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Density Functional Theory Studies of the Structures, Energetic and Harmonic Vibrational Frequencies of 5-thioxo-1,4,2-thiazasilolidin-3-one Tautomersin Gas phase andWater.

Thesis

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بسم الله الرحمن الرحيم

﴿ وَيَسْأَلُونَكَ عَنِ الرُّوحِ ۖ قُلِ الرُّوحُ مِنْ أَمْرِ رَبِّي وَمَا أُوتِيتُم مِّنَ الْعِلْمِ إِلَّا قَلِيلًا ﴾

صدق الله العظيم

TO MYdaughters

RenadRemasAnd Reman

your mother

ABSTRACT

The structure, thermodynamic and reactivity of5-thioxo-1,4,2-thiazasilolidin-3-oneisomers were studied in the gas phaseusing density functional theory and complete basis set (CBS-Q). Eight local minimum structure were located (S1-S8) . The global minimum at the B3LYP/6-31++G(dp) // B3LYP/6-31G(d), CBS-Q levels of theory is S5. Natural bond orbital (NBO) analysis reveals that the *S2* has a strong Si-S3 interaction with small d contribution, where as structure *S6* shows a strong Si-S3 bond with substantial d contribution. There is a strong $n_{O6} \rightarrow \sigma^{*}_{C2-N5}$ interaction in most of the structures. For example, the second order energy for *S1* is (40.67 kcal/mol). This interaction increases the C_2-N bond strength and elongates theC_4-N bond length. The bond critical point (BCP) results showed that for all Si-C2 and Si-H bonds the Laplacian is positive. These values strongly support the assumption that bonding between silicon atom and carbon C2 and hydrogen attached to the silicon atoms is predominantly ionic .This result is supported by the natural atomic charges since the silicon atoms bear high positive charges, while the oxygen, nitrogen and hydrogen attached to the silicon atoms have negative charges. The solvation of the structures was calculated using SCRF keyword with Tomasi's polarized continuum (PCM) model. The hydration reactions showed a high equilibrium constant values which means that the reactions at this temperature favor the products. The solvation process has no effect in the order of stability in comparison with the gas phase investigation. The geometries of 5-thioxo-1,4,2-thiazasilolidin-3-one and its isomers were completely reoptimized at MP2(FC)/6-31G(d) level within the

CBS-Q theory. ΔH and ΔG are reported related to S5 in the 5-thioxo-1,4,2-thiazasilolidin-3-one molecule because *S5* possessed the lowest ΔH and ΔG values. The S2OAshowed the highest relative enthalpy and S3SAshowed the highest relative Gibbs free energy (ΔH= 24.65 kcal/mol, ΔG=24.32 kcal/mol) in the anions section and the *S2NC* showed the highest relative enthalpy and Gibbs free energy (ΔH= 50.25 kcal/mol, ΔG=47.07 kcal/mol) in the cations section. Finally, the calculated frequencies of optimized structures showed the OH stretching frequencies in *S1, S2, S3, S4* and *S8* are in the range of (3474-3606 cm^{-1}) consistent with the usual OH frequency in the absence of hydrogen bonding. The shift in *S8* (3474 cm^{-1}) towards the lower frequency can be attributed to the charge delocalization over nitrogen and oxygen atoms. The SiH and SH vibrational frequencies are in agreement with the experimental values reported previously.

<u>Acknowledgement</u>

*In the name of **Allah** , most gracious, most merciful. A. word of thanks giving to god , the source of all knowledge, by whose abundant grace this work has   come to fruition.*

*I would like to express my greatest appreciation and indebtedness to the person who always ease the difficulties and solve the problems that obstruct my way toward the best to candles burning to light my way , My **Mother** and ask god to sustain her with health and extend her live*

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AIM OF STUDY

The aim of this study is to provide a consistent and reliable set of gas-phase structures and in aqueous solution for the 5-thioxo-1,4,2-thiazasilolidin-3-one and its cations and anions using different level theories. The supervisor has been investigating the proton transfer (PT) process for numerous acyclic compounds, so there is attraction to switch to cyclic heterocyclic compound. Of particular interest are molecular geometries, activation barriers, natural bond orbital analysis, enthalpies, Gibbs free energies, vibrational frequencies and how these properties change upon isosteric substitution of the carbon atom in 2-thioxothiazolidin-4-one (rhodanine) molecule by silicon.

الهدف من الدراسة

الهدف من هده الدراسة هو الحصول علي تراكيب موثقه و ثابتة لمركب 5-thioxo- 1,4,2-thiazasilolidin-3-one وايوناته الموجبة والسالبة في الحالة الغازية وكذلك محلوله المائي و تحت مستويات نظريه مختلفة , في إطار انتقال البروتون (PT)

للمركبات الحلقية , والاهتمام بهندسة الجزيئات و نشا طها وطبيعة المدرات الرابطة و المحتوي الحراري و طاقاتها والترددات الهتزازيه و كيفية تغيير خواص الجزيئات عند استبدال درة الكربون في مركب 2-thioxothiazolidin-4-one (الرودنين) بدره السليكون

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ABBREVIATION

SE: Schrödinger equation

BO: Born-Oppenhiemer approximation

HF: Hartree-Fock

DFT: Density functional theory

AO :Atomic Orbitals

TST: Transition State theory

PES: Potential energy surface

BS: Basis set

STO : Slater type orbital

GTO : Gaussian type orbital

LCAO: Liner combination of atomic orbitals

CBS-Q :Complete basis set

B$_3$lyp :Becke three Lee–Yang

NBO : Natural bond orbital

NHOs :Natural hydride orbitals

E$^{(2)}$: Second- order delocalization energy

QTAIM : Quantum theory atoms in molecules

PCM :Polarized continuum model

ZPVE : Zero point vibration energy

RMSD: Root mean square deviation

SCRF: Self consistent reaction filed

CHAPTER ONE

INTRODUCTION

1.1 Theoretical Chemistry

Chemistry is a part of the physical science dealing with construction, transformation and properties of molecules. The subfield where mathematical methods are combined with fundamental laws of physics to study process of chemical relevance is known as theoretical chemistry. The computational chemistry is a branch of theoretical chemistry that uses a digital computer to model systems of chemical interest and also defined as a branch of chemistry that uses the results of theoretical chemistry incorporated into efficient computer programs to calculate the structures and properties of molecules. Examples   of   such properties are structure ,energy, dipole moment, vibrational frequencies, reactivity, heats of formation and ionization potentials [1,2].

1.2 The Theories

1.2.1 The Schrödinger equation

The Schrödinger equation is one of the fundamental equations of quantum mechanics. The Schrödinger equation takes several different forms depending on its physical situation. The Schrödinger equation gives the wave functions and energies of a molecule.

1.2.1.1 Time–dependent equation:

This is the equation of motion for the quantum state, in the most general form it is written as:

$$i\mathbf{h}\frac{\partial}{\partial t}\Psi(x,t)=\hat{H}\Psi(x,t)..(1.1)$$

Where, $\hat{H}$ is Hamiltonian operator acting on wave function Ψ x is the position (x,y,z).

t is the time.

i is square root of -1.

ℏ is a Planck's constant divided over 2π.

1.2.1.2 Time–independent equation:

This equation is used for the standing waves the eigenvalue equation for H abstract form, for a general equation system it is written as[2,8]

$$Hy = Ey \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1.2)$$

Where H is the molecular Hamiltonian, Ψ is the wave function, and E is the energy.

1.2.2 Born-Oppenheimer approximation

Under typical physical conditions the nuclei of molecular systems are moving much more slowly than the electrons (recall that protons and neutrons are about 1836 times more massive than electrons) and note the appearance of mass in the denominator of the kinetic energy terms of the Hamiltonian. For practical purposes electronic relaxation with respect to nuclear motion is instantaneous.

$$\text{H} \quad = \quad -\sum_i \frac{\mathbf{h}^2}{2m_e}\nabla_i^{\,2} - \sum_k \frac{\mathbf{h}^2}{2m_k}\nabla_k^{\,2} - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k>l} \frac{e^2 Z_k Z_L}{r_{kL}} \dots\dots\dots(1.3)$$

Where, i and j run over electrons, k and *l* run over nuclei,

m_e is mass of the electron,

m_k is mass of the nucleus k,

∇^2 is the laplacian operator,

e is the charge on the electron,

Z is an atomic number

r_{KL} is the distance between particles K and L.

As such, it is convenient to decouple these two motions and compute electronic energies for fixed nuclear positions. That is the nuclear kinetic energy term is taken to be independent of the electrons correlation in the attractive electron-nuclear potential

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energy term becomes a simply evaluated constant for a given geometry. Thus according to the theory[9], the electronic Schrödinger equation is taken to be:

$$(H_{el} + V_N)\Psi_{el}(q_i, q_K) = E_{el}\,\Psi_{el}(q_i, q_K) \dots\dots\dots\dots\dots\dots\dots(1.4)$$

Where the subscript (el) emphasizes the invocation of the Born-Oppenheimer approximation, H_{el}, V_N is the nuclear-nuclear repulsion energy, q_i electronic coordinates, q_k nuclear coordinates, and without the Born-Oppenheimer we would lack the concept of a potential energy surface.

1.2.3 Hartree-Fock

The Hartree-Fock method assumes that the exact N-body wave functions of the system can be approximated by a single Slater determinant. The Hartree-Fock method finds its typical application in the solution of the electronic Schrödinger equation for atoms, molecules and solids. The Hartree-Fock is typically used to solve the time-independent Schrödinger equation for a multi-electron atom or molecule as described in the Born-Oppenheimer approximation. Since there are no known solutions for many-electron systems (the diatomic hydrogen cation being notable one-electron exceptions), the problem is solved numerically. The Hartree-Fock method makes five major simplifications in order to deal with this task.

Firstly, the Born-Oppenheimer approximation is inherently assumed. The full molecular wave function is a function of the coordinates of each nuclei, in addition to those of the electrons. Secondly, relativistic effects are completely neglected .The momentum operator is assumed to be completely non-relativistic. Thirdly, the variational solution is assumed to be a linear combination of a finite number of basis functions which are usually (but not always) chosen to be orthogonal. The finite basis set is assumed to be approximately complete. Fourthly, each energy eigenfunction is assumed to be describable by a single Slater determinant ,an anti-symmetrized product of one-electron wave-functions (orbitals). Finally, the mean-field approximation is implied. Effects arising from deviations from this assumption, known as electron correlation, are

completely neglected. This assumption can lead to large deviations from experimental results.

The starting point for the Hartree-Fock method is a set of approximate one-electron wave functions known as spin-orbitals. For an atomic orbital calculation, these are typically the orbitals for a hydrogenic atom. For a molecular orbital or crystalline calculation, the initial approximate one-electron wave functions are typically a linear combination of atomic orbitals (LCAO). The orbitals above only account for the presence of other electrons in an average manner.

In modern Hartree-Fock calculations, the one-electron wave functions are approximated by a linear combination of atomic orbitals. These atomic orbitals are called Slater-type orbitals. Furthermore, it is very common for the atomic orbitals in use to actually be composed of a linear combination of one or more Gaussian-type orbitals rather than Slater-type orbitals, in the interest of saving large amounts of computation time. Among the five simplifications outlined under Hartree-Fock algorithm, the fifth is typically the most important neglecting electron correlation can lead to large deviations from experimental results.[9,10]

1.2.4 Density Functional Theory

The basis for density function theory is the proof by Hohenberg and Koh[11] that the ground-state electronic energy is determined completely by the electron density $"\rho"$. A wave function for an N-electron system contain 3N coordinates ,three for each electron The electron density is the square of the wave function , integrated over N-1 electron coordinates, this only depends on three coordinates , independently of the number of electrons. The goal of DFT methods is to design function connecting the electron density with the energy. A function is a prescription for producing a number from a set of variables (coordinates).A functional is similarly a prescription for producing a number from a function, which in turn depends on variables. A wave function and electron density are thus functions, while an energy depending on a wave function or an electron density is a functional .

A function: is a prescription for producing a number from a set of variables (coordinates). A functional is similarly a prescription for producing a number from a function.

A function depending on: a set of variables with parentheses f(x), while a functional depending on a function is denoted with brackets F[f].

The energy functional may be divided into three parts, kinetic energy T $[\rho]$, attraction between the nuclei and electrons, $E_{ne}[\rho]$ and electron-electron repulsion $E_{ee}[\rho]$, (the nuclear-nuclear repulsion is a constant in the Born-Oppenhiemer approximation) furthermore, the $E_{ee}[\rho]$ term may be divided into a coulomb and an exchange part J $[\rho]$ and K$[\rho]$, implicitly including correlation energy in all terms. The $E_{ne}[\rho]$ and J $[\rho]$ functionals are given by their classical expressions, where the factor of 1/2 in J $[\rho]$ allows the integration to run over all space for both variables. [1]

The foundation for the use of DFT methods in computational chemist was the introduction of orbital's by Kohn and Sham. The basic idea in the Kohn and Sham formalism is splitting the kinetic energy functional into two parts

-One of which can be calculated exactly

-A small correction term

$$H_1 = T + V_{ext}(1) + 1V_{ee} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1.5)$$

The key to the Kohn and Sham theory is thus the calculation of the kinetic energy under the assumption of non-interacting electrons.

The same of HF orbitals in wave mechanics, the HF theory provides ~ 99% of the correct answer. The difference between the exact kinetic energy and that calculated by assuming non-interacting orbital is small. The remaining kinetic energy is absorbed into an exchange-correlation term , and a general DFT energy expression can be written as[1]

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \dots\dots\dots (1.6)$$

$T_S[\rho] = $ kinetic energy calculated from a slater determinat

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$E_{ne}[\rho]$= attraction between the electron-nuclei

$J[\rho]$ = term of the potential energy

$E_{xc}[\rho]$ = the exchange and correlation energy

$E_{xc}[\rho]$=($T[\rho]$ - $T_S[\rho]$) + ($E_{ee}[\rho]$ - $J[\rho]$)

($T[\rho]$ - $T_S[\rho]$)= the kinetic correlation energy

($E_{ee}[\rho]$ - $J[\rho]$) = exchange and potential correlation energy

1.2.5 The basis sets

      The basis set is defined as the set of mathematical function from which the wave function is constructed , where is each MO in HF theory is expressed as a Linear combination of basis function, the coefficients for which are determined from the iterative solution of the HF self consist field equation. There are two types of basis functions (also called Atomic Orbitals, AO although in general they are not solutions to an atomic Schrödinger equation) commonly used in electronic structure calculations. Slater type orbitals (STO) and Gaussian type orbital (GTO).

Slater type orbitals[12] have the functional form:

$$STO = \frac{z^3}{p^{0.5}} e^{(-zr)} \dots\dots\dots\dots\dots\dots\dots\dots (1.7)$$

Slater type orbitals do not have any radial nodes; nodes in the radial part are introduced by making linear combinations of STOs. Slater type orbitals are primarily used for Gaussian type orbitals[13] can be written in terms of polar or Cartesian coordinates.

$$GTO = \frac{2c}{p^{0.75}} e^{(-cr^2)} \dots\dots\dots\dots\dots\dots\dots(1.8)$$

1.2.5 .1.Classification   of basis set:

Having decided on the type of function (STO / GTO) and the location (nuclei), the

most important factor is the number of functions to be used. The smallest number of

functions possible is minimum basis set, only enough functions are employed to

contain all the electrons of neutral atoms. The next improvement in the basis set is

a doubling of all basis functions producing extended basis set, polarization functions

higher angular momentum functions are also important. Once a p-orbital has been

added to hydrogen S-orbital, it may be argued that the p-orbital now should be

polarized by adding a d-orbital, which should be an f- orbital, …etc.

   For   single   determinant   wave functions, where electron   correlation   is   not

considered, the first set of polarization functions (p-functions for hydrogen and d-

function   for heavy atoms) is by far the most important, and will in general describe

all the important   charge polarization effects[14].

1.2.6 The linear combination of atomic orbitals (LCAO)

     Quantum mechanics systems have temporarily restricted to systems of one
electron, if in addition, these systems were to have only one nucleus, then we   would
not need to guess wave functions, but instead we could solve Born-Oppenheimer
equation   exactly. The eigenfunction that are determined in that instance are the
familiar hydrogenic atomic orbitals, 1s, 2s, 2p, 3s, 3p, 3d.etc;we will not investigate the
mathematical representation but will simply hypothesize that, as a function they may
be useful in the construction of more complicated molecular orbitals. We constructed a
guess wave function f as a linear combination of atomic wave functions j_i.

$$ f \ = \ \sum_{i=1}^{N} \ a_{\ i} j_{\ i} \ \ldots\ldots..\ldots\ldots\ldots\ldots\ldots..(1.9) $$

Where, the set of N functions $j_{\ i}$ is called the ' basis set ' and each has associated with it some coefficient a_i. This construction is known as the linear combination of atomic orbitals (LCAO) approach. One should also note that the summation in the previous equation has an upper limit N; we cannot work with an infinite basis in any convenient way[9].

1.2.7 Potential Energy Surface.

The course of a chemical reaction is determined by the potential-energy function for nuclear motion U(q) where q indicates the coordinates of the N nuclei of the reactant molecules. For two atoms coming together to form a diatomic molecule, U is a function of one variable, the inter nuclear distance R, and U(R) is the usual potential-energy curve. for more interesting chemical reaction, U is a function of 3N-6 variables, we subtract 6 because the three translational and three rotation degrees of freedom of the system leave U uncharged. for a two –atom system , there are only two rotational degrees of freedom U give what is called the potential-energy surface (PES) for the reaction. If U depends on two variables ,then a plot of U(q,q) in three dimensions give a surface in ordinary three-dimensional space, because of the large number of variables , U(R) is a surface in an abstract space of 3N-5 dimensions. To find U(R) ,we must solve the electronic Schrodinger equation at a large number of nuclear configuration , a truly formidable task. Once U is found, we look for the path of minimum potential energy on U connecting reactants and products. The point of maximum potential energy U on the minimum-energy path is called the transition state; this is a saddle point on the U surface ,since it is a maximum point on a minimum-energy path. The transition state is not a stable structure and the transition from reactants to products is a smooth one, or the reverse reaction the surface U is the same as for the forward reaction[9].

1.2.8 Transition state theory (TST)

Transition state theory is developed in the early 1930s by Eyring[15]. It assumes that a reaction proceeds from one energy minimum to another via an intermediate maximum. The transition state is the configuration which divides the reactant and product parts of the surface (molecule which has reached the transition state will continue on to product) while the geometrical of the energy maximum is called transition structure. Within standard TST the transition state and transition structure are identical, but this is not necessarily the case for more refined models. The reaction proceeds via a (reaction coordinate) usually taken to be negative at reactant zero at the TS and positive for the product. Transition state theory assumes an equilibrium energy distribution among all possible quantum states at all points along the reaction coordinate. The probability of finding a molecule is a given quantum state is proportional to

$$ e^{-\Delta E / K_B T} $$ ………………..………………. (1.10)

This is Boltzman distribution. Assuming that the molecule at the TS is in equilibrium with the reactant, the microscopic rate constant can be expressed as:

$$ K = K_B T / h \ e^{-\Delta G^{\#}/RT} $$ ………………………(1.11)

Where, $\Delta G^{\#}$ is the activation Gibbs free energy difference between the TS and reactant.

k_B is Boltzman's constant.

h is a Planck's constant.

R is a gas constant and

T is the absolute temperature.

k is the reaction rate constant, from the TST expression.

If the free energy of the reactant and TS can be calculated, the reaction rates follow trivially, so that the equilibrium constant for a reaction can be calculated from the free energy difference between the reactants and products.

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$$K_{eq} = e^{-\Delta G° /RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1.12)$$

The Gibbs free energy is given in term of the enthalpy and entropy[1]

$$\Delta G = \Delta H - \Delta TS \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1.13)$$

1.3 The Chemistry of Rhodanine and Rhodanine derivatives

Rhodanine (2-thioxothiazolidin-4-one) and rhodanine derivatives are used as vulcanizing agents, pharmaceuticals and intermediates in the synthesis of dyes. The absorption spectra of rhodanine have been studied in connection with interesting physiological properties of some

4-thiazolidone derivatives [16]. Another interesting aspect of the chemistry of these compounds is their donor ability toward metal ions, which makes them suitable as ligands in coordination compounds[17]. Rhodanine and its derivatives are used as highly sensitive reagents for the elements of Pt, Pb and Hg[18,19].

The prototropic tautomerism and rotamerization of heterocyclic compounds are including, in particular, biologically active compounds, is of great importance in many areas of chemistry and biochemistry. The term (tautomerism) refers to a compound existing in an equilibrium between two or more isomeric form called tautomers[20,21], and biological activities including antibacterial[22,23],antiviral[24],antidiabetical[25] and anti-inflammatory action[26]. These compounds are also used in analytical chemistry as highly sensitive reagents for heavy metals[27,28]. Again the rhodanine and it derivatives have been used as highly sensitive and selective reagents for Pt, Pd[29,30] and Ag[31.32].

Semiempirical (MINDO/3 ,AMI ,MINDO ,PM3) and ab initio calculations on the relative stabilities and structures of the five potential tautomeric forms of rhodanine are considered, it is shown that all methods excepting (PM3) predict that the 2-thioxo-4-thiazolidnone is the most stable structure, these results especially those extracted from AM1 are comparable with the know experimental infrared spectrum of

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rhodanine, the transition states between five pairs of all possible tautomeric forms of the rhodanine were found by the AMI method[33]. Eleven tautomers and rotamers of rhodanine were studied, the optimized geometrical parameters of all the eleven forms were computed and compared with the available X-ray results, The thermodynamic parameters for the eleven forms were calculated in the gas phase and water utilizing PCM method. Tautomer R1 is the most stable tautomer in all cases both in gas phase and in aqueous solution as also known from experimental data. Consideration of the solvent causes some reordering of the relative stability of rhodanine conformers. Energy barriers of rotamerization processes are only that for the proton transfer tautomerization processes[34].

Prototropic tautomerism of substituted thiazolidine and oxazolidine heterocycles were studied theoretically attheB3LYP/6-311G(2d,p)level. The thermodynamic parameters for the molecules were calculated in the gas phase and in two different solvent utilizing IPCM methods. The study revealed that the same tautomer is the most stable both in gas phase and in solution (DMSO and cyclohexane)[35]. The steady state absorption and emission studies of the rhodanine derivative((5-(dimethylaminobenzylidene)rhodanine)) have been investigated. Adual fluorescence associated with an intramolecular charge transfer (ICT) phenomenon is reported. In support of the experimental results ab initio and DFT calculations have been performed. The theoretical calculations also indicate that the chosen compound has significant non-linear optical (NLO) properties[36]. The structure of rhodanine has been determined by three dimensional Fourier and least squares methods using an I.B.M electronic computer the crystal structure showed that the molecule is planar, and there are two strong N….O hydrogen bonds around the center of symmetry, binding the molecules in pairs[37]. A novel use of cluster analysis is presented to compare the output from different levels of theory. The relative energies of the tautomer of methylidene

rhodanine (5-methylene-2-thioxo-thiazolidin-4-one) computed by the semiempirical molecular orbital method AM1 are remarkable similar to ab initio values which involves effective core potentials augmented by plarization and diffuse function[38].A new series of rhodanine based on phosphodiesterase-4 inhibitors is described. The structure-activity relationship directed toward improving potency led to the development submicromolar inhibitors.Thereplacementofrhodaninewithtructurallyrelatedheterocyclicwas alsoconsidered[39].Thepush-pullbehaviorofnovel2-(1,1-dicyanomethylene)rhodanine bearing an electron donor N,N-dimethyl aniline or tetra thiafulvene group on the C-5 of the heterocyclic ring was studied using electrochemical, spectroscopic analysis and theoretical methods. Calculations showed a remarkable push-pull trend with the HOMO mainly located on the donor moiety and the LUMO on the acceptor dicyanomethylene moiety. In agreement with the theoretical predictions ,a solvatochromic behavior intramolecular charge transfer band was observed in the visible region[40].

CHAPTER TWO

EXPERIMENTAL SECTION

2.1 The Machine

The calculations were preformed for both gas and aqueous phases using DELL OPTIPLEX 320 Pentium 4 (CPU 3 GHz and 2GB RAM) computer.

2.1.2 The Software(s)

2.1.2.1 The Gaussian 03W Software

Gaussian 03W is one of the latest in the Gaussian series of electronic structure program. Gaussian 03W Version 6, was made by Gaussian Inc. (1995-2004). The Gaussian program predicts the energies, molecular structures and the vibrational frequencies of molecular systems, along with numerous molecular properties derived from these basic computation types. It can be used to study molecules and reactions, including stable and unstable species or non-observable species such as (short-lived intermediates and transition stat structures).

2.1.2.2 The Chemcraft Software

Chemcraft windows version is used to read the Gaussian output files. It is a graphical program for working with quantum chemistry computations. It is a convenient tool for visualization of computed results and preparing new jobs for the calculation. Chemcraft is mainly developed as a graphical user interface for Gamess and Gaussian program packages.

2.2 The Methodology Section

The calculations investigated the relative stabilities of the various isomeric forms of (5-thioxo-1,4,2-thiazasilolidin-3-one)and the reaction paths leading from one structure to another. Even though, numerous experimental and theoretical properties have been reported (as mentioned in the previous chapter)for 2-thioxothiazolidin-4-one (rhodanine) in the literature, we have failed to find any reported experimental or theoretical results of 5-thioxo-1,4,2-thiazasilolidin-3-one.The root mean square deviation (RMSD) analysis has been used to validate our methodology by comparing the X-ray structural

data of 2-thioxothiazolidin-4-one with eight structural data which are reproduced by using different basis sets including three basis sets with effective core potential, different exchange and correlation functional also employed. No identical (RMSD=0) structure was found but 6-31G(d) basis set is produced a comparable variables, The nature of the structure may impose certain specific requirements for packing within the crystal structure that would not be mimicked by any gas-phase calculation. The monomer-monomer specific interactions, such as hydrogen bonding or strong London dispersion interactions between atoms on separate neighboring molecules may reveal that the crystal packing forces are causing the gas-phase structure to be slightly different.

Therefore, all DFT calculations were performed with the B3LYP three parameter density functional, which includes Becke's gradient exchange correction[41] and the Lee–Yang–Parr correlation functional[42,43]. The geometries of all conformers, products and transition states were fully optimized at the B3LYP/6-31G(d) level of theory. This was followed by harmonic frequency calculations at this level ; the optimized structures were confirmed to be real minima by frequency calculation (no imaginary frequency). The vibrational frequencies were scaled by a factor of 0.9614 as introduced by Radom[44]. The zero-point vibrational energy contribution is also considered. Single-point calculations were then performed at the B3LYP/6-31++G(d,p) level for the geometries optimized at the B3LYP/6-31G(d) level.

Natural bond orbital analysis was then performed using the NBO 3.1 program[45] included in GAUSSIAN 03 package of programs at B3LYP/6-311++G(d,p) level of theory . Using this approach the orbital interactions can be quantitatively described in terms of the second-order perturbation interaction energy ($E^{(2)}$) [46,47]. The charge density generated at the B3LYP/6-311++G(d,p) level of theory has been analyzed using the quantum theory atoms in molecules (QTAIM) developed by Bader[48]. The charge density ($\rho(r)$) and Laplacian ($\nabla^2\rho(r)$) of the charge density at all bond critical points (BCPs) is considered.

Free energy of salvation of the structures was calculated using SCRF keyword with Tomasi's polarized continuum (PCM) model[49,52]. Mon-water molecule with dielectric constant (ε) of 78.39 has been used as a solvent.

The study included the analysis of the reaction enthalpies and Gibbs free energies. The geometries of 5-thioxo-1,4,2-thiazasilolidin-3-one and its isomers were completely optimized at MP2(FC)/6-31G(d) level within the CBS-Q theory[53,56]. The gas-phase basicity was defined as the enthalpy of protonation [$\Delta H(298)$] for reaction (2.1).

$$B(g) + H^+(g) \rightarrow BH^+(g) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2.1)$$

The enthalpy of protonation, ΔH_{298}, was computed using Eqs. (2.2) and (2.3).

$$\Delta H_{298} = \Delta E_{298} + \Delta(pV) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.2)$$

$$\Delta E_{298} = E_{298}(XH^+) - [E_{298}(X) + 3/2RT] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.3)$$

The gas-phase acidity was defined as the enthalpy of deprotonation (ΔH_{298}) for reaction below

$$AH\ (g)\ \rightarrow\ A^-\ (g) + H^+\ (g) \dots\dots \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2.4)$$

The enthalpy of deprotonation, ΔH_{298} was computed using the following two equations (2.5) and (2.6)

$$\Delta H_{298} = \Delta E_{298} + \Delta(pV)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2.5)$$

$$\Delta E_{298} = [E_{298}(A^-) + 3/2RT] - E_{298}(AH)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2.6)$$

Notice that there is an inverse relationship between the magnitude of the ΔH^{298} and the strength of the acid. E^{298} stands for the total energies of the most stable conformations of acids and their anions (including the thermal energy correction at 298.15 K). In equation 2, the substitution of $\Delta(pV)=-RT$ is carried out since, one mole of gas is lost in reaction 1). Again In equation 5, the substitution of $\Delta(pV)=RT$ is carried out since, one mole of gas is obtained in reaction 4). The equilibrium constants (K_{eq}) of the reactions were calculated from Gibbs free energies using $\Delta G= -RT\ln K_{eq}$. The calculations were performed using Gaussian03 version 6.0 package

CHAPTER THREE

RESULTES AND DISCUSSION

3.1. The Geometries

We have located eight local minima of 5-thioxo-1,4,2-thiazasilolidin-3-one *S1-S8*. We have also identified seven transition structures (*TS1* to *TS7*) that connect these minima via proton transfer. The eight local minima and seven corresponding transition structures are presented in Fig (1). The structural parameters (bond length) from the full optimized geometry of each of these stationary points are given in Table (1) , along with the bond order of the structures

| S1 | TS1 | S2 | TS2 |

| S3 | TS3 | S4 | TS4 |

| S5 | TS5 | S6 | TS6 |

| S7 | TS7 | S8 |
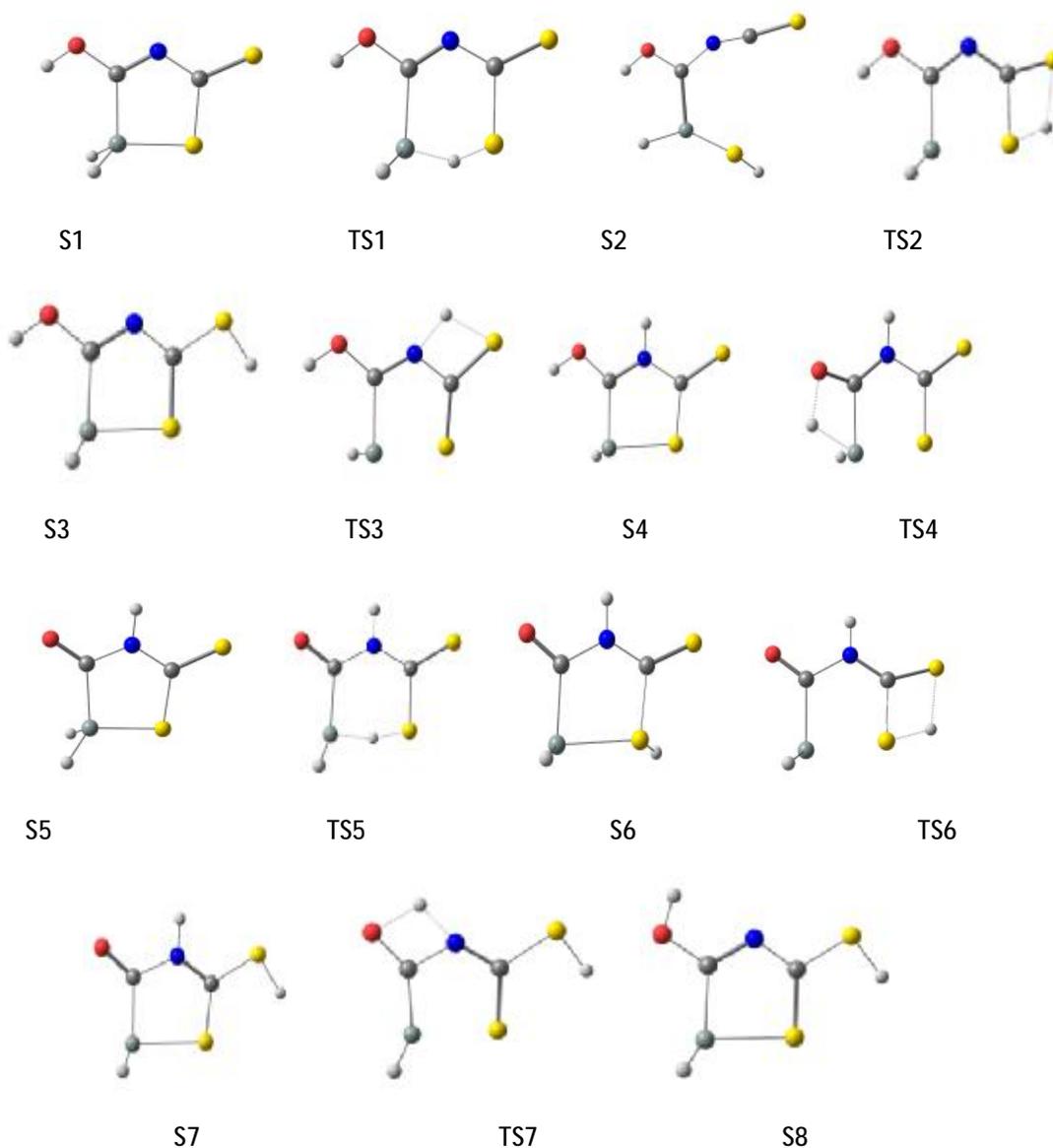
Fig 1: The compound structures and the transition states interconnecting them.

Table (1): Geometrical parameters of the structures, bond length (Ắ), bond order (in parentheses) at B3LYP/6-31G(d) level.

Sys.	Si1-S3	S3-C4	C4-S7	C4-N5	N5-C2	C2-O6	C2-Si1	Si-H	S-H	N-H	O-H
S1	2.128	1.857	1.635	1.376	1.288	1.342	1.928	1.485	-	-	0.970
	(0.994)	(0.997)	(1.766)	(1.174)	(1.635)	(1.099)	(0.800)	(0.913)			(0.758)
S2	2.175	-	1.573	1.209	1.349	1.346	1.857	1.504	1.350	-	0.974
	(0.957)		(1.964)	(1.838)	(1.164)	(1.090)	(1.188)	(0.882)	(0.964)		(0.745)
S3	2.256	1.735	1.758	1.326	1.333	1.338	1.923	1.512	1.350	-	0.972
	(0.792)	(1.285)	(1.162)	(1.389)	(1.368)	(1.118)	(0.983)	(0.881)	(0.964)		(0.754)
S4	2.261	1.746	1.651	1.412	1.335	1.333	1.912	1.515	-	1.020	0.972
	(0.805)	(1.215)	(1.643)	(1.021)	(1.302)	(1.126)	(0.974)	(0.870)	-	(0.759)	(0.736)
S5	2.166	1.800	1.643	1.378	1.401	1.215	1.926	1.481	-	1.018	-
	(0.918)	(1.087)	(1.713)	(1.120)	(1.077)	(1.770)	(0.806)	(0.925)	-	(0.759)	-
S6	2.403	1.869	1.635	1.342	1.458	1.212	1.968	1.519	1.348	1.019	-
	(0.572	(0.904)	(1.747)	(1.248)	(0.943)	(1.778)	(0.810)	(0.893)	(0.931)	(0.765)	-
S7	2.351	1.700	1.764	1.333	1.480	1.210	1.958	1.518	1.348	1.020	-
	(0.659)	(1.388)	(1.143)	(1.306)	(0.904)	(1.775)	(0.852)	(0.886)	(0.957)	(0.776)	-
S8	2.273	1.727	1.759	1.331	1.337	1.331	1.910	1.508	1.349	-	0.980
	(0.768)	(1.309)	(1.154)	(1.367)	(1.359)	(1.131)	(0.982)	(0.883)	(0.964)	-	(0.732)

The structural parameters from the full optimized geometry of the structures are given in appendixB. All the minima structures are exhibited cyclic structure except *S2* which was clearly acyclic species? The optimized structures at the B3LYP/6-31G(d) level of theory gave good agreement with the available experimental data for related compounds[57] since the extracted bond length of S-C, C=S, C-N and C=O are valued as 1.800Ắ (1.735Ắ), 1.642Ắ (1.645Ắ), 1.392Ắ (1.374Ắ) and 1.209Ắ (1.220Ắ) and the bond angles of SCN

and CNC are valued as $109.35°$ $(111.08°)$ and $120.47°$ $(117.69°)$ assigned for the *S1* structure and the X-ray structure.

the X-ray data are given between parentheses. The structures under consideration have not been observed experimentally .so the *S5* ,re-optimized at the different level of theory to examine the effect of a larger basis set and different exchange and correlation parameters on the geometries of the structures Appendix A. The root mean square deviation (RMSD) between structures optimized at the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels is very small (0.0065). Again the RMSD of 0.004 was extracted for the structures optimized at two different basis sets with effective core potential (SDD and LANL2DZ) routine. The opening of heterocyclic structure *S2* seems to concentrate the electronic density on C2-Si1 bond, and thus the C2-Si1 bond length was the shortest among the structures.

3.2. Charge Distribution and Dipole moment

The charge distribution of the structures in the gas phase has been examined using calculated natural bond orbital charges. Natural atomic charges for the minimum structures and the dipole moments obtained with B3LYP/6-311++G(d,p) method are shown in Table (2).

Table (2): Natural Atomic charges of the structures at B3LYP/6-311++G(d,P) level

Sys.	qSi1	qC2	qS3	qC4	qN5	qO6	qS7	qH_Si	qH_S	qH_N	qH_O	μ
S1	0.794	0.278	-0.089	-0.129	-0.521	-0.618	0.087	-0.139	-	-	0.477	6.09
S2	0.537	0.169	-0.384	0.228	-0.482	-0.629	0.114	-0.176	0.138	-	0.486	1.53
S3	0.402	0.255	-0.004	-0.073	-0.580	-0.624	0.177	-0.157	0.127	-	0.479	0.96
S4	0.411	0.279	0.012	-0.171	-0.600	-0.642	-0.043	-0.161	-	0.419	0.496	5.19
S5	0.829	0.355	-0.036	-0.116	-0.647	-0.547	-0.003	-0.130	-	0.423	-	2.32
S6	0.432	0.310	0.154	-0.075	-0.646	-0.566	0.006	-0.201	0.165	0.421	-	2.69
S7	0.414	0.317	0.029	-0.064	-0.638	-0.574	0.137	-0.181	0.153	0.408	-	5.44
S8	0.470	0.258	-0.001	-0.084	-0.626	-0.634	0.166	-0.153	0.130	-	0.477	2.69

It can be seen in Table (2) that the C4, N, O and H atoms attached to the silicon atom acquire negative charges, whereas the Si, C2 and the remaining hydrogen are positively charged. Natural population analysis indicated that charge distribution of all structures forms of 5-thioxo-1,4,2-thiazasilolidin-3-one shows that the C4, nitrogen and oxygen atoms have more negative charges, where as the hydrogen atoms of oxygen and nitrogen have positive charges. The result suggests that the atoms bonded to nitrogen or oxygen atoms are electron donors, and that charge transfer from hydrogen to oxygen or nitrogen is significant. In addition, the oxygen atom is the most negative in most compounds and as a result will most effectively interact with electrophiles *S1*, *S4* and *S7* have the largest dipole moments in the gas phase (6.09 D, 5.19 D and 5.44 D respectively). The dipole moment of *S3* was the lowest (0.96 D), and is notable that these dipole moments correlate with the stability of compounds: the dipole moment of *S1* is at least six times greater than that of *S3*, and the latter molecule is much less stable.

3.3. The Energy analysis

The potential energy surface for the conversion of *S1* to *S8* is plotted schematically in Fig (2).
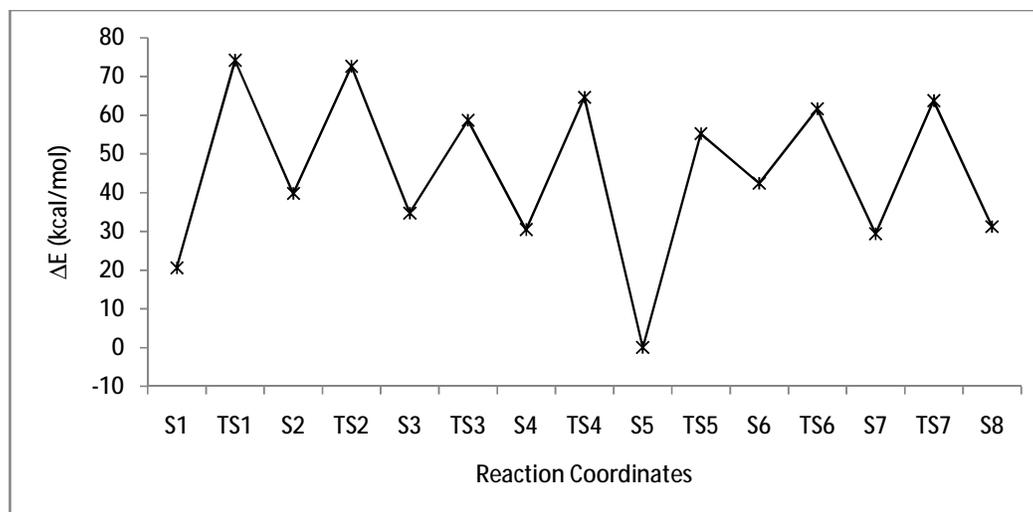
Fig (2): The relative energies of the structures and the transition states interconnecting

The *S5* structure is identified as the global minimum at all levels of calculations, and the energies of all other isomers are reported relative to *S2*. The *S5* structure has the same atoms arrangement in comparison with the X-ray structure of rhodanine. The relative energies are listed in Table (3). *S2* and *S6* have the highest energies (39.78 kcal/mol and 42.42 kcal/mol) above the global minimum *S5*, respectively and the overall stability order for the local minima is *S5 > S1 > S7 > S4 > S8 > S3 > S2 > S6*. The energy difference among the structures is no greater than a (63.72 kcal/mol).

Table (3): The total energy, ZPVE in Hartree, relative energy and activation energy, in (kcal/mol) and HOMO-LUMO gap in ev.

Sys.	Energy	Energy+ZPVE	ZPVE	ΔE	Ea	H-L g
S1	-1294.0002	-1293.9487	0.0515	20.58		3.413
TS1	-1293.9102	-1293.8633	0.0469	74.17	53.59	3.366
S2	-1293.9679	-1293.9181	0.0498	39.78		2.848
TS2	-1293.9134	-1293.8658	0.0476	72.60	32.82	3.455
S3	-1293.9777	-1293.9262	0.0515	34.70		3.320
TS3	-1293.9364	-1293.8880	0.0484	58.67	23.97	3.348
S4	-1293.9879	-1293.9330	0.0549	30.43		3.248
TS4	-1293.9274	-1293.8786	0.0488	64.57	34.14	3.639
S5	-1294.0338	-1293.9815	0.0523	0.00		4.083
TS5	-1293.9410	-1293.8935	0.0475	55.22	55.22	3.600
S6	-1293.9655	-1293.9139	0.0516	42.42		3.682
TS6	-1293.9305	-1293.8833	0.0472	61.62	19.20	3.450
S7	-1293.9855	-1293.9347	0.0508	29.37		3.275
TS7	-1293.9261	-1293.8800	0.0461	63.72	34.35	3.501
S8	-1293.9832	-1293.9318	0.0514	31.19		3.274

Note : Relative energy for structure S5

It is clear that the highest energy point is TS1, which lies (74.17 kcal/mol)above the global minimum, *S5* and is involved in the rate-determining step. The transition state

energies are not affected by the ring strain since,TS1 and *TS7* with a five-membered rings structure have the highest and lowest energies (74.17kcal/mol and 55.22kcal/mol) respectively. Furthermore, *TS2* and *TS3* with 3-membered rings showed the same energy pattern (72.60kcal/mol and 58.67kcal/mol) respectively. The transformation of *S1* to *S2* via *TS1* and *S5* to *S6* via TS5 involves a proton transfer from silicon to sulfur atom. These steps are involves the highest barriers of (53.59 kcal/mol and 55.22 kcal/mol) via *TS2* and *TS5* respectively. Judging from the transition barriers it seems that the highest energy barriers are assigned for the endothermic steps. Thus, *S5-TS5-S6* is the slowest reaction step and it is endothermic with an energy barrier equal to (55.22 kcal/mol). *S6-TS6-S7* and *S1-TS1-S2* steps are again endothermic with energy barriers of (19.20 kcal/mol and 53.59 kcal/mol) respectively. The remaining steps in the potential energy surface are exothermic. The exothermic steps of *S4-TS4-S5* and *S6-TS6-S7* with enthalpies equal to (-30.43kcal/mol and -13.05kcal/mol) respectively are located**.** The transformation of *S1* to *S5* involves first a proton transfer (Si→S) leading to *S2* via *TS1*, secondly a proton transfer (S→S) leading to *S3* structure via TS2, thirdly a proton transfer (S→N) leading to *S4* via TS3, finally another proton transfer (O→Si) leading to the global minimum *S5* via *TS4*. Therefore, the reaction coordinate involves a pathway (S1→S2→S3→S4→S5) that has an overall activation barrier of (55.22 kcal/mol). The HOMO-LUMO separation has been used as a simple indicator of kinetic stability[23,24] because a large HOMO-LUMO gap(4.083eV) implies that it is energetically unfavorable to add an electron to a high-lying LUMO to extract electrons from the low-lying HOMO [24]. Indeed the largest HOMO-LUMO gap (4.083 ev) is found for *S5* structure, whereas *S2* has the lowest gap (2.848 ev). This difference in the energy gap is largely due to a relative stabilization of the LUMO, which is at (2.7478 ev and 3.15917 ev) assigned for *S5* and *S2*, respectively.

3.4. NBO analysis

Natural bond orbital analysis is a influential tool for under standing electron delocalization between different orbitals. Natural atomic hybrid (NHOs) and the polarization coefficients of the structures are given in Table (4). Important second order delocalization energies $E^{(2)}$ that are representative of the extent of electron delocalization are given in Table (5).

Table (4): Calculated natural atomic hybrid (NHOs) and the polarization coefficient for the structures with B3LYP/6-311++G(d,p), polarization coefficient (in parentheses).

Sys.	Si1-C2		Si1-S3	
	Si1	C2	Si1	S3
S1	$sp^{3.72}d^{0.04}$ (0.5589)	$sp^{1.67}$ (0.8292)	$sp^{3.16}d^{0.04}$ (0.5988)	$sp^{5.31}d^{0.03}$ (0.8009)
S2	$sp^{1.83}d^{0.03}$ (0.5681)	$sp^{1.74}$ (0.8230)	$sp^{2.55}d^{0.03}$ (0.5772)	$sp^{5.15}d^{0.03}$ (0.8166)
S3	$sp^{7.29}d^{0.09}$ (0.5142)	$sp^{1.42}$ (0.88577)	$sp^{10.22}d^{0.14}$ (0.5028)	$sp^{4.97}d^{0.02}$ (0.8644)
S4	$sp^{7.92}d^{0.10}$ (0.4900)	$sp^{1.30}$ (0.8717)	$sp^{9.25}d^{0.11}$ (0.5285)	$sp^{5.96}d^{0.02}$ (0.8489)
S5	$sp^{3.38}d^{0.04}$ (0.5702)	$sp^{1.79}$ (0.8215)	$sp^{3.73}d^{0.05}$ (0.5783)	$sp^{5.53}d^{0.03}$ (0.8158)
S6	$sp^{8.00}d^{0.10}$ (0.5117)	$sp^{1.51}$ (0.8592)	$sp^{24.47}d^{0.30}$ (0.4117)	$sp^{5.51}d^{0.01}$ (0.9113)
S7	$sp^{7.64}d^{0.09}$ (0.5130)	$sp^{1.40}$ (0.8584)	$sp^{15.04}d^{0.20}$ (0.4443)	$sp^{7.04}d^{0.02}$ (0.8959)
S8	$sp^{6.80}d^{0.09}$ (0.5090)	$sp^{1.44}$ (0.8508)	$sp^{11.97}d^{0.17}$ (0.4894)	$sp^{5.05}d^{0.02}$ (0.8721)
	C2-N5		C4-N5	
	C2	N5	C4	N5
S1	$sp^{1.83}$ (0.6332) $sp^{1.0}$ (0.6103)	$sp^{1.68}d^{0.01}$ (0.7740) $sp^{1.0}$ (0.7921)	$sp^{1.91}$ (0.6318)	$sp^{1.99}d^{0.01}$ (0.7751)
S2	$sp^{2.58}d^{0.01}$ (0.6003)	$sp^{1.04}$ (0.7998)	$sp^{1.23}$ (0.6168)	$sp^{1.01}$ (0.7871)
S3	$sp^{2.11}$ (0.6251) $sp^{99.99}d^{0.29}$ (0.5719)	$sp^{1.88}d^{0.01}$ (0.7805) $sp^{1.00}$ (0.8203)	$sp^{1.82}$ (0.6351)	$sp^{1.74}d^{0.01}$ (0.7724)
S4	$sp^{2.37}$ (0.6024) $sp^{99.99}d^{2.15}$ (0.4894)	$sp^{1.65}$ (0.7982) $sp^{1.00}$ (0.8720)	$sp^{2.46}$ (0.6005)	$sp^{1.79}$ (0.7996)
S5	$sp^{2.30}$ (0.5984)	$sp^{1.84}$ (0.8012)	$sp^{2.16}$ (0.6110)	$sp^{1.66}$ (0.7916)
S6	$sp^{2.62}d^{0.01}$ (0.5802)	$sp^{1.91}$ (0.8145)	$sp^{1.96}$ (0.6145)	$sp^{1.57}$ (0.7889)
S7	$sp^{2.92}d^{0.01}$ (0.5705)	$sp^{1.97}$ (0.8213)	$sp^{2.00}$ (0.6186) $sp^{99.99}d^{6.15}$ (0.5259)	$sp^{1.56}$ (0.7857) $sp^{99.99}d^{1.16}$ (0.8506)
S8	$sp^{2.08}$ (0.6233) $sp^{99.99}d^{0.34}$ (0.5632)	$sp^{1.92}d^{0.01}$ (0.7820) $sp^{1.00}$ (0.8263)	$sp^{1.85}$ (0.6339)	$sp^{1.69}d^{0.01}$ (0.7734)

C4-S7		
	C4	S7
S2	$Sp^{0.99}$ (0.7453)	$Sp^{4.52} d^{0.03}$ (0.6667)
	$Sp^{20.17}d^{0.05}$(0.5706)	$Sp^{34.67} d^{0.12}$ (0.8212)
	$sp^{99.99}d^{18.30}$(0.5503)	$sp^{99.99}d^{19.23}$(0.8349)

Inspection of the results presented in Table (4) reveals that the increasing d character in the silicon natural hybrid orbital (NHO) σ_{Si-S3} and increasing p character on the sulfur NHO σ_{Si-S3} bond orbitals result in a lengthening of the Si1-S3 bond and as expected to simultaneously decrease the bond order as noted for *S6* and *S7* structures. *S2* shows a strong Si-S3 interaction with small d contribution, whereas structure *S6* shows a strong Si-S3 bond with substantial d contribution. Small and nearly equal values of the calculated d contribution at the sulfur atom indicate that 3d orbitals have little importance in bonding for the structures. The size of the polarization coefficients of σ_{Si-S3} shows the importance of the two hybrids in the formation of the bond. In all structures the sulfur has larger percentage in the NBO and gives the larger polarization coefficient because it has higher electronegativity . Similar results are found in all the bonding Si-C2, C2-N and C4-N orbitals. *S6* and *S7* showed the largest polarization coefficients on sulfur atoms (0.9113 and 0.8959) among the structures under consideration . The same trends have been noted in Si-C2, C2-N and C4-N bond. The second order delocalization energies ($E^{(2)}$) for the structures are given in Table(5). There is a strong $n_{O6} \rightarrow \sigma^{*}_{C2-N5}$ interaction in most of the structures. For example, the second order energy for S1 is (40.67 kcal/mol). This interaction increases the C_2-N bond strength and elongates the C_4-N bond length.This is accompanied by an $n_{S3} \rightarrow \sigma^{*}_{C4-S7}$ interaction ($E^{(2)}$ = 24.51 kcal/mol), which introduces partial π character. The NBO analysis for isomer *S2* with acyclic structure demonstrates that the $n_{N5} \rightarrow \sigma_{C4-S7}$ interaction between the nitrogen lone pair and the C_4-S_7 gives strong stabilization. This is accompanied by an $n_{N5} \rightarrow \sigma_{C4-S7}$ ($E^{(2)}$ = 160.55 kcal/mol). A very important interaction for *S2* is the $n_{N5} \rightarrow \sigma_{C4-S7}$ interaction where the N5 lone pair has low occupancy (1.4121) and highest energy (-0.2668 a.u.) and is primarily delocalized into anti-bonds (σ^{*}_{C2-Si1}). This interaction elongates the C2-O6 to (1.346 Å) and the Wiberg bond index is (1.09) . In addition, the sulfur *S7* lone pair is the lowest

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occupancy (1.9787) and highest energy orbital (-0.7531 a.u) and is interacting with σ^*_{C4-N5}. Generally, the lone pair of O, N and sulfur atoms is involved in a strong hyper conjugative interaction.

Table (5): Second order delocalization energies ($E^{(2)}$) of the structures with B3LYP/6-311++G(d,p), all values are in (kcal/mol).

	S1	S2	S3	S4	S5	S6	S7	S8
$nO6{\rightarrow}\sigma^*C2\text{-}N5$	40.67		41.39	47.68		33.09	35.05	44.07
$nS3{\rightarrow}\sigma^*C4\text{-}S7$	24.51			43.34				
$nN5{\rightarrow}\sigma^*C4\text{-}S7$		160.55			64.33	65.64		
$nS7{\rightarrow}\sigma^*S3\text{-}C4$			41.42					39.88
$nN5{\rightarrow}\sigma^*C2\text{-}O6$					45.86			
$nS3{\rightarrow}\sigma^*C4\text{-}N5$							45.81	

Another important indicator of the bonding character is the second derivative of the charge density at the bond critical point, the Palladian of the charge density $\nabla^2\rho(r)$. If the Laplacian is negative and large in magnitude, atoms are bound covalently. A positive Laplacian indicates electrostatic or ionic bonding. The characteristics of the density at the bond critical point ($\rho(r)$ and $\nabla^2\rho(r)$) are represented in Table(6). The bond critical point results showed that for all Si-C2 and Si-H bonds the Laplacian is positive. These values strongly support the assumption that bonding between silicon atom and carbon (C2) and hydrogen attached to the silicon atoms is predominantly ionic. This result is supported by the natural atomic charges since the silicon atoms bear high positive charges, while the oxygen, nitrogen and hydrogen attached to the silicon atoms have negative charges, Table (2). The Laplacian is negative and large for N-H and O-H bonds, this Laplacian confirm the covalent bond nature. The trend in $\rho(r)$, S-H > N-H > O-H, can be related to the bond lengths with the shortest bond (O-H) displaying the largest $\rho(r)$ values. The high electronegativity of O and N relative to S means that the former plays the role of anions in structures

Table(6): The values of the electron density $\rho(r)$ (in parentheses), and the Laplacian of charge density $\nabla^2\rho(r)$ at bond critical points at B3LYP/6-311++G(d,p) level of theory.

Sys	Si1-C2	Si1-S3	S3-C4	N5-C2	N5-C4	O6-C2	S7-C4	Si-H	S-H	N-H	O-H
S1	0.189	0.056	-0.183	-1.060	-0.943	-0.351	-0.044	0.206	-	-	-2.494
	(0.110)	(0.104)	(0.164)	(0.378)	(0.316)	(0.298)	(0.229)	(0.121)		-	(0.360)
S2	0.335	0.024	-	-0.638	-0.500	-0.419	0.410	0.191	-0.601	-	-2.477
	(0.112)	(0.093)	-	(0.304)	(0.408)	(0.299)	(0.232)	(0.114)	(0.211)	-	(0.356)
S3	0.236	0.012	-0.358	-1.080	-1.096	-0.321	-0.370	0.172	-0.642	-	-2.488
	(0.105)	(0.079)	(0.202)	(0.347)	(0.353)	(0.301)	(0.201)	(0.112)	(0.217)	-	(0.359)
S4	0.275	-0.008	-0.358	-0.908	-0.756	-0.336	-0.063	0.168	-	-1.669	-2.499
	(0.102)	(0.081)	(0.201)	(0.336)	(0.283)	(0.305)	(0.221)	(0.111)	-	(0.332)	(0.355)
S5	0.177	0.043	-0.274	-0.786	-0.876	-0.170	-0.017	0.207	-	-1.662	-
	(0.114)	(0.097)	(0.183)	(0.291)	(0.308)	(0.407)	(0.223)	(0.123)	-	(0.332)	-
S6	0.158	-0.003	-0.200	-0.619	-0.946	-0.153	-0.028	0.164	-0.656	-1.650	-
	(0.101)	(0.058)	(0.164)	(0.256)	(0.332)	(0.410)	(0.223)	(0.113)	(0.219)	(0.331)	-
S7	0.180	-0.015	-0.410	-0.541	-0.954	-0.150	-0.353	0.163	-0.644	-1.610	-
	(0.101)	(0.066)	(0.212)	(0.242)	(0.339)	(0.411)	(0.197)	(0.112)	(0.217)	(0.330)	-
S8	0.250	0.005	-0.376	-1.051	-1.074	-0.314	-0.367	0.172	-0.642	-	-2.402
	(0.107)	(0.076)	(0.205)	(0.344)	(0.349)	(0.306)	(0.200)	(0.113)	(0.217)	-	(0.349)

3.5. The Higher Level Theory (CBS-Q) analysis.

The eight local minimum structures (*S1-S8*) were reproduced for 5-thioxo-1,4,2-thiazasilolidin-3-one molecule. The description of the anions (A) and the cations (C) for the structures are as follows, deprotonation of O-H in *S1* is labelled *S1OA* and the protonation of N atom in *S1* molecule is labelled *S1NC* (i.e. *S1OA* is an anion form of *S1* structure in which the proton is dissociated from oxygen atom and *S1NC* is a

cation form of *S1* structure in which the proton is added to nitrogen atom). The relative energies, enthalpies and free energies are given in Table(7). The energies of the structures are often calculated for geometries optimized at a lower level due to the large computational time required for geometry optimization; however in this section the optimized structures at CBS-Q level of theory gave an identical geometrical parameters with lower level theory B3LYP/6-31G(d) ,The relative energies at different level of theory and in solution are schematically plotted in Fig (3). The *S5* structure is located as a global minimum on the reaction coordinates at the CBS-Q level of calculation and the energy values are reported related to *S5* structure. The *S1* and *S7* structures have the lowest energies (28.23 kcal/mol and 37.16 kcal/mol) respectively above the *S5* energy. The *S2* and *S6* have the highest energies (60.17 and 52.73 kcal/mol) above the global minimum *S5*.

Table (7): The relative energies, enthalpies and free energies (kcal/mol) for the structures at CBS-Q level of theory.

Sys.	$\Delta E°$	$\Delta H°$	$\Delta G°$
S1	28.23	18.72	18.58
S2	60.17	46.53	43.51
S3	46.25	35.39	35.17
S4	38.74	31.63	31.60
S5	0.00	0.00	0.00
S6	52.73	45.60	44.85
S7	37.16	31.51	30.76
S8	40.09	32.35	32.13
Note: The relative energy for structure S5			
The anions			
S1OA	0.384	0.001	0.006
S2OA	16.72	24.65	20.58
S3OA	24.16	24.18	23.59
S3SA	26.24	24.26	24.32

S4OA	0.00	6.53	6.48
S5NA	0.384	0.00	0.00
S6SA	0.00	6.53	6.48
S7NA	24.16	24.18	23.59
S8OA	24.16	24.18	23.59
Note: The relative energy for structures S4OA, S6SA			
The cations			
S1NC	0.0	0.0	0.0
S1SC	5.39	4.25	4.16
S2NC	62.15	50.25	47.07
S3NC	24.72	16.13	15.85
S4SC	24.72	16.13	15.85
S5OC	1.35	2.07	2.09
S6OC	42.19	36.94	36.41
S7OC	24.72	16.13	15.86
S8NC	31.71	17.50	17.07

Note: The relative energy for S1NC structure.
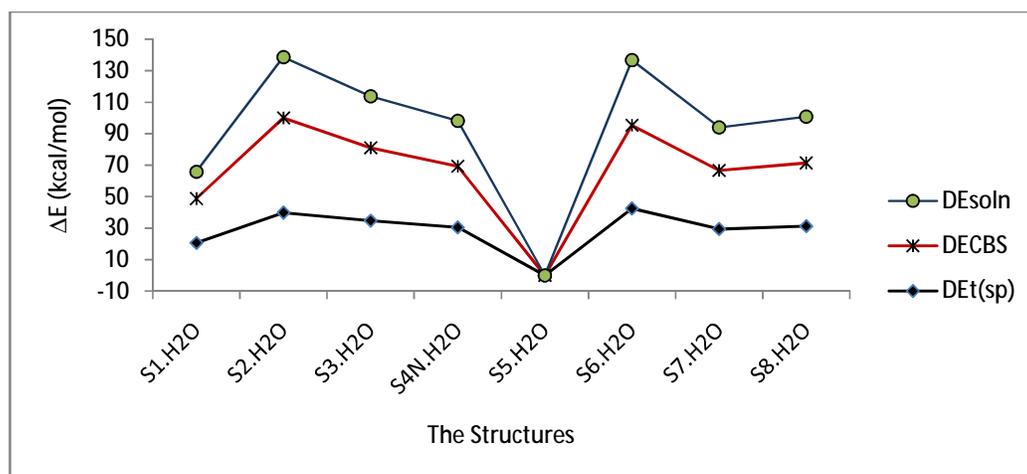
Fig (3): The Relative energies at different level of theory and in solution.

The stability order of the structures are pursued the same pattern located for earlier calculations. The related energies for all the structures considered at this level of theory are presented in Fig (4). The anions study revealed that the *S5NA* has the lowest energy (0.384 kcal/mol) above the *S4OA* structure. The *S3SA* possessed the highest energy (26.24 kcal/mol) related to global minimum in anions section *S4OA*. The cations energies exhibited the *S1NC* as a global minimum in the cation section. The *S5OC* structure had the lowest energy (1.35 kcal/mol) above the cation global minimum *S1NC* structure. The relative enthalpies and Gibbs free energies are listed in Table (7).
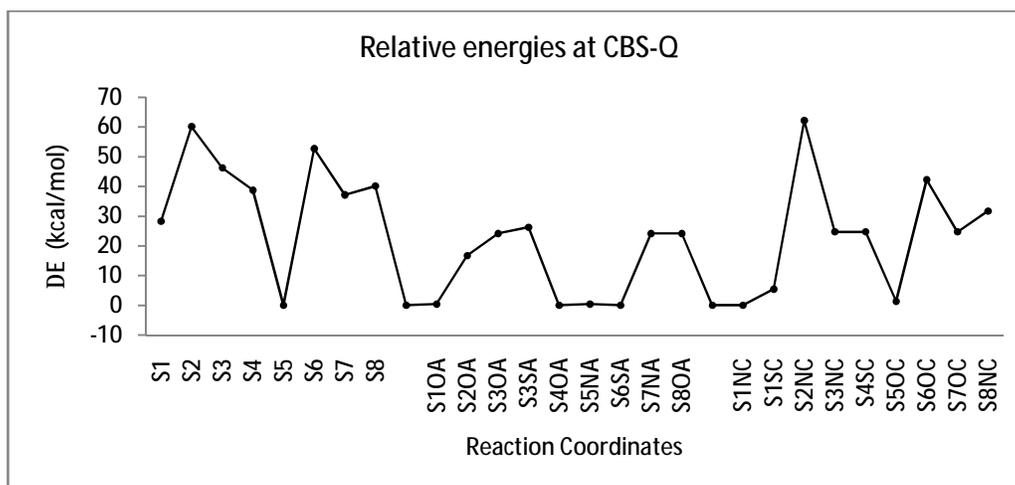
Fig (4): The relative energies of the structures and their anions and cations at CBS-Q level of theory.

Again, the values of ΔH and ΔG are reported related to *S5* in the 5-thioxo-1,4,2-thiazasilolidin-3-one structure because *S5* possessed the lowest ΔH and ΔG values Fig (5,6).
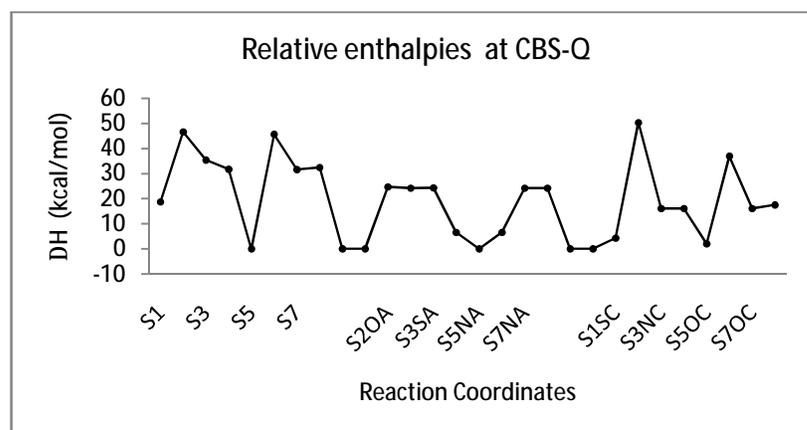
Fig(5): The relative enthalpies of the structures and their anions and cations at CBS-Q level of theory.
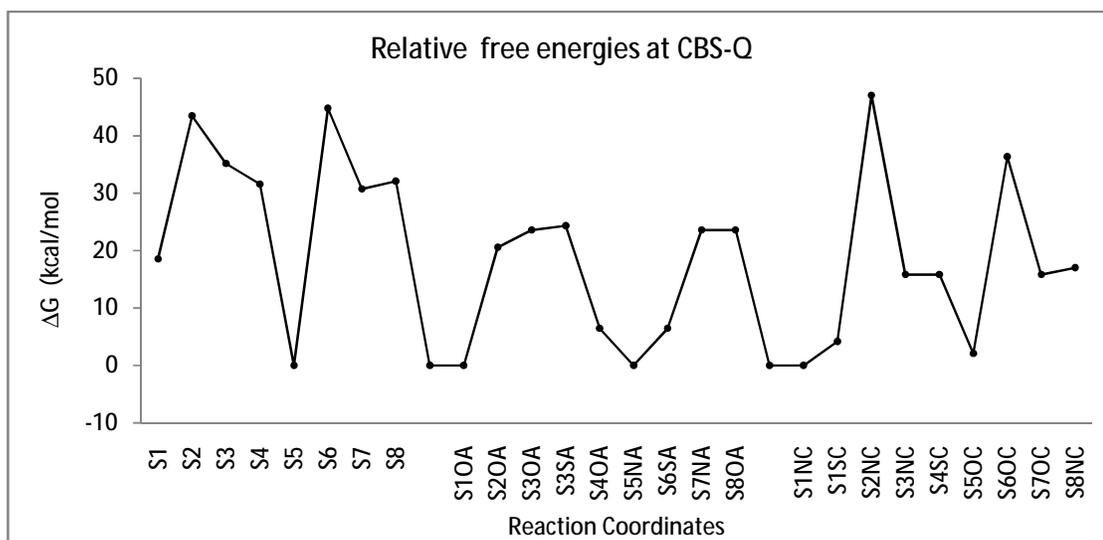
Fig(6): The relative free energies of the structures and their anions and cations at CBS-Q level of theory.

The *S2OA* showed the highest relative enthalpy and *S3SA* showed the highest relative Gibbs free energy (ΔH= 24.65 kcal/mol, ΔG=24.32 kcal/mol) in the anions section and the *S2NC* showed the highest relative enthalpy and Gibbs free energy (ΔH= 50.25 kcal/mol, ΔG=47.07 kcal/mol) in the cations section.The acidities and basicities of 5-thioxo-1,4,2-thiazasilolidin-3-one structure are presented in Table (8).The enthalpy of deprotonation may be computed between two arbitrary species. Those between two species with most similar structures *S1* and *S1OA*, for example, the reaction ($S1 \rightarrow S1OA + H^+$) might be of theoretical interest, but only the differences between the most stable species can have physical meaning and can be compared with experiments. Of the nine anions of 5-thioxo-1,4,2-thiazasilolidin-3-one structure *(S1OA,S2OA, S3OA, S3SA, S4OA, S5NA ,S6SA,S7NA* and *S8OA)* three anions with equal energies (24.16 kcal/mol) are located in deprotonation processes namely *S3OA, S7NA* and *S8OA*. Energetically easiest process is the deprotonation of *S6SA* with the computed enthalpy and Gibbs free energy of (66.72 kcal/mol and 67.12 kcal/mol). The equilibrium constants of the processes are given in Table(8).The equilibrium constants at 298.15 K of the deprotonation reactions are very small which means the reaction at this temperature favor the reactants and the protonation reactions at the same temperature showed a reverse trend.

Table (8): The gas-phase acidity, basicities (enthalpies ΔH , Gibbs free energies ΔG in kcal/mol) and the equilibrium constants of the reactions at CBS-Q level of theory at 298K.

The Reaction	ΔH_{298}	ΔG_{298}	K_{eq}
The cations			
S1+ H$^+$ → S1NC	-48.66	-48.72	5.15×10^{35}
S1+ H$^+$ → S1SC	-48.18	-48.28	2.44×10^{35}
S2+ H$^+$ → S2NC	-43.56	-43.77	1.21×10^{32}
S3+ H$^+$ → S3NC	-48.91	-49.62	2.35×10^{36}
S4+ H$^+$ → S4SC	-48.53	-48.77	5.60×10^{35}
S5+ H$^+$ → S5OC	-43.81	-43.93	1.50×10^{32}
S6+ H$^+$ → S6OC	-46.33	-46.35	9.40×10^{33}
S7+ H$^+$ → S7OC	-47.94	-47.84	1.16×10^{35}
S8+ H$^+$ → S8NC	-47.93	-48.15	1.96×10^{35}
The anions			
S1 - H$^+$ → S1OA	71.09	71.22	6.25×10^{-53}
S2 - H$^+$ → S2OA	70.31	69.88	5.99×10^{-52}
S3 - H$^+$ → S3OA	72.90	72.23	1.13×10^{-53}
S3 - H$^+$ → S3SA	73.39	73.02	2.99×10^{-54}
S4 - H$^+$ → S4OA	69.58	69.64	8.99×10^{-52}
S5 - H$^+$ → S5NA	75.47	75.54	4.25×10^{-56}
S6 - H$^+$ → S6SA	66.72	67.12	6.32×10^{-50}
S7 - H$^+$ → S7NA	73.87	74.01	5.63×10^{-55}
S8 - H$^+$ → S8OA	73.63	73.52	1.28×10^{-54}

3.6. The Vibrational Frequencies investigation.

In Table (10), the calculated frequencies of optimized structures are revealed after correction by the scaling factor of 0.9614 .

The OH stretching frequencies in *S1, S2, S3, S4* and *S8* are in the range of (3474-3606 cm^{-1}), consistent with the usual OH frequency in the absence of hydrogen bonding. This shift in *S8* (3474 cm^{-1}) towards the lower frequency can be attributed to the charge delocalization over nitrogen and oxygen atoms. In the next column, NH frequencies lie between (3408 cm^{-1} and 3373 cm^{-1}), with the *S7* and *S4* structures having the lowest values (3373 and 3377 cm^{-1}). The SiH vibrational frequencies are located between (1999-2201 cm^{-1}), the highest (2201 cm^{-1}) being the asymmetric stretch in *S5* structure .The experimental value for SiH stretching is 2167 cm^{-1} [59,60].which is in agreement with the value of (2168 cm^{-1})calculated for the *S1* structure . Finally, the vibrational frequencies of SH lie between (2580-2603 cm^{-1}). The computed vibrational frequency for **Table (9):** Selected vibrational harmonic frequencies in cm^{-1} of the structures at B3LYP/6-31G(d) level of theory

S7 showed the SH stretch at (2603cm^{-1})which is in excellent agreement with previously reported experimental results[61,62].

	O-H	N-H	S-H	Si-H	C=N	C-O	C=O	C=S
S1	3606			2161 s 2168 as	1571	1299		
S2	3568		2580	2059	2024	1248		
S3	3588		2594	2016				
S4	3580	3377		2002				
S5		3408		2186 s 2201 as			1713	1020
S6		3396	2595	2005			1707	1040
S7		3373	2603	1999			1713	
S8	3474		2597	2039				

3.7. The Solvation Studies

The free energy of solvation for the structures was calculated using water as solvent. The major purpose from considering solvent effect is simulation of real system and determination of the differences between the gas phase and aqueous system. The study of equilibrium in solvent, ΔG solvation of structures and transition states were calculated at 6-311++G(d,p) bases set. The diagram of ΔG_{solv} of structures and transition states are shown in Fig (7) and the final kinetic and thermodynamic data in solvents are presented in Table (11).
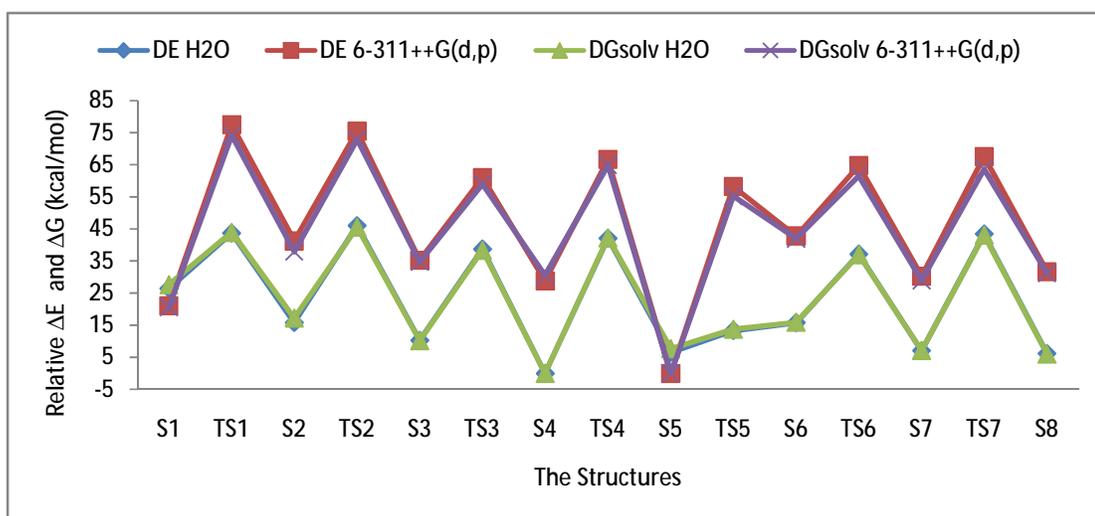
Fig (7): The relative energy and free energies of the structures in water and gas phase at 6-311++G(d,p) level of theory.

The global minimum in water is S4 structure. This figure shows that the (27.68 kcal/mol) value is the highest ΔG_{solv} extracted for S1. S3→S4 conversion provides the highest equilibrium constants (2.95×10^7), which is higher than the gas phase value of (90.79) extracted for the conversion. Comparing these data with the gas phase data shows a large difference between them. For example, the maximum rate constant for S1→S2 structure interconversion in water is(1.75×10^{-7} s^{-1}) very far from the gas phase rate constant of (1.77×10^{-15} s^{-1}). This fact demonstrates that computations in the gas phase cannot deliver comparable results with computations in solvated systems for our structures.

Table (10) : The equilibrium and rate constants for the forward and reverse reactions.

Rxn	Equilibrium constants		Rate constants (s^{-1})	
	H_2O	6-311++G(d,p)	H_2O	6-311++G(d,p)
S1→S2	4.2×10^{7}	1.06×10^{-12}	1.75×10^{-7}	1.77×10^{-15}
S2→S3	1.57×10^{5}	1.62	7.24×10^{-14}	5.42×10^{5}
S3→S4	2.95×10^{7}	90.79	4.35×10^{-16}	3.67×10^{-7}
S4→S5	2.05×10^{-6}	7.06×10^{24}	3.09×10^{-13}	1.35×10^{-34}
S5→S6	9.76×10^{-7}	2.80×10^{-32}	2.59×10^{14}	4.11×10^{3}
S6→S7	2.82×10^{6}	9.99×10^{9}	8.91×10^{-10}	5.37×10^{-11}
S7→S8	7.33	2.88×10^{-3}	3.84×10^{-15}	2.65×10^{-8}
The reverse reactions				
S2→S1	2.38×10^{-8}	9.43×10^{11}	7.36	1.88×10^{-27}
S3→S2	6.35×10^{-6}	0.20	1.14×10^{-8}	2.75×10^{6}
S4→S3	3.39×10^{-8}	0.01	1.28×10^{-8}	3.33×10^{-5}
S5→S4	4.88×10^{5}	1.42×10^{-25}	6.34×10^{-19}	9.53×10^{-10}
S6→S5	1.02×10^{6}	3.58×10^{31}	2.48×10^{8}	1.15×10^{-28}
S7→S6	3.54×10^{-7}	1.00×10^{-10}	2.51×10^{-3}	0.54

Table (11): The relative energy and free energy of solvation (kcal/mol) for the structures.

Sys.	ΔE		ΔG_{solv}	
	H_2O	6-311++G(d,p)	H_2O	6-311++G(d,p)
S1	26.49	21.07	27.68	20.64
TS1	43.731	77.56	43.95	74.21
S2	15.87	41.26	17.28	37.93
TS2	46.05	75.50	45.57	72.93
S3	10.32	35.21	10.19	34.76
TS3	38.79	61.07	38.41	59.00
S4	0.0	28.79	0.0	30.58
TS4	42.12	66.74	42.28	65.00
S5	6.54	0.00	7.76	0.0
TS5	13.37	58.29	13.75	55.31
S6	15.79	42.83	15.96	42.00
TS6	37.20	64.77	36.96	61.50
S7	7.09	30.30	7.16	29.04
TS7	43.47	67.61	43.09	63.65
S8	6.17	31.68	5.98	31.25

3.8. The water-assisted   studies

The free energy of solvation for the structures was calculated using H_2O molecule as solvent. The energies, total energies, enthalpies, free energies, energies in solution, total free energy and the related energies and free energies in solution of the calculated structures are listed in Tables (13,14). The major purpose from considering solvent effect is simulation of real system and determination of the differences between the gas phase and aqueous system. The selected optimized geometries of the hydrated structures are listed in Table (14).

Table (12): The energies, total energy (E_t), free energies (G) and enthalpies(H); energies in water (E_{water})and total free energies in water (G_{water}) all are in Hartree/particle and in atomic

Sys.	6-31g*	SP	E_t	E_{water}	G	H
S1.H_2O	-1370.2888	-1370.4763	-1370.4004	-1370.5092	-1370.4967	-1370.2011
S2.H_2O	-1370.2526	-1370.4403	-1370.3659	-1370.4614	-1370.4467	-1370.1651
S3.H_2O	-1370.2655	-1370.4518	-1370.3753	-1370.4763	-1370.4630	-1370.1775
S4N.H_2O	-1370.2739	-1370.4610	-1370.3813	-1370.4868	-1370.4742	-1370.1830
S4O.H_2O	-1370.2806	-1370.4656	-1370.3856	-1370.4934	-1370.4814	-1370.1895
S5.H_2O	-1370.3195	-1370.5042	-1370.4274	-1370.5249	-1370.5110	-1370.2314
S6.H^2O	-1370.2511	-1370.4379	-1370.3613	-1370.4586	-1370.4448	-1370.1630
S7.H_2O	-1370.2738	-1370.4601	-1370.3837	-1370.4797	-1370.4658	-1370.1860
S8.H_2O	-1370.2706	-1370.4572	-1370.3805	-1370.4743	-1370.4605	-1370.1827
H2O	-76.4090	-76.4584	-76.4373	-	-	-76.3840

Table (13): free energies and equilibrium constants for the hydration reaction (kcal/mol).

The reaction	$\Delta H°$	$\Delta G°$	K_{eq}
$S1 + H_2O \rightarrow S1.H_2O$	-13.15	-4.55	2.17×10^3
$S2 + H_2O \rightarrow S2.H_2O$	-12.69	-3.42	3.21×10^2
$S3 + H_2O \rightarrow S3.H_2O$	-13.72	-4.15	1.10×10^3
$S4N + H_2O \rightarrow S4N.H_2O$	-12.06	-2.21	4.17×10^1
$S4O + H_2O \rightarrow S4O.H_2O$	-16.13	-6.35	1.07×10^1
$S5 + H_2O \rightarrow S5.H_2O$	-10.29	-0.70	3.26×10
$S6 + H_2O \rightarrow S6.H_2O$	-11.88	-1.84	2.23×10^1
$S7 + H_2O \rightarrow S7.H_2O$	-13.17	-2.89	1.31×10^2
$S8 + H_2O \rightarrow S8.H_2O$	-13.27	-3.12	1.94×10^2

The relative energies and relative free energies of the hydrated structures are given in Fig (8). The equilibrium constants of hydrated reactions were calculated from Gibbs free energies using $\Delta G = -RT \ln K_{eq}$. The equilibrium constant at 298.15 K of the hydration reactions are listed in Table (14). all the hydration reactions showed a high equilibrium constant values which means that the reactions at this temperature favor products.
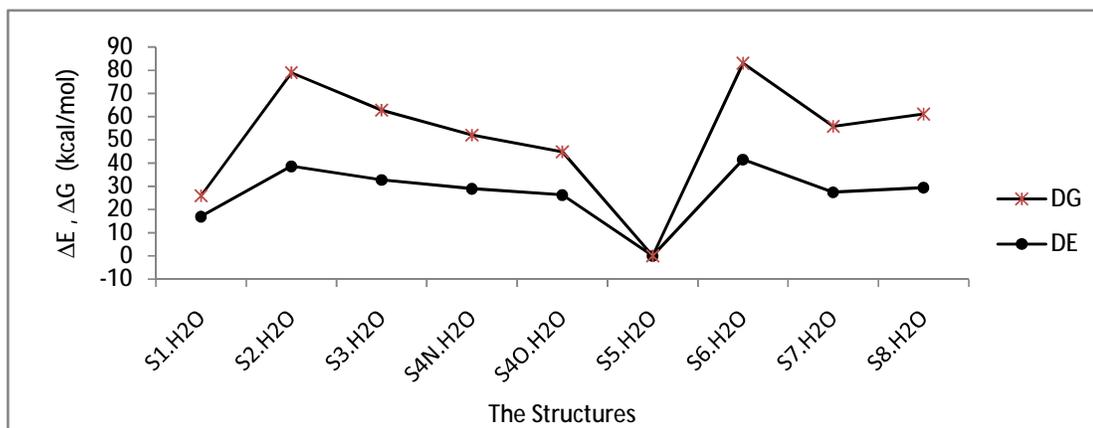
Fig (8): The relative energies and free energies of the solvated structures.

The solvation process has no effect in the order of stability. The *S1 + H₂O* reaction is quantitative and has the largest value (2.17×10^3). The Gibbs free energy difference (ΔG) between hydrated structures at B3LYP/6-311++G(d,p) level of theory lie between(-6.35kcal/mol and -0.70kcal/mol). From the free energies of various structures in aqueous solution it was found that the values for *S5.H₂O*, *S6.H2O* and *S4N.H₂O* are (-0.70kcal/mol ,-1.84 kcal/mol and -2.21kcal/mol) where as the values for *S1.H₂O*,*S3.2H₂O* and *S2.3H₂O* are(-4.55kcal/mol , -4.15kcal/mol and -3.41kcal/mol) respectively at 298.15 K and 1 atmosphere pressure. Therefore, the *S5.H₂O* is the not favored in aqueous solution as expected since *S5* is the most stable structure. The relative energy and free energy in water assissent for the structures in Table(14). On contrast the *S1* structure is very reactive with water molecule and the formation of *S1.H₂O* species will be favored. The calculated enthalpies for hydration process in one water molecule is added; The *S4* molecule has two sites available for binding with water molecule, one site through OH giving the *S4O.H₂O* and the other site through NH giving the *S4N.H₂O*. The enthalpy of *S4O.H₂O* is the lowest (-16.13 kcal/mol) Thus, hydrogen binding with water stabilized *S4O.H₂O* to greater extent than *S4N.H₂O* structure. The high stability of *S5* structure is clearly detectable since the *S5.H₂O* structure possessed the highest enthalpy. The enthalpies were estimated by adding the thermal corrections to the energy to account for translational, vibrational and

rotational motion at 298.15 K and 1 atmosphere pressure.

Table (14): The relative energy and free energy in water assissent (kcal/mol) for the structures

Sys.	ΔE°	ΔH°	ΔG°
S1.H₂O	16.95	19.030	8.97
S2.H₂O	38.59	41.60	40.35
S3.H₂O	32.69	33.68	30.12
S4N.H₂O	28.93	30.35	23.09
S4O.H₂O	26.23	26.28	18.574
S5.H₂O	0.00	0.00	0.00
S6.H₂O	41.48	42.902	41.54
S7.H₂O	27.42	28.47	28.36
S8.H₂O	29.43	30.56	31.69

Note: The relative energy for structure S5.H₂O

<u>CONCLUSION</u>

The present study systematically analyzed the tautomers stability of the 5-thioxo-1,4,2-thiazasilolidin-3-one molecule, the activation barriers for rearrangements, the infrared spectra and the electronic structure through NBO, electron density, its Laplacian and the equilibrium and rate constants were investigated. The S5 isomer is the global minimum in gas phase and S4 is global minimum in water. S2 is acyclic structure which is resulted from ring-opening tautomerizm. The effect of the solvent is clearly seen since by looking to S1-S2 interconversion the equilibrium constant in water is$(4.20\times10^{7})$and in the gas phase is (1.06×10^{-12}). The bonding properties have been analyzed; the results have been strongly supported by the bond length, Wiberg bond index, natural atomic charges and dipole moment. For example, since the silicon atoms bear high positive charges, while the oxygen, nitrogen and hydrogen attached to the silicon atoms have negative charges. The Laplacian is negative and large for N-H and O-H bonds, this Laplacian confirm the covalent bond nature. The trend in $\rho(r)$, S-H > N-H > O-H, can be related to the bond lengths with the shortest bond (O-H) displaying the largest $\rho(r)$ values. The high electronegativity of O and N relative to S means that the former plays the role of the anions in structures. The computed vibrational frequencies are in conformity with the known stretching range. Since, the OH stretching frequencies in S1, S2, S3, S4 and S8 are in the range of (3474-3606 cm^{-1}), consistent with the usual OH frequency in the absence of hydrogen bonding. This shift in S8 (3474 cm^{-1}) towards the lower frequency can be attributed to the charge delocalization over nitrogen and oxygen atoms.

PUBLICATION WORK

1. Abdulhakim A. Ahmed and N.F.Hassan (*Equilibrium, kinetic and thermodynamic studies of silarhodanine tautomers*) .Chem. Pharm. Res ,Vol 5(6) ,pp 209-214, 2013

2. Abdulhakim A. Ahmed and N.F.Hassan (*Quantum Mechanical Study of Water-Assisted Effect of Intramolecular Proton Transfer Process in Silarhodanine)*, Pelagia.Research.library , vol 4(5), pp58-61, 2013

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APPENDIX

Appendix B: The Cartesian coordinates for the structures.

Atomic Number	X	Y	Z
S1			
14	1.622413000	-0.991810000	0.000138000
6	1.212840000	0.892644000	-0.000369000
16	-0.439404000	-1.518879000	-0.000183000
6	-0.991020000	0.254280000	0.000089000
7	-0.027818000	1.237111000	0.000449000
8	2.118388000	1.883427000	-0.000122000
16	-2.599011000	0.549390000	-0.000036000
1	2.400523000	-1.367217000	-1.208104000
1	2.398612000	-1.364807000	1.210526000
1	3.018427000	1.520454000	-0.001339000
S2			
14	1.856407000	-0.057992000	0.510814000
6	0.664187000	1.234907000	-0.084608000
16	1.182476000	-1.940633000	-0.343803000
6	-1.658983000	0.393320000	-0.017458000
7	-0.677477000	1.093240000	-0.102871000
8	1.008517000	2.524744000	-0.254709000
16	-3.022681000	-0.381918000	0.092523000
1	3.075377000	0.387642000	-0.248374000
1	1.043522000	-2.609691000	0.820594000
1	1.977672000	2.574770000	-0.332969000

S3

14	-1.809238000	-0.998224000	-0.227503000
6	-1.270744000	0.828027000	0.040493000
16	0.360459000	-1.518057000	0.107503000
6	0.862009000	0.142219000	0.045234000
7	0.019141000	1.165967000	0.033791000
8	-2.091424000	1.884339000	0.056759000
16	2.557365000	0.594201000	-0.061570000
1	-2.348723000	-1.223232000	1.167355000
1	3.056624000	-0.656838000	0.021911000
1	-3.013932000	1.578952000	0.055887000

S4

14	1.804188000	-1.018208000	-0.212544000
6	1.276773000	0.803804000	0.029286000
16	-0.374989000	-1.533713000	0.101260000
6	-1.023266000	0.085798000	0.020389000
7	-0.027279000	1.086265000	-0.008082000
8	2.040929000	1.895618000	0.067986000
16	-2.618061000	0.508896000	-0.041068000
1	-0.356573000	2.050919000	-0.042062000
1	2.350739000	-1.143208000	1.195371000
1	2.978481000	1.637859000	0.073881000

S5

14	-1.745137000	-0.889690000	0.000027000
6	-1.320962000	0.989238000	0.000000000
16	0.328599000	-1.515672000	-0.000031000
6	1.000261000	0.154251000	-0.000016000
7	0.068734000	1.169729000	-0.000050000

50

8	-2.096829000	1.924386000	0.000005000
16	2.621293000	0.419102000	0.000028000
1	0.426075000	2.122756000	-0.000039000
1	-2.487421000	-1.283046000	-1.219355000
1	-2.487308000	-1.283068000	1.219473000

S6

14	-1.999125000	-0.882956000	-0.326502000
6	-1.345850000	0.939899000	0.025733000
16	0.255287000	-1.460702000	0.270634000
6	1.046704000	0.218172000	0.049180000
7	0.092964000	1.160389000	0.104561000
8	-2.054828000	1.920590000	0.091697000
16	2.663063000	0.389270000	-0.130831000
1	0.392995000	2.134058000	0.105436000
1	-2.358518000	-1.077262000	1.136039000
1	0.842421000	-1.988364000	-0.822282000

S7

14	-1.979613000	-0.934986000	-0.197748000
6	-1.424709000	0.929232000	0.023559000
16	0.284435000	-1.502026000	0.082073000
6	0.886349000	0.086283000	0.021533000
7	0.042938000	1.117149000	-0.019943000
8	-2.088778000	1.939757000	0.079685000
16	2.606613000	0.469461000	-0.045332000
1	0.374402000	2.081090000	0.006042000
1	-2.307294000	-1.103312000	1.274422000
1	3.030532000	-0.798118000	0.131737000

S8

14	-1.841336000	-0.984579000	-0.238711000
6	-1.279267000	0.818618000	0.046013000
16	0.338019000	-1.524173000	0.118513000
6	0.858327000	0.121400000	0.048431000
7	0.015910000	1.151440000	0.034498000
8	-2.142524000	1.832093000	0.063513000
16	2.556129000	0.567634000	-0.069529000
1	-1.625978000	2.664268000	0.075609000
1	-2.398947000	-1.249142000	1.137277000
1	3.051718000	-0.683330000	0.029077000

TS1

14	-1.834105000	-0.961199000	-0.124247000
6	-1.210720000	0.869995000	0.015173000
16	0.443420000	-1.512649000	0.094365000
6	1.015363000	0.283910000	0.005492000
7	0.039721000	1.217419000	0.006525000
8	-2.080753000	1.892188000	0.032098000
16	2.633061000	0.529822000	-0.023485000
1	-2.363084000	-1.303135000	1.235578000
1	-0.648856000	-1.659886000	-1.068184000
1	-2.994171000	1.562172000	0.011524000

TS2

14	-1.595278000	1.114972000	0.525630000
6	-1.325837000	-0.751725000	-0.059420000
16	0.511161000	1.344092000	-0.438721000
6	0.865318000	-0.426150000	-0.170194000
7	-0.120263000	-1.297515000	-0.174371000

8	-2.326884000	-1.624474000	-0.159868000
16	2.498422000	-0.591034000	0.254273000
1	-2.334791000	1.495699000	-0.745713000
1	1.914462000	1.158475000	0.273768000
1	-3.179073000	-1.167061000	-0.058494000

TS3

14	1.883612000	-0.880970000	-0.217522000
6	1.160589000	0.898802000	0.043657000
16	-0.253867000	-1.646473000	0.092799000
6	-0.947672000	-0.090893000	0.041784000
7	-0.157476000	1.038616000	0.042230000
8	1.839140000	2.047116000	0.053293000
16	-2.562078000	0.479160000	-0.055853000
1	-1.381878000	1.678565000	-0.025017000
1	2.385399000	-1.024142000	1.205002000
1	2.792737000	1.861465000	0.039586000

TS4

14	1.833290000	-0.868277000	0.103372000
6	1.194361000	0.904799000	0.068219000
16	-0.322032000	-1.490202000	-0.187019000
6	-1.033769000	0.126447000	0.041524000
7	-0.108148000	1.197405000	0.158303000
8	2.151709000	1.682783000	-0.234329000
16	-2.648028000	0.406313000	0.032312000
1	-0.487477000	2.139321000	0.080656000
1	2.029486000	-1.217382000	1.551721000
1	2.892697000	0.544592000	-0.496228000

TS5

14	-2.053804000	-0.847287000	-0.164631000
6	-1.338020000	0.937482000	0.022554000
16	0.442267000	-1.523540000	0.122348000
6	1.027168000	0.165883000	-0.040535000
7	0.061611000	1.125853000	-0.110778000
8	-2.062105000	1.908841000	0.143539000
16	2.648667000	0.449074000	-0.009191000
1	0.380068000	2.093908000	-0.119852000
1	-2.398310000	-1.204990000	1.248804000
1	-0.752776000	-1.607316000	-0.899609000

TS6

14	-1.849101000	-1.052653000	-0.433726000
6	-1.474252000	0.832795000	0.065120000
16	0.454674000	-1.348929000	0.345856000
6	0.907360000	0.336450000	0.120578000
7	-0.055647000	1.243307000	0.146547000
8	-2.307182000	1.704860000	0.125628000
16	2.567336000	0.460807000	-0.213381000
1	0.157255000	2.236255000	0.065435000
1	-2.333484000	-1.387225000	0.966196000
1	1.959809000	-1.259442000	-0.224110000

TS7

14	-2.003998000	-0.907642000	-0.211370000
6	-1.351538000	0.888836000	0.035782000
16	0.243048000	-1.539301000	0.098200000
6	0.866597000	0.060330000	0.023767000
7	0.022991000	1.081471000	-0.015047000

8	-1.811260000	2.076975000	0.080030000
16	2.580117000	0.442494000	-0.053803000
1	-0.464696000	2.291159000	0.045149000
1	-2.417685000	-1.086975000	1.232316000
1	3.006491000	-0.829361000	0.079160000

Appendix C : The Vibrational frequencies or the structures.

S1

Frequency cm^{-1}	IntensityIR	Frequency cm^{-1}	IntensityIR
75.7582	0.9953	667.7054	24.3604
167.6565	2.5988	686.8867	19.3849
248.9854	167.6565	794.9153	107.5339
332.3375	0.7335	974.2041	263.1897
358.9275	16.4706	1007.5079	177.3187
362.9392	65.8159	1184.2172	103.7773
472.8622	36.9539	1315.0191	629.6563
474.6927	31.5797	1351.3435	122.7492
491.5032	1.4681	1633.88	247.2217
565.5743	12.3408	2247.5083	150.985
570.6419	3.171	2254.5898	115.3215
597.7422	3.1351	3750.9534	112.8855

S2

Frequency cm^{-1}	Intensity	Frequency cm^{-1}	Intensity
48.3296	0.2334	572.4734	70.3463
67.477	1.9288	578.6939	67.9645
118.7346	0.4521	755.7766	20.3324
142.555	5.5544	849.3583	67.144
214.9785	20.9856	881.0253	113.5056
293.4027	55.5926	1196.5733	40.1582
351.9711	76.4423	1298.5456	517.529
426.0385	37.8009	1423.1621	106.3087
455.2512	19.233	2105.1618	1952.2745
482.0739	12.6756	2142.6793	41.2804
521.9304	10.3924	2684.4175	4.3251
551.2287	13.1584	3711.8996	77.9494

S3

Frequency cm^{-1}	Intensity	Frequency cm^{-1}	Intensity
107.3833	2.0147	632.784	1.9721
180.1127	6.6323	712.3504	31.7617
225.195	2.9463	754.2937	29.5635
304.1605	29.9644	948.2129	86.3352
335.934	9.3082	1045.3145	66.7645
356.3077	8.001	1201.4735	119.8533
388.2947	32.5432	1344.4468	591.6449
417.9765	4.8553	1421.9963	328.2947
483.0904	10.6783	1469.6156	141.9739
557.2295	61.4884	2097.5835	176.2416
578.0977	10.8659	2698.2179	2.8575
593.8423	3.8035	3732.1063	73.6259

S4

Frequency cm⁻¹	Intensity	Frequency cm⁻¹	Intensity
98.9733	3.2026	717.7918	30.4084
170.538	0.7475	740.3981	61.2828
236.6944	1.0391	770.5254	48.4816
310.8214	8.3115	1088.9052	204.9166
353.2051	11.6743	1149.8406	56.2819
401.4544	35.9196	1211.9461	207.5538
422.7998	2.2691	1325.7457	241.5995
505.8746	1.2891	1450.6525	212.3482
521.7262	97.7929	1549.5838	301.7477
541.1952	19.1451	2081.798	202.9116
569.3206	19.8975	3512.9356	53.7149
634.2833	7.5057	3726.0057	85.3258

S5

Frequency cm⁻¹	Intensity	Frequency cm⁻¹	Intensity
85.417	1.0734	682.097	13.0207
130.1903	3.9561	716.388	44.8482
248.0306	5.8718	798.0236	79.8383
330.9239	10.5529	963.4126	204.0829
363.9206	23.7062	1061.1381	109.1683
412.5788	6.7799	1186.6031	400.2796
478.2007	6.1512	1259.6351	79.7113
508.1135	22.7871	1452.5279	258.3668
540.0526	0.5288	1781.6622	321.9795
584.3235	4.2431	2288.7948	96.9301
591.2129	21.9302	2273.9986	113.1907
672.4913	58.8328	3545.1852	50.8332

S6

Frequency cm⁻¹	Intensity	Frequency cm⁻¹	Intensity
67.7705	3.0692	716.1838	114.1396
123.7009	3.232	755.2062	19.8113
223.0052	8.0361	802.3704	25.6058
289.8626	14.3124	926.445	13.5871
309.9827	0.4175	969.9479	75.7579
340.6496	24.0049	1082.1459	452.8461
429.0458	9.8182	1307.9285	29.416
462.6212	13.5191	1499.5753	458.8908
491.2188	12.579	1776.1111	269.1478
544.6224	7.165	2084.7137	199.4439
559.4886	6.5642	2699.1866	2.0459
651.8596	11.1556	3531.5763	45.8083

S7

Frequency cm^{-1}	Intensity	Frequency cm^{-1}	Intensity
93.1042	1.4508	664.5962	57.924
130.3462	1.3365	712.8268	3.998
213.0371	1.8385	770.9519	0.754
245.9198	33.5364	880.0124	94.7771
302.9032	14.8231	959.4505	30.6038
350.0462	11.5459	1047.8604	197.385
357.3281	1.8676	1363.9734	63.4471
409.8622	17.3875	1491.1354	157.1489
467.6804	3.1545	1782.4035	309.0353
545.9954	2.2854	2079.0433	197.8995
574.7081	4.1906	2706.5884	0.0635
659.1174	49.6735	3507.5781	36.9563

S8

Frequency cm^{-1}	Intensity	Frequency cm^{-1}	Intensity
113.9305	1.9002	657.594	109.8198
185.9486	0.9531	760.3648	3.9824
223.1879	1.9566	712.8436	13.1922
298.2855	15.2685	950.4398	81.0247
324.881	18.8006	1201.1687	114.0061
350.5597	4.8062	1388.2934	243.375
388.6122	22.8747	1041.875	70.4151
404.321	9.2453	1414.9214	665.9833
478.4832	2.9296	1442.3189	59.1985
573.2794	18.3192	2120.9068	165.6654
584.2435	15.2169	2700.5734	2.3567
632.0159	2.2991	3612.6735	62.9229

S5 IR spectrum
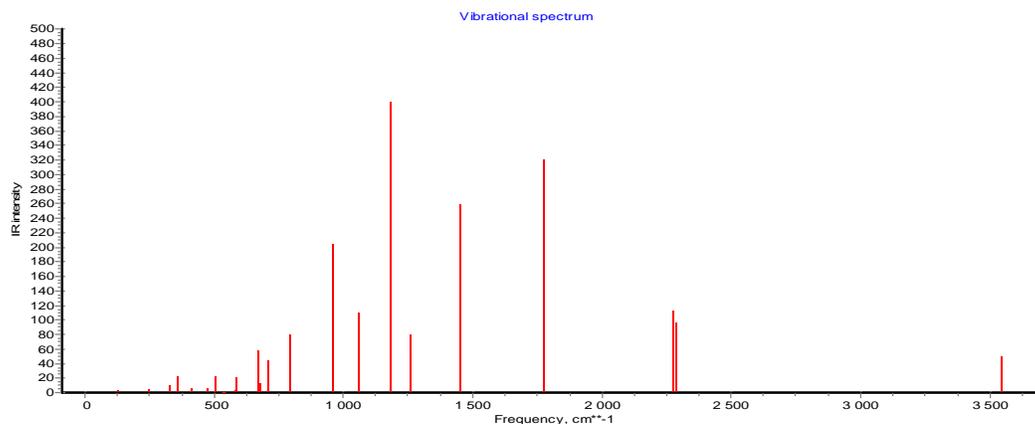
parameter	1	2	3	4	5	6	7	8	9	10	11	EXP.
Bond length (Å)												
C1-C2	1.524	1.525	1.524	1.521	1.528	1.528	1.521	1.528	1.528	1.523	1.520	1.506
C1-N5	1.389	1.391	1.390	1.385	1.392	1.403	1.388	1.390	1.403	1.387	1.385	1.374
C=O	1.205	1.203	1.212	1.204	1.209	1.241	1.218	1.204	1.242	1.208	1.205	1.220
C2-S3	1.834	1.833	1.840	1.823	1.835	1.893	1.813	1.831	1.889	1.821	1.815	1.805
C2-H8	1.091	1.090	1.096	1.088	1.093	1.092	1.093	1.101	1.092	1.094	1.094	0.979
C2-H9	1.091	1.090	1.097	1.088	1.093	1.092	1.092	1.101	1.092	1.094	1.094	0.982
S3-C4	1.770	1.771	1.774	1.763	1.774	1.832	1.761	1.773	1.827	1.763	1.758	1.735
C4-N5	1.378	1.375	1.378	1.373	1.377	1.391	1.379	1.379	1.391	1.374	1.371	1.367
C4=S6	1.638	1.640	1.646	1.636	1.642	1.680	1.627	1.635	1.671	1.636	1.634	1.645
N5-H10	1.013	1.012	1.015	1.010	1.015	1.017	1.018	1.018	1.017	1.014	1.013	0.861
Bond angle (°)												
C2-C1-N5	110.08	109.83	110.40	110.21	109.85	111.03	109.57	109.76	110.96	109.70	109.68	111.56
C2-C1-O7	125.38	125.56	125.35	125.36	125.63	125.17	125.61	125.48	125.14	125.65	125.65	124.45
C1-C2-S3	107.14	107.28	106.90	106.91	107.21	107.16	107.71	107.36	107.10	107.36	107.40	106.59
C1-C2-H8	109.30	109.29	109.39	109.46	109.42	109.99	108.86	109.31	110.01	109.31	109.22	109.88
C1-C2-H9	109.30	109.28	109.37	109.47	109.40	110.00	108.83	109.30	110.02	109.30	109.22	109.55
N5-C1-O7	124.53	124.62	124.25	124.43	124.52	123.83	124.81	124.75	123.90	124.65	124.67	123.99
C1-N5-C4	120.21	120.40	120.16	120.14	120.47	120.97	120.01	120.45	120.91	120.29	120.20	117.69
C1-N5-H10	120.17	120.00	120.26	120.23	119.99	119.63	120.32	120.18	119.72	120.15	120.21	120.25
S3-C2-H8	111.03	110.98	111.05	111.08	111.14	110.04	111.38	111.33	110.02	111.20	111.27	110.16
S3-C2-H9	111.03	110.97	111.02	111.08	111.11	110.04	111.35	111.33	110.02	111.21	111.27	110.78
C2-S3-C4	93.09	93.04	93.09	93.25	93.12	91.82	93.27	93.09	92.02	93.23	93.24	93.05

H8-C2-H9	109.00	109.01	109.07	108.80	108.53	109.60	108.65	108.19	109.65	108.44	108.44	109.83
S3-C4-N5	109.47	109.46	109.45	109.49	109.35	109.04	109.42	109.34	109.01	109.42	109.48	111.08
S3-C4-S6	26.39	124.73	125.02	124.92	125.09	125.00	124.97	124.88	125.02	124.97	124.90	124.43
N5-C4-S6	29.74	125.81	125.52	125.59	125.56	125.97	125.62	125.78	125.97	125.62	125.62	124.49
C4-N5-H10	119.62	119.60	119.58	119.63	119.55	119.41	119.67	119.38	119.37	119.57	119.59	122.06
RMSD	0.075	0.074	0.079	0.072	0.077	0.096	0.073	0.079	0.094	0.074	0.072	0.00

Appendix A 1 (B3LYP/6-311++G**), 2 (B3LYP/6-311G**), 3 (B3LYP/6-311G**), 4 (B3LYP/AUG-CC-pvtz), 5 (B3LYP/AUG-CC-pvdz), 6 (B3LYP/6-31G*), 7 (MP2(full)/6-31G*), 8 (B3LYP/SVP), 9 (B3LYP/SDD), 10 (B3PW91/6-31G*), 11 (PBE1PBE/6-31G*), EXP. (X-ray structure)

جامعة بنغازي

كلية العلوم

قسم الكيمياء

استخدام نظرية دالة الكثافة لدراسة تراكب وطاقات و الترددات الاهتزازيه لمركب 5-thioxo-1,4,2-thiazasilolidin-3-one وازومراته في الطور الغازي والماء

قدمت هذهالأطروحةاستكمالالمتطلباتالاجازه العالية (درجة الماجستير) في علم الكيمياء

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بنغازي – ليبيا

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