CHAPTER V

A Quantum Chemical Study on Monothioformic Acid and Monothioformic Acid...Water Complex

5.1 Introduction 98
5.2 Geometry 100
5.3 Monomer Energies 101
5.4 The Monothioformic Acid...Water Complex 102
   5.4.1 Hydrogen Bonding Characteristics 103
   5.4.2 Binding Energy of the Molecular Complexes 105
   5.4.3 The Density Functional Theory Considerations 106
   5.4.4 Charge Transfer and Dipolemoment 107
References 109
5.1. Introduction

The existence of monothioformic acid HCOSH has been known since the pioneering work of Engler and Gattow [1] who prepared it by the treatment of sodium or potassium monothioformate (which was obtained from the hydrolysis of phenyl formate with NaHS or KHS) with 18% HCl and distilled from solution in vacuum at 5°C. The UV, IR and proton NMR spectra of the molecule have been studied and indicated that the HCOSH, like monothioacetic acid [2], exists preferentially in the thiol form [1,3]. Hocking and Winnewisser [4], measured the microwave and millimetre wave spectrum, and found two distinct but similar spectra of HCOSH molecule and established that these were most likely due to the trans and cis rotamers of HCOSH, even though the possible presence of the HCOSH isomer could not be completely ruled out. They have also reported the IR spectrum of HCOSH in the vapour phase, and a force field and torsional potential function for the molecule. The geometries of the trans and the cis HCOSH rotamers have also been determined by analysing the microwave spectra of three isotopic molecules HCOSD, HCOS\(^{34}\)H and DCOSH on the assumption of a planar structure [4].

Since the two planar rotamers, trans HCOSH and cis HCOSH have a relative abundance of roughly 3:1 in the gas phase at room temperature, the molecule is well suited for the study of rotameric effects. The pure rotational spectrum obtained by
Hocking and Winnewisser [5] yielded the slightly different substitution structures of the two rotamers, a large difference in the dipole moment and precise relative intensity measurements at room temperature, from which the energy difference between the ground states of the two rotamers was determined [6]. In addition the quartic centrifugal distortion constants have been determined for the parent species and five of its simply substituted isotopic species [4,5,7]. In the gas phase IR spectrum [8] most of the absorptions are found to be due to the trans conformer and only some of those have been found to be due to the cis one. The observed torsional transitions from these studies gave a barrier height of 40.77 kJ/mol for the internal rotation. The NMR result [9] for the barrier to isomerization of thioformic acid in CD$_2$Cl$_2$ solution is compatible with the microwave results, while in the gas phase, the barrier is suggested to be 32 kJ/mol. For many molecules, the conformers can be stabilized in low temperature matrices and the species can be interconverted using IR irradiation [10]. The main activity is usually in the vibrational fundamental region, even though the excitation of the overtones is also important. The previous estimates of the energetics of thioformic acid suggest that this molecule could not be interconverted by excitation of the fundamental vibrations. The preliminary studies of Raaska et al., [11] about matrix-isolated thioformic acid indicate that the process from trans to cis can be induced by both IR and UV excitation, the former case indicating that overtone, mostly the C=0 stretching overtone excitation is involved.

In the present investigation, the molecule HCOSH has been optimized in both trans and cis structures. The obtained geometrical parameters, total energies and one electron properties are used to study conformational stability of the molecule. The hydrogen bonding between the HCOSH and H$_2$O molecules has been studied through
ab initio and density functional theories. The computations have been performed employing the MICROMOL MARK V [12] computer program.

5.2 Geometry

The geometrical parameters of the HCOSH molecule were optimized by using the split valance basis sets 3-21G, 3-21G* and 6-31G at HF level of theory for trans and cis structures and are given in the Table 5.1. The geometry optimization yields a planar structure for the trans and cis form of HCOSH molecule in support of the assumption of molecular planarity used in the spectral analysis [1] (Fig. 5.1). Pietro et al., [13] have demonstrated that the HF/3-21G* level of theory predicts, the equilibrium structures of both normal valent and hyper-valent molecules containing second row elements are uniformly in good agreement with experimental data. Accordingly, the calculated bond lengths and bond angles at HF/3-21G* level of theory have been found to be in good agreement with the experimental values [4]. It can be seen from the Table 5.1 that the bond lengths are systematically shortened when polarization functions are added to the basis sets, except for the C-H bondlengths for both trans and cis structures. However, the C-S bondlength is found to be the most sensitive, in which the inclusion of d type polarization functions for the heavy atoms results in the decrease of 0.07-0.08 Å of the C-S distance. The effect of p type polarization functions to the hydrogen atoms is less significant. Altogether this bond shortening brings the calculated values much closer to the experimental values. The calculated C=O and C-H distances are found to be about 0.02 Å short in all the three basis sets. The addition of polarization functions to the basis set causes an increase of 1.97 degrees in the SCH angle and a slight increase in CSH angle. The intramolecular hydrogen bond length between the oxygen atom of the C=O bond and the hydrogen atom of the OH bond is
Table 5.1

The optimized structure of trans-and cis HCOSH at different basis sets (bondlengths in Å and bond angles in degrees and total energy in a.u.)

<table>
<thead>
<tr>
<th></th>
<th>HCOSH (trans)</th>
<th></th>
<th>HCOSH (cis)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3-21G</td>
<td>3-21G*</td>
<td>6-31G</td>
<td>Exp(^a)</td>
</tr>
<tr>
<td>(r_{CS})</td>
<td>1.855</td>
<td>1.781</td>
<td>1.821</td>
<td>1.768</td>
</tr>
<tr>
<td>(r_{SH})</td>
<td>1.351</td>
<td>1.329</td>
<td>1.352</td>
<td>1.354</td>
</tr>
<tr>
<td>(r_{CO})</td>
<td>1.197</td>
<td>1.175</td>
<td>1.201</td>
<td>1.205</td>
</tr>
<tr>
<td>(r_{CH})</td>
<td>1.078</td>
<td>1.098</td>
<td>1.080</td>
<td>1.104</td>
</tr>
<tr>
<td>(\angle_{CSH})</td>
<td>96.0</td>
<td>96.3</td>
<td>97.0</td>
<td>92.5</td>
</tr>
<tr>
<td>(\angle_{HCS})</td>
<td>110.0</td>
<td>109.8</td>
<td>111.4</td>
<td>110.0</td>
</tr>
<tr>
<td>(\angle_{OCS})</td>
<td>124.0</td>
<td>125.4</td>
<td>124.5</td>
<td>125.9</td>
</tr>
<tr>
<td>Total energy</td>
<td>-508.78499</td>
<td>-508.99593</td>
<td>-511.29044</td>
<td>-508.78055</td>
</tr>
</tbody>
</table>

\(^a\) From Ref [4]. Microwave Spectra.
Fig. 5.1 Molecular structures of trans and cis HCOSH molecule
obtained as 2.67 Å in HF/6-31G basis set and 2.61 Å in the HF/3-21G basis set. The experimental value of this parameter is found to be 2.53 Å through microwave spectroscopy [4]. In general the differences in bondlengths and bond angles between the trans and cis structures follow the same trend, as observed in experimental values [4]. The difference between the trans and cis structures is prominent in the case of SCH angle due to the interaction of H(C)...H(S), that occurs in the cis structure.

5.3 Monomer Energies

The rotational spectrum of Hocking and Winnewisser [5] shows that the trans conformation was deduced as the main conformer, with it being in equilibrium with the cis form. It has been estimated that the ground state of the cis conformer is $0.6613 \pm 0.0017$ kcal/mol higher than the ground state of the trans conformer. This energy difference is much smaller than that of formic acid HCOOH, where the experimental energy difference between the cis and trans forms is 3.902 kcal/mol [14]. For the HCOSH molecule, the theoretical calculations with or without polarization function of double zeta basis sets, at HF and MP2 levels of theory have predicted that the energy difference to be higher by a factor of two to five [9,15]. At the HF level, the energy difference between the cis and trans conformers of thioformic acid is in the range 1.2 - 3.3 kcal/mol. Inclusion of polarization functions to the basis sets has reduced this energy separation to a value of 1.2 - 1.9 kcal/mol [11]. In the present study the total energy of the HCOSH molecule in trans and cis structures have been calculated at HF/3-21G, HF/3-21G$^*$ and HF/6-31G levels and given in the Table 5.1. From these calculations, the trans structure is found to be more stable than the cis structure by 2.8, 1.4 and 3.0 kcal/mol in HF/3-21G, HF/3-21G$^*$ and HF/6-31G basis.
sets respectively. These figures clearly demonstrate the importance of polarization functions in calculating the HF energies of sulphur containing molecules [11].

The height of the barrier indicate primarily the role of conjugation in the C-S bond towards stabilizing the two planar confirmations of trans and cis form. The corresponding barrier in HCOOH molecule in the same basis set has been obtained as 7.22 kcal/mol [16], which is higher, as expected since the C-O bond should have more double bond character than the C-S bond. The dipole - dipole repulsion of the nearly parallell CH and SH bonds in the cis rotamer and the stabilizing interaction between the C=O and S-H bonds in the trans rotamer can also be expected. But both of the these effects will be smaller in HCOSH due to the length of the C-S bond. (The length of the C-S bondlength is 1.86 Å and the C-O bond length of HCOOH has been obtained as 1.35 Å [16] at HF/3-21G basis set level).

5.4 The Monothioformic Acid ....Water Complex

The interaction of HCOSH....H₂O complex has been studied at the HF/3-21G level by keeping the HCOSH and H₂O monomers in the optimized structural parameters at the HF/3-21G level and by varying the intermolecular distance and HOH angle of water molecule due to the fact that the hydrogen bond energies are always small and the identity of the monomer in the complex structures is usually largely retained.

For both HCOSH(T)....H₂O and HCOSH(C)....H₂O complexes, the hydrogen bonding of S-H ....O is considered as linear (Fig.5.2) since the usual form of the hydrogen bond is always linear and this linearity has been supported both experimentally
Fig. 5.2 Molecular structure of HCOSH[T]...H$_2$O and HCOSH[C]...H$_2$O molecular complexes.
and computationally [17]. This is mainly because due to small energies of hydrogen bonds and a large change in angle corresponds to only a few tenth of a kilocalorie [17]. The 3-21G calculated potential energy surface of HCOSH(T)...H₂O and HCOSH(C)...H₂O complexes are presented in Fig. 5.3 (a & b) and 5.4 (a & b) respectively. The optimized hydrogen bondlength and HOH angle were found to be 1.84 Å and 109.8° respectively for the HCOSH(T)...H₂O complex and the same values were found to be 1.97 Å and 109.0° for the HCOSH(C)...H₂O Complex.

5.4.1. Hydrogen Bonding Characteristics

Using the definitions based of the molecular orbital representation, Allen [17] has established three monomer quantities \( \mu_{A-B} \) (dipolemoment), \( \Delta I \) (difference in ionization potential) and \( R \) (heavy atom internuclear separation) that characterize a physical model of the normal hydrogen bond. This model has organized the results computed from ab initio wave functions and rationalized the qualitative characteristics of the hydrogen bond like dimerization energy, charge transfer, dipolemoment, internuclear separation, etc., For the HCOSH...H₂O interaction, the above three monomer quantities can be explained as follows.

\( \mu_{S-H} \) represents the bond dipolemoment along the S-H bond, which is the principal characterizing factor for the total dipolemoment. To form the hydrogen bond, it is necessary that the sulphur atom (proton donor) should have the bond dipole, with the hydrogen slightly positive and the hydrogen orbital not entirely filled. The experimental S-H bond dipole moment is 0.53 D and for the O-H bond it is 1.13 D.
Fig. 5.3a. The 3-D potential energy surface (contour plot) of HCOSH(T)...H₂O complex, relative energy (r,θ), relative energy in kcal/mol, r in Å and θ in degrees.
Fig. 5.3b. The 3-D potential energy surface (surface plot) of HCOSH(T)...H₂O complex, relative energy (r,θ), relative energy in kcal/mol, r in Å and θ in degrees.
Fig. 5.4a. The 3-D potential energy surface (contour plot) of HCOSH(C)...H2O complex, relative energy (r,θ), relative energy in kcal/mol, r in Å and θ in degrees.
Fig. 5.4b. The 3-D potential energy surface (surface plot) of the HCOSH(C)...H₂O complex, relative energy (r,θ), relative energy in kcal/mol, r in Å and θ in degrees.
[17]. The total dipole moment of HCOSH(T)….H₂O and HCOSH(C)….H₂O hydrogen bonding complexes are found to be 3.02 D and 7.16 D respectively and for the HCOOH(T)….H₂O and HCOOH(C)….H₂O complexes, the values are 3.84 D and 8.10 D respectively [16].

ΔI is the difference between the first ionization potential of the monomer (electron donor) and that of the noble gas atom in its row; for the water molecule its value is given by 8.94 eV [17]. Since ΔI measures the lone pair distortability, in the interaction HCOSH….H₂O, it measures the extent to which the sulphur atom can induce a charge polarization of the oxygen atom of the water molecule. The value of ΔI for H₂O is higher compared with the values of other electron donors like PH₃ and SH₂ for which it is given by 5.16 eV and 5.29 eV respectively [17].

The third factor that influences the hydrogen bonding character is R, the heavy atom internuclear separation. For the HCOSH(T)….H₂O and HCOSH(C)….H₂O complexes, the value of R has been obtained as 3.191 Å and 3.321 Å respectively. Comparing to HCOSH(C)….H₂O complex, the HCOSH(T)….H₂O complex is strongly bound since the bonding is inversely proportional to the distance between the heavy atoms. The value of R also gives the measure of charge density since charge distribution is occurring between S and H, H and O(H₂O) and between O and its ligands. Further with respect to normal hydrogen bond model, in the charge distribution, the center of charge loss is between O (H₂O) and its ligands and the center of charge gain is near S.
5.4.2 Binding Energy of the Molecular Complexes

The complex energies, monomer energies and interaction energies ($\Delta E$) for the HCOSH(T)...H$_2$O and HCOSH(C)...H$_2$O complexes are given in the Table 5.2, along with BSSE values. The interaction energy $\Delta E$ is determined from

$$\Delta E = E^{TW} - (E^T + E^W) \quad (5.1)$$

where $E^{TW}$, $E^T$ and $E^W$ are total energies of the complex system, HCOSH monomer and H$_2$O monomer systems respectively. The counterpoise method of Boys and Bernardi [18] was used for $\Delta E$ and all the occupied and virtual orbitals of the 'ghost' system were used. Interaction energy defined by Eq.(5.1) contains the deformation energy (i.e.) energy needed to deform the subsystems from their optimized geometry to the geometry they have in the complex system. The interaction energy corrected for BSSE is evaluated from

$$\Delta E (\text{BSSE}) = \Delta E + \text{BSSE} \quad (5.2)$$

The counterpoise corrected binding energy values for the HCOSH(T)...H$_2$O and HCOSH(C)...H$_2$O complex systems were obtained as 3.97 kcal/mol and 4.10 kcal/mol respectively, without electron correlation and vibrational zero point considerations. The HCOSH(T)...H$_2$O complex is found to be more stable than the HCOSH(C)...H$_2$O complex by 3.5 kcal/mol. The barrier height of the cis complex is rather less by 0.72 kcal/mol than the trans complex whereas in the case of formic acid the two barrier heights were found to be equal [16]. (The difference is only 0.07 kcal/mol) With the BSSE correction, the interaction energy of the HCOSH(T)...H$_2$O complex becomes 3.97 kcal/mol and for the HCOSH(C)...H$_2$O complex it is 4.10 kcal/mol. Hence it follows that the BSSE correction makes the barrier height of the HCOSH(T)...H$_2$O complex to be reduced by 0.13 kcal/mol than the HCOSH(C)...H$_2$O complex.
Table 5.2
Monomer energies, complex energies $E_{\text{complex}}$, reaction energies $\Delta E$ and BSSE at the HF/3-21G level.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Optimized Monomer energy (a.u.)</th>
<th>$E_{\text{complex}}$ (a.u.)</th>
<th>$\Delta E$ (kcal/mol)</th>
<th>BSSE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOSH (T)</td>
<td>-508.78499</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCOSH (C)</td>
<td>-508.78055</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-75.58596</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCOSH(T)...H$_2$O Complex</td>
<td>-584.38328</td>
<td>7.74</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td>HCOSH(C)...H$_2$O Complex</td>
<td>-584.37770</td>
<td>7.02</td>
<td>2.92</td>
<td></td>
</tr>
</tbody>
</table>


5.4.3 The Density Functional Theory Considerations

The density functional theory (DFT) calculations were made on the HCOSH monomer and HCOSH....H$_2$O complex systems and the results are given in the Table 5.3. The DFT provides a very interesting framework for the quantitative description of global and local indices that allow one to study the inherent reactivity of chemical species [19]. The two important parameters of the DFT theory are the electronic chemical potential $\mu$ [20] and the absolute hardness $\eta$ [21] that characterize the given chemical system [19]. Operational definitions for these quantities are given by $\mu = (I+A)/2$ and $\eta = (I-A)/2$ where $I$ and $A$ are referred as Ionization potential and electron affinity respectively. If the two systems B and C are brought together, the fractional number of electrons transferred, $\Delta N$ is given by [21],

$$\Delta N = \frac{\chi_C - \chi_B}{2(\eta_C + \eta_B)}$$

(5.3)

Where the absolute electronegativity $\chi$ is equal to $-\mu$. The electron flow is continued in a complex system from that of lower $\chi$ to that of higher $\chi$ until the chemical potentials are equal.

The interaction between the two systems becomes strong and more favourable with an increase in the value of $\Delta N$. The Table 5.3 shows the HCOSH(C)....H$_2$O interaction is more favourable with $\Delta N$ value of 0.02 than the HCOSH(T)....H$_2$O interaction. The HOMO-LUMO (highest occupied MO - Lowest unoccupied MO) energy gap and the absolute hardness values are found to be more for the trans HCOSH molecule by 0.01 eV than the cis HCOSH molecule; Hence the trans HCOSH molecule
Table 5.3

Density functional theory calculations of the thioformic acid monomer and the thioformic acid... water complex (all values except $\Delta N$, are in eV).

<table>
<thead>
<tr>
<th>Complex</th>
<th>-$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>-2$\mu$</th>
<th>-2$\eta$</th>
<th>$\chi$</th>
<th>$\eta$</th>
<th>$\Delta N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOSH (T)</td>
<td>10.87</td>
<td>3.66</td>
<td>7.21</td>
<td>14.53</td>
<td>3.61</td>
<td>7.27</td>
<td></td>
</tr>
<tr>
<td>HCOSH (C)</td>
<td>10.89</td>
<td>3.63</td>
<td>7.26</td>
<td>14.52</td>
<td>3.63</td>
<td>7.26</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>12.95</td>
<td>7.1</td>
<td>5.85</td>
<td>20.05</td>
<td>2.93</td>
<td>10.03</td>
<td></td>
</tr>
<tr>
<td>HCOSH(T)...$\text{H}_2\text{O}$ Complex</td>
<td>9.97</td>
<td>4.30</td>
<td>5.67</td>
<td>14.27</td>
<td>2.84</td>
<td>7.14</td>
<td>0.0197</td>
</tr>
<tr>
<td>HCOSH(C)...$\text{H}_2\text{O}$ Complex</td>
<td>10.06</td>
<td>4.23</td>
<td>5.83</td>
<td>14.29</td>
<td>2.92</td>
<td>7.15</td>
<td>0.0202</td>
</tr>
</tbody>
</table>
can be considered to be more stable but less reactive since its higher hardness contributes to less polarizability. But at the same time, for the complex systems the HOMO-LUMO energy gap and the hardness values gave an exactly opposite trend. The HOMO-LUMO energy gap and hardness values are found to be more for HCOSH(C)....H₂O complex by 0.02 and 0.01 eV respectively. Hence it follows that among the two interactions, the HCOSH(C)....H₂O complex can be considered to be more stable since an increase in hardness is always accompanied with a more stable configuration [22].

5.4.4 Charge Transfer and Dipolemoment

The recent study [24] on the chemical hardness for the hydrogen bonded system shows that the higher values of chemical hardness could not able to predict for the higher stability of the system. Hence the bonding and stability of the molecular complexes have also been studied in view of the electron population around the atoms and the determined atomic charges of the monomer and complex systems are given in the Table 5.4. The hydrogen bond between the two monomers and the enhancement of the dipolemoment are always characterized by the charge distribution between different atoms of the complex system. The net charge transfer from the H₂O molecule to the HCOSH molecule is more by 0.013 electronic units for the HCOSH(T)....H₂O complex than the HCOSH(C)....H₂O complex. Hence the value of hydrogen bond dipolemoment μO-H should be more in the case of HCOSH(T)....H₂O complex and hence the penetration of lone pair also becomes more. This penetration leads to shorten the internuclear separation; the hydrogen bond length between the trans HCOSH and H₂O molecules has been found to be less by 0.13 Å than the hydrogen bondlength of cis HCOSH and H₂O molecule.
The more stability of trans HCOSH might be due to the intramolecular interaction that is present in the trans monomer. This fact has been supported from the calculated atomic charges for both the monomers from the Table 5.4. Both sulphur and oxygen atoms are found to be more negative in trans HCOSH when they are compared with those of cis form. The sulphur atom in the cis form has a charge +0.093 and that in the trans form +0.052. The charge on the oxygen atom is -0.476 in cis HCOSH and -0.488 in the trans form. Conversely, the S-H hydrogen atom charge is more positive (+0.112) in the trans HCOSH than in the cis HCOSH (+0.065) that leads to stabilization by electrostatic attraction.

An overestimation of dipolemoment in HF calculations is the usual trend observed for compounds containing a heteroatom [23]. This is due to the difficulty in describing the charge distribution correctly. The experimental dipolemoments are 1.536 D and 2.868 D for the trans and cis HCOSH molecule respectively [6]. In the present calculations, the dipolemoments have been obtained as 0.97 D and 3.48 D respectively. The accuracy of the dipolemoment values are also found to be basis set dependents. The best values of the dipolemoment have been obtained by Raaska et al., [11], 1.517 D for trans structure using HF/6-31G** basis set and 3.333 D for cis structure, using HF/6-311G** basis set [11].
Table 5.4

Atomic net charges (electronic units) of HCOSH (trans and cis) monomers, HCOSH(T)...H₂O and HCOSH(C)...H₂O Complexes.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Monomer</th>
<th>HCOSH(T)...H₂O Complex</th>
<th>HCOSH(C)...H₂O Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>trans</td>
<td>cis</td>
<td></td>
</tr>
<tr>
<td>H(HC)</td>
<td>+0.246</td>
<td>+0.237</td>
<td>+0.230</td>
</tr>
<tr>
<td>C</td>
<td>+0.078</td>
<td>+0.081</td>
<td>+0.083</td>
</tr>
<tr>
<td>O</td>
<td>-0.488</td>
<td>-0.476</td>
<td>-0.511</td>
</tr>
<tr>
<td>S</td>
<td>+0.052</td>
<td>+0.093</td>
<td>-0.062</td>
</tr>
<tr>
<td>H(SH)</td>
<td>+0.112</td>
<td>+0.065</td>
<td>+0.192</td>
</tr>
<tr>
<td>O(H₂O)</td>
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<td></td>
<td>-0.724</td>
</tr>
<tr>
<td>H₁(H₂O)</td>
<td></td>
<td></td>
<td>+0.392</td>
</tr>
<tr>
<td>H₂(H₂O)</td>
<td></td>
<td></td>
<td>+0.400</td>
</tr>
<tr>
<td>Dipolemoment</td>
<td>0.97 D</td>
<td>3.48 D</td>
<td>3.02 D</td>
</tr>
</tbody>
</table>
References