviously correlated with variations in electronic delocalization. A lower delocalization corresponds to a decrease in the electronic density on the =O(S) atom and to an increase in the electronic density on the -O(S)- atom. As it was indicated earlier, the electronic-density analysis reinforced the explanation of the higher stability of the ***syn*** forms, as compared with that of the forms in terms of an increased electronic delocalization [3].

Table 2. Results of the Mulliken atomic charges for CH_3C (=O)SH and $CH_3C(=S)OH$.

Atomic	***DFT(B3LYP)***				***MP2***	
Charges (e)	631+g(d,p)	6-31++g(d,p)	6-311+g(d)	6-311++g(d,p)	6-31+g(d,p)	6-31++g(d,p)
***syn*-thiol**						
C=	0.203	0.208	0.327	0.171	0.228	0.235
O	-0.364	-0.365	-0.246	-0.233	-0.466	-0.471
C	-0.516	-0.541	-0.983	-0.537	-0.374	-0.325
S	0.024	0.043	-0.101	0.023	0.015	0.057
H(S)	0.097	0.086	0.168	0.066	0.085	0.057
H_1	0.190	0.200	0.280	0.185	0.182	0.165
H_2	0.182	0.183	0.276	0.161	0.153	0.127
H_3	0.184	0.185	0.278	0.163	0.178	0.155
***anti*-thiol**						
C=	0.108	0.095	0.204	0.095	0.150	0.133
O	-0.349	-0.346	-0.216	-0.224	-0.450	-0.451
C	-0.424	-0.440	-0.856	-0.437	-0.335	-0.279

S	0.080	0.093	-0.057	0.048	0.091	0.135
H(S)	0.056	0.055	0.123	0.017	0.038	0.024
H_1	0.143	0.143	0.236	0.141	0.139	0.110
H_2	0.193	0.200	0.282	0.180	0.185	0.166
H_3	0.193	0.200	0.283	0.180	0.180	0.162
syn-thione						
C=	-0.060	-0.037	-0.006	0.131	0.069	0.117
O	-0.315	-0.283	-0.162	-0.053	-0.433	-0.409
C	-0.396	-0.496	-0.798	-0.552	-0.304	-0.345
S	-0.133	-0.136	-0.218	-0.312	-0.241	-0.235
H(O)	0.357	0.377	0.352	0.253	0.389	0.400
H_1	0.184	0.194	0.285	0.180	0.176	0.154
H_2	0.182	0.188	0.273	0.176	0.172	0.160
H_3	0.182	0.194	0.273	0.176	0.172	0.160
anti-thione						
C=	-0.049	-0.057	-0.092	-0.114	0.027	0.057
O	-0.304	-0.283	-0.153	-0.001	-0.405	-0.385
C	-0.465	-0.446	-0.747	-0.295	-0.323	-0.261
S	-0.046	-0.090	-0.138	-0.285	-0.154	-0.198
H(O)	0.337	0.348	0.329	0.248	0.357	0.365
H_1	0.125	0.209	0.213	0.084	0.116	0.074
H_2	0.201	0.111	0.294	0.181	0.190	0.174
H_3	0.201	0.209	0.294	0.181	0.190	0.174

All conformers have a planar geometry (C_1 point group). The calculated optimized bond lengths and angles for the four conformers were shown in Table 3. The ***syn*** conformer of TAA in the interatomic distances found as: C=O 1.200 Å; C-S 1.822 Å; C-C 1.512 Å; C-H 1.089 Å; S-H 1.348 Å and assumed experimentally by Gordy as C-H=1.09 Å and S-H=1.34 Å [34]. The angle CCO was calculated to be 123.46°, angle CCS, 112.94° and OCS 122.265° (Table 4) and assumed experimentally to be 125° [34]. The thiol and thione forms the structural changes associated with the ***syn***→***anti*** conversion [3, 9-12,14]. The C-S and S-H bonds were lengthened, the C=O bonds are shortened and the O=C-S angles decreased, while the C-C-S and C-S-H angles increased. These changes suggest both the opening of the heavy atom backbone in the ***syn*** forms to make way for the hydrogen atom and the importance of CH_3•••H repulsions in the ***anti*** forms as indicated in the literature [3]. The S-C bond lengths were considerably shortened by including these functions in the DFT calculation in both thiol and thione forms. This feature may be originated from a stronger overlap between the carbon and sulphur atoms when polarization functions were used and reflects also in the calculated charges of sulphur and oxygen atoms.

Table 3. Results of the optimized geometries for $CH_3C(=O)SH$ and $CH_3C(=S)OH$.

Parameter	***syn***-thiol	***anti***-thiol		***syn***-thione	***anti***-thione
Bond length (ppm)			Bond length (ppm)		
C_2=O_5	1.200	1.200	C_2-O_1	1.342	1.344
S_1-H_8	1.348	1.350	O_1-H_8	1.498	1.512
C_2-C_3	1.512	1.515	C_2-C_3	0.970	0.966
C_2-S_1	1.822	1.820	C_2=S_5	1.642	1.634

C_3-H_4	1.089	1.089	C_3-H_4	1.086	1.095
C_3-H_6	1.093	1.093	C_3-H_6	1.094	1.091
C_3-H_7	1.093	1.093	C_3-H_7	1.094	1.091
Bond angle (°)			Bond angle (°)		
O_5=C_2-C_3	123.465	122.475	C_2-O_1-H_8	110.859	115.782
O_5=C_2-S_1	122.265	119.636	O_1-C_2-C_3	111.002	113.023
C_2-S_1-H_8	94.174	97.459	O_1-C_2=S_5	122.720	120.098
C_3-C_2-S_1	112.946	116.844	C_3-C_2=S_5	109.465	109.566
C_2-C_3-H_4	109.063	110.260	C_2-C_3-H_4	109.465	109.565
C_2-C_3-H_6	110.024	110.424	C_2-C_3-H_6	107.934	110.551
C_2-C_3-H_7	110.024	110.424	C_2-C_3-H_7	109.375	109.365
H_4-C_3-H_6	110.260	109.063	H_4-C_3-H_6	109.465	108.966
H_4-C_3-H_7	109.063	109.063	H_4-C_3-H_7	109.465	108.966
H_6-C_3-H_7	107.960	109.280	H_6-C_3-H_7	107.934	108.001
Dihedral angle(°)			Dihedral angle(°)		
O_5=C_2-C_3-H_4	0.000	0.000	O_1-C_2-C_3-H_4	0.0	0.0
O_5=C_2-C_3-H_7	120.000	119.999	O_1-C_2-C_3-H_6	121.263	121.263
O_5=C_2-C_3-H_8	-120.000	-119.999	O_1-C_2-C_3-H_7	-121.265	-121.265
S_1-C_2-C_3-H_4	180.000	180.000	S_5=C_2-C_3-H_4	180.0	180.0
S_1-C_2-C_3-H_6	-59.999	-60.000	S_5=C_2-C_3-H_6	-58.566	-58.566
S_1-C_2-C_3-H_7	-59.999	-60.000	S_5=C_2-C_3-H_7	58.566	58.566
C_3-C_2-S_1-H_8	180.000	0.000	H_8-O_1-C_2-C_3	180.0	0.0
O_5=C_2-S_1-H_8	0.000	180.000	H_8-O_1-C_2=S_5	0.0	180.0

The calculated B3LYP/6-311++g(d,p) wavenumbers and IR intensities for the ***syn***-thiol and ***anti***-thiol conformers of thioacetic acid were shown in Figure 5 and they were given in Table 4 together with the experimental data [14] and IR intensities for the ***syn***-thione and ***anti***-thione conformers of thioacetic acid were included in Table 5. The molecule has 8 atoms and 18 normal modes of fundamental vibrations which were shown in Table 4. Experimental matrix isolation spectra of thioacetic acid were previously studied in an argon matrix at 15 K and theoretical calculation was done by using B3LYP/6-31+G* basis set by Romano and coworkers [14]. The calculated IR spectra we obtained by B3LYP/6-311++g(d,p) basis set fitted nicely the experimental results which were reported in that study.

Table 4. Experimental wavenumbers (ν (cm^{-1})) and relative integral intensities (*I*) of the absorption bands of matrix isolated thioacetic acid ($CH_3C(=O)SH$), compared with wavenumbers (ν (cm^{-1})), absolute intensities (A^{th} (km·mol^{-1})) and B3LYP/6-311++G(d,p) theoretically calculated for ***syn***-thiol conformer of the compound.

Assignment vibrational mode	***syn***-thiol		***anti***-thiol		Argon matrix[c]	
	$\nu^{a,b}$ (cm^{-1})	A^{th} (km mol^{-1})	$\nu^{a,b}$ (cm^{-1})	A^{th} (km mol^{-1})	ν (cm^{-1})	*I*
2ν (C=O, *anti*)					3444.0	
2ν (C=O, *syn*)					3432.0	
ν (CH_3) as	3072.5	5.0	3070.8	6.8	3020.6	0.050
ν (CH_3) as	3040.0	3.9	3039.2	3.3	2986.2	0.025
ν (CH_3) s	2974.0	0.7	2974.0	1.4	-	-

ν (S-H)	2622.5	0.4	2610.6	4.6	2606.5	0.134
OCS					2049.6	0.004
ν (C-O) +ν (C-S)					1749.2	0.711
ν (C=O, *syn*)	1751.1	334.9			1722.5	3.045
ν (C=O, *anti*)			1754.2	358.9	1728.7	0.537
δ (CH_3) as	1443.7	121.8	1442.7	15.1	1441.2 1435.5	0.163
δ (CH_3, *anti*) as			1435.8	11.5	1426.6	0.022
δ (CH_3, *syn*) as	1432.6	15.0			1422.2	0.455
δ (CH_3, *syn*) s	1357.9	25.2			1355.2	0.372
δ (CH_3, *anti*) s			1355.2	24.4	1353.0	0.035
ν (C-C)	1108.8	153.5	1114.9	151.8	1126.6	2.976
γ (CH_3)	1005.6	4.8	1006.3	0.8	1056.6	0.064
γ (CH_3, *anti*)			978.3	31.5	987.2	0.042
γ (CH_3, *syn*)	981.6	40.0			983.6	0.543
δ (CSH)	822.3	30.3	822.8	21.9	821.8 819.9 814.4	0.340
ν (C-S, *syn*)			604.8	72.1	624.5	0.102
ν (C-S, *anti*)	600.8	85.4			617.3 614.7	1.291
γ (C-O)	512.7	3.0	517.4	0.0	-	
δ (OSC, *syn*)	431.5	3.4			445.4	0.035
δ (OSC, *anti*)			415.6	7.1	427.6	
τ (HSCO, *syn*)	355.8	21.0			350.7	0.147
τ (HSCO, *anti*)			329.1	0.1	-	-
δ (CCS)	313.8	6.1	297.7	14.1	-	-
τ (CH_3)	56.1	0.1	90.0	0.1	-	-

[a] wavenumbers of the strongest bands were underlined.

[b] theoretical wavenumbers were scaled by a factor of 0.978.

[c] Ref 14.

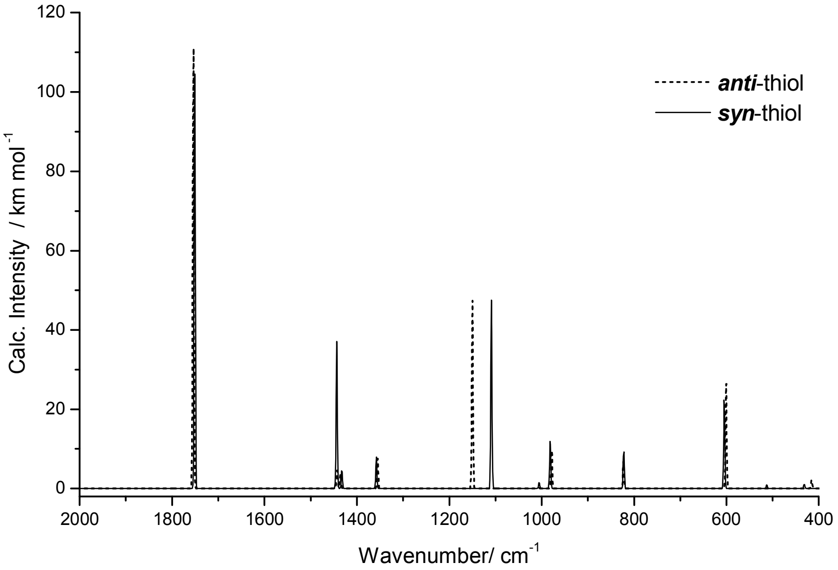


Figure 5. Theoretical spectra of ***syn*** and ***anti***-thiol conformer of the thioacetic acid calculated at the DFT/B3LYP/6-311++G(d,p) level. The calculated wavenumbers were scaled by a factor of 0.978 (between 2000-400 cm^{-1}).

Table 5. The wavenumbers (ν (cm^{-1})) and absolute intensities (A^{th} (km·mol^{-1})) theoretically calculated by DFT(B3LYP)/6-311++g(d,p) of ***syn*** and ***anti***-thione conformers of thioacetic acid ($CH_3C(=S)OH$) .

Assignment vibrational mode	***syn***-thione		***anti***-thione	
	ν^a (cm^{-1})	A^{th} (km mol^{-1})	ν^a (cm^{-1})	A^{th} (km mol^{-1})
ν(O-H)	3691.6	58.0	3678.7	54.3
ν(HCH_2)s	3098.0	2.2	3093.0	1.1
ν(HCH_2)as	3017.6	4.0	2991.9	8.1
ν(CH_3)	2966.9	4.6	2942.0	13.7
δ(HCH_2)as	1452.9	24.1	1450.4	11.1
δ(HCH_2)s	1440.6	11.8	1447.4	18.8
δ(CH_3)s+ν(C-C)	1379.3	102.0	1373.1	117.6
δ(CH_3)as+ν(C-C)	1354.3	147.8	1364.3	7.9
δ(COH)+γ (CH_3)+ν(C-O)	1263.3	254.2		
δ(COH)+γ (CH_3)+ν(C-C)			1230.6	347.6
γ (CH_3) as+ν(C-C)	1085.0	95.7	1086.3	115.1
γ (CH_3) s	1006.1	0.0	1003.4	0.0
γ (CH_3) s+ν(C-O)	990.4	49.8	980.4	49.5
ν (C=S)+γ(CH_3)	719.1	1.7	717.3	0.9
δ(O-H)+γ(CH_3)	648.5	86.2	505.4	11.0
δ(OCS)+τ(O-H)+γ (CH_3)	496.8	10.4	449.9	5.4

γ (CC=S)+τ(C-O)+γ(CH_3)	445.6	17.1	445.2	108.1
δ (CC=S) + γ (CH_3)	368.1	1.5	375.4	0.5
τ (CH_3)	91.0	0.7	111.5	0.2

[a] theoretical wavenumbers were scaled by a factor of 0.978.

4. CONCLUSIONS

Energies and structures of thioacetic acid were investigated by using theoretical methods of quantum chemistry. In consonance with the theoretically predicted relative energies of the four conformers, ***syn***-thiol conformer was found to be the most stable one (***anti***-(thione)< ***syn***-(thione)< ***anti***-(thiol)< ***syn***-(thiol)). Taken into consideration the topology of the potential energy surface around the different minima and the calculated relative energies estimated at the DFT/6-311++g(d,p) level of theory (Table 1), the populations of ***syn***-thiol acid conformers were estimated for the gaseous phase equilibrium at room temperature (297 K) using the Boltzmann distribution equation. At room temperature the equilibrium mixture contains mainly two forms, ***syn*** (93.75%) and ***anti*** (6.25%) thiol acid. Barrier energies for conformational interconversion have been calculated using the density functional theory [DFT(B3LYP)/6-311++G(d,p)] method. Infrared spectra of thioacetic acid were investigated via density functional theory compared with matrix isolation spectroscopy. The results of spectra of thioacetic acid indicated in the present work are in good agreement with high levels of theory.

ACKNOWLEDGMENT

Our research group is greatly in debt to the Board of Scientific Research Projects of Eskişehir Osmangazi University for providing the Gaussian 03W program and we would like to thank Dr. Nihal Kuş for her kindly help to use the program.

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