Evidence of sulfur centered hydrogen bond with sulfur atoms as a donor in aromatic thiols and aliphatic thiols on complexation with water using quantum mechanical methods

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Abstract

It has been more than a century since the discovery of hydrogen bonds, but the knowledge about its impact on day to day life of people is getting enhanced even now. It has a pivotal role in the stabilization of various biomolecules and subsequent bioactivity. Sulfur cantered hydrogen bond (SCHB), which is a weak interaction, has attracted the attention of many scientists in the last few decades. In this work, we report the nature of the SCHB between aliphatic/aromatic thiols and water. B3LYP-D3(BJ) with cc-pVTZ level was used for modeling the hydrogen bonded thiol-water complexes. Domain-based local pair natural orbitals coupled-cluster theory with single, double, and perturbative triple excitation DLPNO-CCSD(T) method was used for local energy decomposition analysis. QTAIM analysis helped to examine hydrogen bonds, weak non-covalent interactions, and the various electron density delocalization. Natural Bond Orbital (NBO) analysis explains the reason for the sulfur atom being the H-bond donor. Second-order perturbation energy from NBO findings supports the data obtained by LED and AIM calculations. Aromatic thiols form stronger hydrogen bonds than aliphatic thiols. The effect of substituents was also explored by studying aromatic systems with electron-withdrawing groups and donating groups. EDG substituted have more vital interaction, and EWG substituted thiols form stronger S-H…O hydrogen bonds.

Keywords: Sulfur cantered hydrogen bond; Thiol-water; DLPNO-CCSD(T); Local energy decomposition (LED); AIM; NBO

Introduction

The hydrogen bond (HB) is still an essential field of research after more than a century of its discovery [1,2]. It is one of the most studied non-covalent interactions due to its omnipresence in many chemical and biological processes. The recent developments in the study of supramolecular chemistry accelerated further basic research of hydrogen bonds. Gerlt and coworkers showed the role played by short, strong HBs in enzymatic catalysis [3]. Perrin and Nielsen reviewed the importance of short hydrogen bonds in chemical and biological processes [4]. Other essential roles played by Hydrogen bonding can be seen in binding between substrate and enzyme [5] shown by Fersht. Hydrogen bonds play a vital role in the structure of the DNA helix [5,6]. Lehn showed that hydrogen bonds help in self-organising in supramolecular chemistry [7] and Xanthes [8], Albrecht and coworkers [9] and Zabardasti and coworkers [10] showed that hydrogen bonding is involved in molecular cluster formations. Jiang and Lai reported that there is the presence of CH-O hydrogen bonds even at the protein-protein interfaces and showed that this type of hydrogen bond contributed 17% to the overall non-covalent interactions between a series of protein-protein systems [11]. Sheiner used *abinitio* calculations to study the ability of the aromatic groups in aminoacids to form hydrogen bonds[12]. N−H···π hydrogen bond was also detected between the pi-electron cloud of aromatic rings and N-H residues of amino acids [13].

Hydrogen bonds play a major role in many physical, biological and chemical phenomenons, and in this manuscript, we discuss the study about weak sulfur centred hydrogen bonds (SCHB). According to the recommended definition of Hydrogen bond by IUPAC [14], it can be described as attractive interaction of hydrogen atom attached to a donor atom (Dn) and an acceptor atom (Ac) and can be written as Dn-H---Ac [10]. The donor and acceptor atoms are generally electronegative atoms, but non-conventional hydrogen bonds have carbon, sulfur or pi electrons as the donor or acceptor which forms weak hydrogen bonds, are reported in the literature [15–17].

Biswal and coworkers have performed extensive experimental studies using ultrafast laser spectroscopy to study the nature and strength of sulphur centred hydrogen bonds

[18]. They have pointed out the importance of the S and Se centred hydrogen bonds in tuning orgaic molecules for even organoelectronic applications [19]. They have recently studied the hydrogen bond driven thiouracil dissolution in ionic liquids using both experimental and computational tools [20]. Arunan and coworkers studied the rotational spectra of SCHBs with H_2S and compared it with its oxygen counterpart. SCHBs are generally weak bonds compared to the more conventional oxygen centred hydrogen bonds (OCHB) because of the low electronegativity difference between sulfur and hydrogen atom [21]. Goswami and Arunan did a theoretical and spectroscopic study of SCHBs with H_2S [22]. Sarkar and coworkers studied the cooperativity of SCHBs in H_2S clusters [23]. van Bergen and coworkers used the NCI index to identify hydrogen bonds involving sulfur in proteins [24]. Juanes and coworkers [25] studied the stabilization of thienyl mercaptan hydrates due to O_w---HS hydrogen bond and secondary O_w--H...π interactions with the ring. A lot of research in hydrogen bonds involving sulfur have been reported in literature earlier but not much work has been done on Hydrogen bonds with oxygen as the acceptor atom. In our work, we have studied the donor capability of sulfur with methanethiol, ethanethiol and 1-propanethiol for the formation of sulfur centred hydrogen bonds (SCHB) with the oxygen of water molecule as the acceptor atom, S-H---O.

Domain-based local pair natural orbitals coupled-cluster theory with single, double and perturbative triple excitation DLPNO-CCSD(T) have been used in this work. This method gives results approaching its parent CCSD(T) method and with the Normal PNO truncation threshold, it is possible to approach the CCSD(T) results with a 1kcal/mol range [26]. DLPNO-CCSD(T) method provides accuracy closer to its parent canonical form CCSD(T), which is considered as the gold standard but is computationally very less expensive than CCSD(T) and this method scales linearly to modern DFT methods [26]. Local Energy Decomposition (LED) method breaks down the DLPNO-CCSD(T) energies into meaningful physical contributions from the fragments, including electrostatic energy, electron exchange energy, strong pair contributions and other important contributions [27]. LED analysis has been done in this work to study the interactions of weak SCHBs in thiols and water systems. QTAIM analysis [28] have been employed in earlier studies by Hajji and coworkers to examine hydrogen bonds, weak non-covalent interactions, electron density delocalization and aromaticity [29,30]. In this work, the quantum theory of atoms in molecules analysis was done in which topological analysis of bond critical points based on electron density was used to assess the binding energies of the SCHBs. Natural Bond Orbital (NBO) analysis was done to highlight the reasons for sulfur atom acting as the hydrogen bond donor.

Computational Details

Geometry optimization for all eight system, methanethiol – water, ethanethiol – water, 1-propanethiol – water, benzylthiol - water, thiophenol - water, 4-nitrothiophenol - water, 4-cyanothiophenol - water and 4-chlorothiophenol - water was done using B3LYP exchange correlational functional with Grimme's empirical dispersion correction method DFT-D3 with Becke-Johnson damping, commonly known as B3LYP-D3(BJ) [31,32]. Dunning's correlation consistent basis set cc-pVTZ was used for all calculations [33][34]. Frequency calculations were done at the same level on the optimized geometries for all the systems to make sure all stationary points are at true minima and do not have any imaginary frequencies. Avogadro software was used for visualising the optimised geometries and vibrational frequencies [35]. DLPNO-CCSD(T) and LED studies for all three systems were done with Tight PNO settings using the cc-pVNZ (N = T,Q) basis sets [36]. For the localisation of Molecular Orbitals, Foster-Boys localisation scheme was applied [37]. All geometry optimizations, frequency calculations and DLPNO-CCSD(T) calculations were performed on ORCA version 4.2.1 [38]. LED energies were extrapolated to CBS limit by the two point scheme [39].

$$E_{CBS} = \frac{n^3 E_{corr}^{(n)} - m^3 E_{corr}^{(m)}}{n^3 - m^3} \qquad .....(1)$$

Here $E_{corr}^{(n)}$ and $E_{corr}^{(m)}$ are energies obtained with cc-pVTZ and cc-pVQZ basis set respectively. Basis set super position error(BSSE) was not corrected because after extrapolation the BSSE-corrected and BSSE-uncorrected energies converge as the BSSE is cancelled out by the basis set convergence error (BSCE) in short range [40]. The optimised geometry at the B3LYP-D3(BJ)/cc-pVTZ theory was used for generation of wavefunction file for QTAIM studies using Multiwfn version 3.7 code [41]. Natural bond orbital analysis was performed using the optimised geometry at B3LYP/cc-pVTZ level using the NBO 3.0 [42] suite incorporated in Gaussian 09W suite [43].

Results and discussions

LED of Interaction Energies

The theory of Local Energy Decomposition and its uses have been described in many papers [26,27,44–46]. The energy of a molecular system XY relative to the energies of non-interacting fragments X and Y can be written as

$$\Delta E = \Delta E_{geo-prep} + \Delta E_{int} \quad ....(2)$$

where ΔEgeo−prep is the geometric preparation energy needed to distort the fragments X and Y from their equilibrium structures at infinite separation to their geometry in the complex. ΔEint is the interaction energy of the fragments X and Y at a given geometry of the complex XY. ΔEint is further decomposed into ΔE_{int}^{ref}, which accounts for the interaction energy at the reference level and ΔE_{int}^{C}, which accounts for correlation contribution.

$$\Delta E_{int} = \Delta E_{int}^{ref} + \Delta E_{int}^{C} \quad .....(3)$$

Since occupied orbitals are localised in DLPNO-CCSD(T) framework ΔE_{int}^{ref} can be further decomposed into electronic preparation, electrostatic and exchange interactions.

$$\Delta E_{int}^{ref} = \Delta E_{el-prep}^{ref} + E_{elstat} + E_{exch} \quad .....(4)$$

The electronic preparation $\Delta E_{el-prep}^{ref}$ corresponds to the energy needed to bring the electronic structures of the isolated fragments from ground states to one which is optimal for interaction. The contribution from the correlation term to the interaction energy can be further described as a sum of Strong pair ΔE_{int}^{C-SP}, weak pair ΔE_{int}^{C-WP} and triples correction $\Delta E_{int}^{C-(T)}$.

$$\Delta E_{int}^{C} = E_{int}^{C-SP} + \Delta E_{int}^{C-WP} + \Delta E_{int}^{C-(T)} \quad ......(5)$$

The weak pair triples correction contribution is very less in comparison to strong pair contribution to the correlation interaction energy. Further decomposition of strong pair contribution can tell us about London dispersion forces and charge transfer energies, which are reported in literature [46] and not discussed here.

Here the LED calculations are done to find the interactions of different molecular adducts, which are methanethiol – water, ethanethiol – water, 1-propanethiol – water and benzylthiol - water systems for aliphatic thiols. Thiophenol - water, 4-chlorothiophenol - water, 4-cyanothiophenol - water and 4-nitrothiophenol - water systems have been studied as representative aromatic thiol systems.

The binding energy in all the eight systems are mostly due to electrostatic energy in addition to electron exchange and strong pair correlation energies, which is typical for a hydrogen bonded system (see Table 1). The total binding energy obtained is not just the strength of the hydrogen bond but the total interaction energy between the thiol molecule and water molecule, including but not limited to ionic interactions, covalent interactions and van der Waals interaction energy. The local energy decomposition analysis tells us that Dispersion effects are also shown in the table as the correlation energy of strong pairs and interfragment dispersive interactions of weak pairs. Triples correction for the interaction energy is also reported for the fragments.

The interaction energy for thiols with a benzene rings, thiophenols and benzylthiol, have much higher interaction energy compared to the thiols not containing a benzene ring. Among the aromatic thiols, we see that substituted thiolphenols have greater interaction energy than the thiophenol - water system. Among the substituted thiophenols, Chlorothiophenol and water system is observed to have the highest interaction. Systems with electron-withdrawing groups (-nitro and -cyano) have lesser interaction than thiophenol with electron-donating groups (-chloro). Para isomers of aromatic systems are only studied as ortho isomers could being steric effects also.

The LED terms for interaction energy and its decomposition into reference energy and correlation energy is reported. The reference energy is further decomposed into electrostatic interaction energy, electronic preparation energy and electron exchange interaction energy. Electronic preparation energy, which is the energy required for the molecules to be in a geometry where they can interact, is the biggest repulsive interaction. Electronic preparation energy counters the strong electrostatic interaction between the molecules. The correlation term, which tells us about the dispersion effects is further decomposed into strong pair contribution and interfragment dispersive interactions of weak pair contribution. Triples correction for the interaction energy, also provides a non-negligible contribution to the binding energies of the system. Electrostatic interaction is the largest among other reference energy and correlation terms, which is an indication that these are hydrogen bonded systems. In all eight systems the correlation energy terms are dominated by the reference energy terms, which are decomposed and reported in meaningful terms in table 1. The coordinates of the optimised geometry and the vibrational modes are given in the Supplementary information Tables S1 –S16.

Table 1 – DLPNO-CCSD(T)based Local energy decomposition (LED) of energy terms for the thiol water systems.

Molecule system	ΔE_{int}	ΔE_{int}^{ref}	$E_{el-prep}^{ref}$	E_{elstat}	E_{exch}	ΔE_{int}^{C}	E_{int}^{C-SP}	ΔE_{int}^{C-WP}	$\Delta E_{int}^{C-(T)}$
Methanethiol - water	-5.89	-4.53	13.54	-15.09	-2.98	-1.36	-1.16	-0.04	-0.15
Ethanethiol - water	-6.61	-4.96	11.49	-13.55	-2.91	-1.64	-1.41	-0.04	-0.18
1-propanethiol - water	-6.98	-5.25	11.72	-13.95	-3.01	-1.72	-1.45	-0.08	-0.19
Thiophenol - water	-10.03	-8.01	14.72	-19.19	-3.54	-2.02	-1.65	-0.13	-0.23
4-Nitrothiophenol - water	-12.47	-10.10	19.54	-25.30	-4.34	-2.37	-1.96	-0.13	-0.27
4-Cyanothiophenol - water	-12.01	-9.67	19.03	-24.45	-4.25	-2.33	-1.93	-0.13	-0.26
4-Chlorothiophenol - water	-14.08	-11.85	14.79	-22.59	-4.05	-2.23	-1.83	-0.14	-0.25
Benzylthiol - water	-11.62	-7.78	21.55	-24.03	-5.30	-3.84	-3.28	-0.09	-0.47

All energies are in kcal/mol

The optimised structure of the thiol complexes are given in figures 1 (aliphatic thiols) and 2 (aromatic thiols).

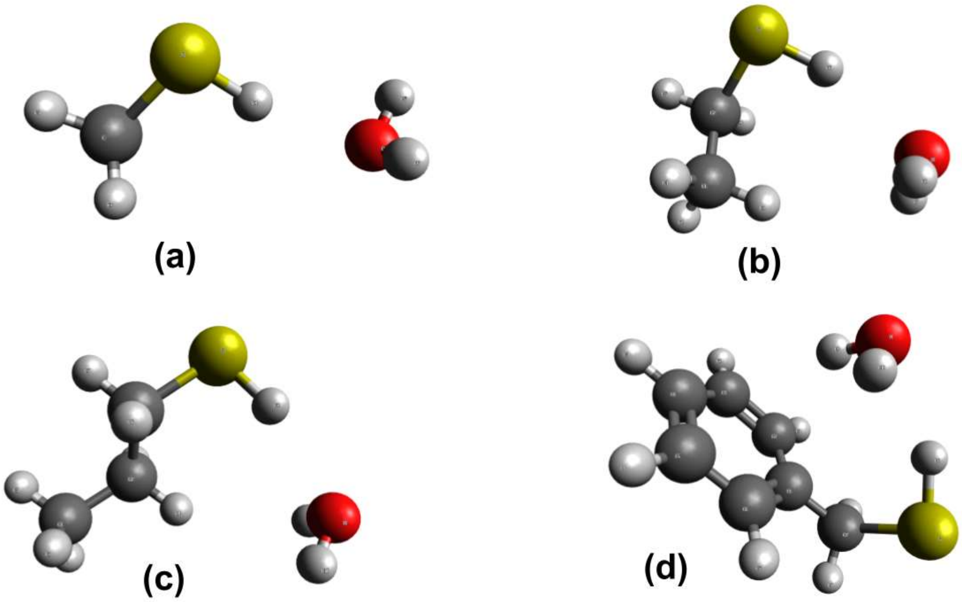

Figure 1 - Optimised geometry of aliphatic thiol - water complex (a) Methanethiol – water, (b) Ethanethiol – water, (c) 1-Propanethiol – water and (d) Benzylthiol - water at B3LYP-D3(BJ)/cc-pVTZ level of theory.

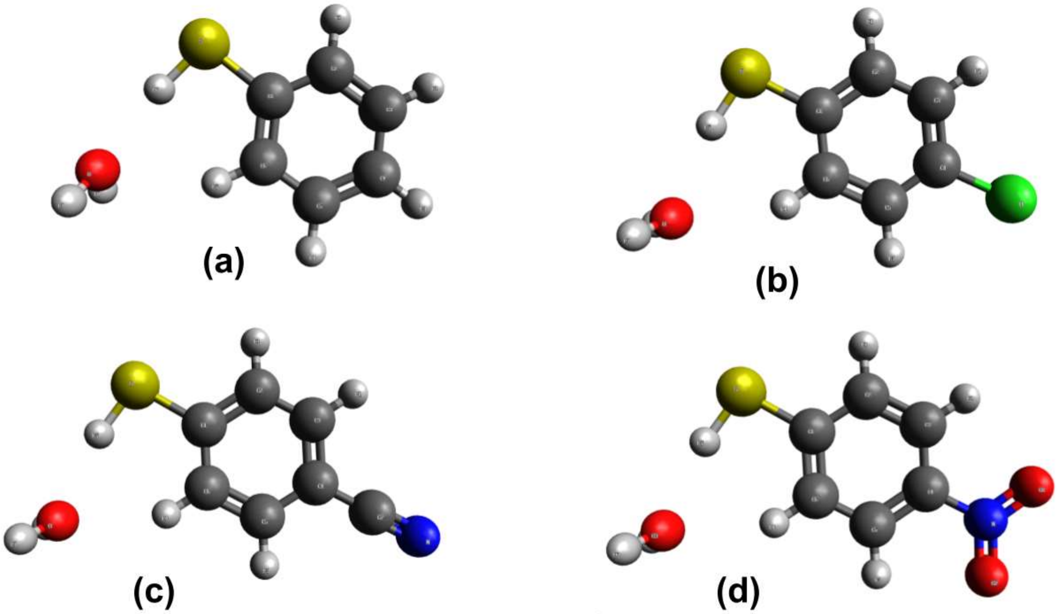

Figure 2 - Optimised geometry of aromatic thiol - water complex (a) Thiophenol - water, (b) 4-Chlorothiophenol - water, (c) 4-Cyanothiophenol - water and (d) 4-Nitrothiophenol - water at B3LYP-D3(BJ)/cc-pVTZ level of theory.

Frontier molecular orbital data can be used to support the above observations. The HOMO LUMO energy gap is low for the aromatic thiols than the aliphatic thiols. Also the aromatic thiol- water have a positive electron affinity and a low global hardness with enhanced softness, which supports the arugument of enhanced polarisation in the systems due to hydrogen bond. Plots of the HOMO and LUMO of the system is given in Figs S1-S8 (Supplementary Information).

Table 2: Frontier Molecular Orbital properties data of the complexes

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
HOMO	-6.15	-6.17	-6.15	-6.40	-5.68	-6.41	-6.23	-5.77
LUMO	0.36	0.11	0.08	-0.87	-0.18	-2.30	-1.34	-0.49
Energy Gap ΔE	6.51	6.28	6.23	5.53	5.50	4.10	4.89	5.29
Electron Affinity (A= εLUMO = -LUMO)	-0.36	-0.11	-0.08	0.87	0.18	2.30	1.34	0.49
Global Hardness (η = (I-A)/2)	3.25	3.14	3.12	2.76	2.75	2.05	2.44	2.64
Global Softness (S = 1/η)	0.31	0.32	0.32	0.36	0.36	0.49	0.41	0.38

(a) methanethiol - water, (b) ethanethiol - water, (c) 1-propanethiol - water, (d) benzylthiol - water, (e) thiophenol - water, (f) 4-nitrothiophenol - water, (g) 4-cyanothiophenol - water, (h) 4-chlorothiophenol - water

Hydrogen bond analysis using Quantum Theory of Atoms in Molecules (QTAIM)

Topological analysis of the systems for electron density at bond critical points was done based on quantum theory of atoms in molecules. Wavefunctions were generated from the B3LYP/cc-pVTZ geometry using Multiwfn software [41]. Topological parameters for selected important bond critical points (BCPs) are reported in table 2. The total number of critical points follow the Poincaré - Hopf relation which was satisfied here. Figures 3 and 4 show the paths connecting the (3,-1) critical points for aliphatic and aromatic thiols respectively.

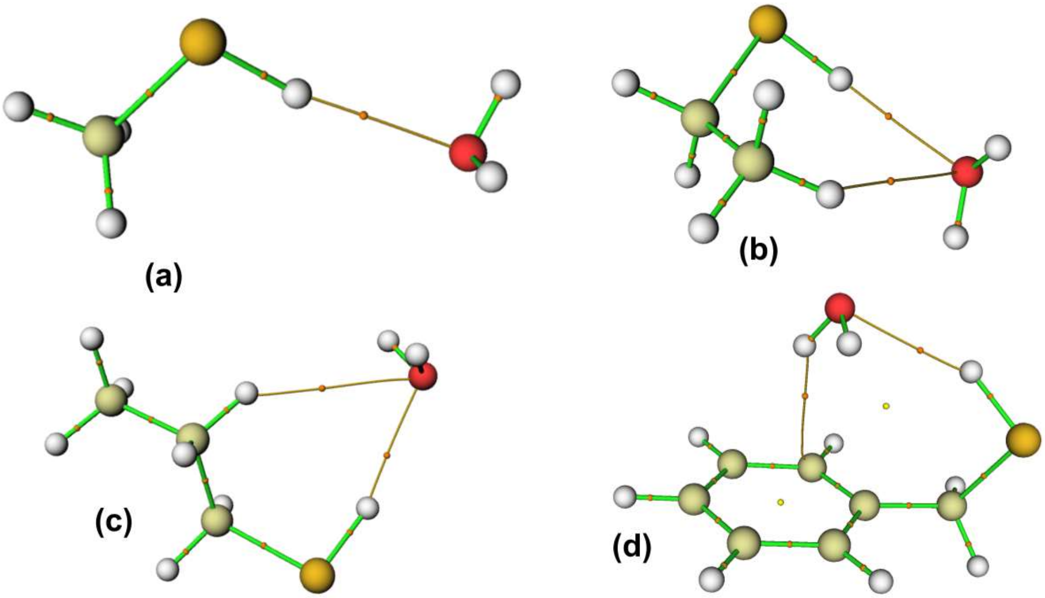

Figure 3 : AIM graphs for different aliphatic thiols - water complexes showing the paths connecting the BCPs. (a) is Methanethiol - water system, (b) is Ethanethiol - water system, (c) is 1-propanethiol - water system and (d) is Benzylthiol - water system

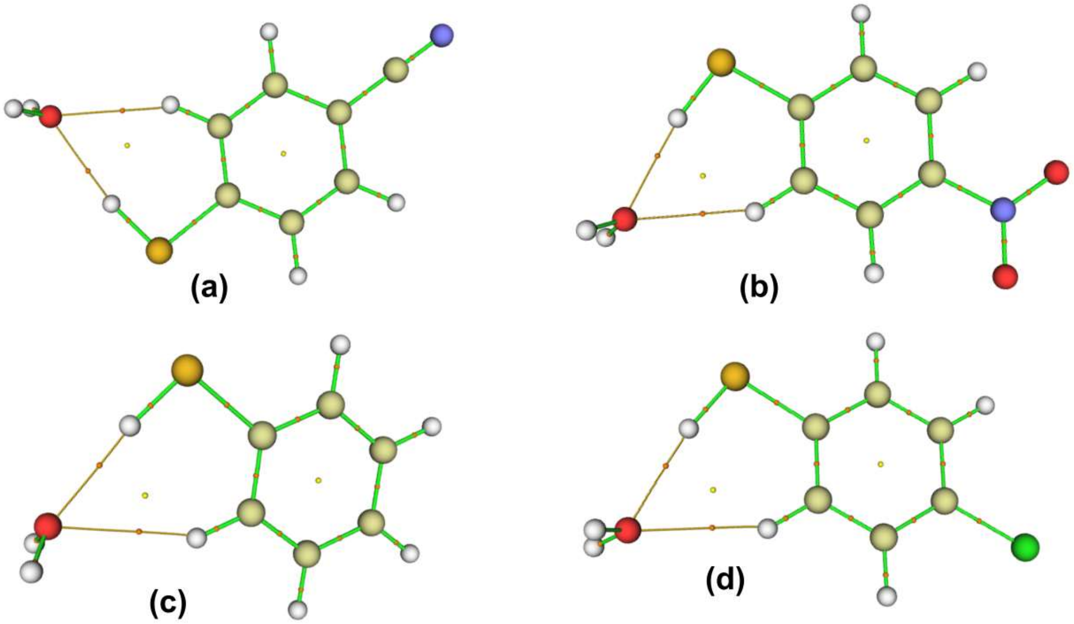

Figure 4 - AIM graphs for different aromatic thiols - water complexes showing the paths connecting the BCPs. (a) is 4-cyanothiophenol - water system, (b) is 4-nitrothiophenol - water system, (c) is thiophenol - water system and (d) is 4-chlorothiophenol - water system

The relations developed by Emamian et al [47]] have been used for estimating the hydrogen bond energies. Espinosa and co workers [48] method of estimating H-Bond energies E = V(r)/2 overestimates the H-bond energy and was not used. The observed Hydrogen bonds are non conventional as the oxygen atom is acceptor and sulfur is the donor atom opposite to regular hydrogen bonds. The hydrogen bond energies for all the systems are not very high and lie from -2.1 kcal/mol to -3.6 kcal/mol, which comes under the category of weak Hydrogen bonds [47]. All these interactions are non-covalent in nature as $\nabla^2\rho > 0$ and $|V(r)|/G(r) < 1$. In ethanethiol - water system and 1-propanethiol - water system other weak non covalent interactions were observed, which could be termed as very weak hydrogen bonds. In ethanethiol – water system, C(2)H…O interaction (-0.308 kcal/mol) and in 1-propaethiol – water system C(2)H---O interaction (-0.373 kcal/mol) was observed. Similar secondary interactions were also observed in the substituted and unsubstituted thiophenols, but the interactions are observed to be a little stronger (-1 to -1.4 kcal/mol). Substituted thiophenol - water systems have a greater H-bond strength than unsubstituted thiophenol - water system. Thiophenols substituted with electron withdrawing group (-nitro and -cyano) have stronger hydrogen bonding strength compared to electron donating group (-chloro) substituted thiophenol and water system.

Table 2 – QTAIM topological parameters for selected bond critical points.

Molecule system	BCP	ρ (in a.u.)	$\nabla^2\rho$	V(r) in kcal/mol	G(r) in kcal/mol	H(r) (in kcal/mol)	BE (in kcal/mol
Methanethiol - water	SH---O	0.019	0.053	-5.867	7.141	1.273	-3.614
Ethanethiol - water	SH---O	0.013	0.047	-4.944	6.162	1.211	-2.345
	C(1)H---O	0.004	0.014	-1.449	1.869	0.414	-0.306

1-propanethiol - water	SH---O	0.013	0.047	-5.026	6.275	1.242	-2.374
	C(2)H---O	0.005	0.015	-1.562	1.970	0.407	-0.373
Thiophenol - water	SH---O	0.015	0.058	-6.109	7.681	1.572	-2.751
	C(2)H---O	0.008	0.027	-2.733	3.486	0.753	-1.075
4-Nitrothiophenol - water	SH---O	0.018	0.064	-7.115	8.630	1.514	-3.273
	C(2)H---O	0.009	0.036	-3.380	4.533	1.153	-1.385
4-Cyanothiophenol - water	SH---O	0.0176	0.063	-6.909	8.412	1.502	-3.195
	C(2)H---O	0.009	0.035	-3.333	4.483	1.150	-1.357
4-Chlorothiophenol - water	SH---O	0.017	0.060	-6.561	8.026	1.464	-3.063
	C(2)H---O	0.008	0.033	-3.117	4.210	1.092	-1.230
Benzylthiol - water	SH---O	0.012	0.041	-4.466	5.526	1.059	-2.144

BE - Binding Energy; BCP - Bond critical point; ρ (in a.u.) - electron density; ∇2ρ - laplacian of electron density; V(r) in kcal/mol - Potential energy density; G(r) in kcal/mol - Lagrangian kinetic energy; H(r) (in kcal/mol) - Energy density.

NBO Analysis

NBO analysis was done for the complexes to gain insights into the orbital interactions of the fragments. The optimised geometries at B3LYP/cc-pVTZ was used for the NBO calculations. For a X-H...Y kind of hydrogen bond, a $Y_{n(lp)} \rightarrow \sigma_{X-H}^*$ interaction is observed, which signifies the interaction of lone pair of Y with the empty X-H antibonding orbital. For our thiol water systems, the antibonding orbitals of the S-H bond interacts with the lone pair of the water molecule. The second order perturbation stabilization energy *E*(2) have been reported in table for the $O_{(lp)} \rightarrow \sigma_{S-H}^*$ interaction. These results augments the LED and QTAIM conclusions.

Table 3: Natural orbital interaction (second order perturbation) energies for thiol water complexes (at B3LYP/cc-pVTZ level of theory)

Molecule system	$O_{(lp)} \rightarrow \sigma_{S-H}^*$ orbital interaction (in kcal/mol)
Methanethiol - water complex	4.53
Ethanethiol - water complex	3.60
1-Propanethiol - water complex	3.68
Thiophenol – water complex	4.03
4-Nitrothiophenol – water complex	5.48
4-Cyanothiophenol – water complex	5.36
4-Chlorothiophenol – water complex	5.18
Benzylthiol – water complex	2.99

From the data reported in the Table 3, we can see that there is charge transfer between oxygen of water and the S-H bond of the thiols, which can be seen by the $O_{(lp)} \rightarrow \sigma_{S-H}^*$ for all the complexes. This explains the fact that the sulfur atom acts as hydrogen bond donor while oxygen atom is the acceptor. The interaction energies are a good indicator of the order of strength of the hydrogen bonds. Aromatic thiophenols have greater interaction energy compared to aliphatic thiols, and among the thiophenols, substituted thiophenols have greater $O_{(lp)} \rightarrow \sigma_{S-H}^*$ orbital interaction.

Conclusion

Sulfur centred hydrogen bond is a special type of non-covalent interaction in the major class of hydrogen bonds. In this study, we examined the SCHB formation of various aliphatic and aromatic thiols when complexed with a water molecule using high accuracy abinitio methods like DLPNO-CCSD(T) using Resolution of the Identity formalism, Quantum theory of atoms in molecules and natural bond orbital analysis. All results shows that there is an effect formation SCHB between the thiols and water**.** In hydrogen bonds involving oxygen and sulfur atoms, generally the oxygen atom is the donor and sulfur is the acceptor. But in this case, sulfur atom acts as the donor despite being the less electronegative atom. LED studies tell us that the interaction between aromatic thiol and water is greater than aliphatic thiols and water. EDG substituted thiophenols had greater binding energy with water than EWG substituted thiophenol, however H-Bond strength is observed to higher in EWG thiols and water than compared to EDG thiols and water. LED studies also show that the major contribution to the interaction energies between the thiol and water molecules was from electrostatic energy, which are typical for weak hydrogen bonded systems. QTAIM analysis gave the binding energy of the HBs for the systems in the range of -2.1 to -3.6 kcal/mol, which is classified as weak hydrogen bonds. Aromatic thiols are observed to make stronger hydrogen bonds. Thiophenols substituted with electron withdrawing group (-nitro and -cyano) have stronger hydrogen bonding strength compared to electron donating group (-chloro) substituted thiophenol and water system. The Laplacian of electron density $\nabla^2\rho > 0$ and the ratio of kinetic and potential energy $-G(r)/V(r) > 1$ show that the interactions are of non covalent nature. Findings from NBO analysis reinforces that the Sulfur atom acts as the H-bond donor and oxygen atom of water acts as H-bond acceptor. Second order perturbation energy for the complexes show a significant interaction between the lone pair of oxygen atom and antibonding orbital of S-H bond. Substituted aromatic thiol - water systems show greater interactions than aliphatic thiol - water systems.

The use of local energy decomposition (LED) analysis gave us the information about the binding energies of thiols and water, with a deeper understanding of the type of interactions between thiol and water molecues. QTAIM topological analysis specifically provided us the strength of the hydrogen bond between between sulfur and oxyhen. And NBO analysis gave us insights about the orbitals involved in this unusual S-H…O kind of hydrogen bond. LED, QTAIM and NBO analysis together proved the existence of weak sulfur centered hydrogen bonds. Furthermore, this approach can be used to identify the type and energies of hydrogen bonds.

Supplementary Material

Supplementary material contain tables with the xyz coordinates of the three thiol- water complexes (S1-S8) and simulated IR frequencies (S9-S16)

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Contributions

Arnav Paul : Simualtions, Analysis of data, writing manuscript

Renjith Thomas : Conceiving problem, Supervision, software, editing manuscript, result analysis

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