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QUANTUM CHEMICAL INVESTIGATION OF SELECTED PESTICIDES ADSORPTION OVER SULFONYL HYDRAZIDE BASED ADSORBENTS

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Abstract

Pesticides are frequently used chemicals that control organisms like insects and fungi. A pesticide is a chemical used to remove, deter, or decrease any animal, microbial, or plant pest. Pesticides are frequently chemical agents, but they can also be organic or material agents. A lot of individuals erroneously think that insecticides are pesticides. However, there are other insecticides whose calculated pests do not cover insects. In this work we have investigated the adsorption potential of three selected sulphonyl hydrazides derivatives SH1-SH2 against some selected pesticides i.e. Quintozene, pentachlorophenol (PCP) and Chlorothalonil (CT) which are commonly used in swat region of KP, Pakistan. The title study were carried out through computational chemistry and modeling via Density Functional Theory (DFT) by using B3LYP level of theory with 6-311G(d,p) basis sets. According to our investigation the adsorption mechanism were based on hydrogen bonding and weak Vander Waal forces. The adsorption energies are 6.4-9.38 kcal.mol^{-1}. This study reveles that the complexes with two pesticides coordinated to sulphonyl-hydrazides are more stable than their corresponding substrates and the complex with one molecule of pesticide. Our theoretical findings are good explanation for experimental researchers and we believe that these derivatives will be best adsorbents in future.

INTRODUCTION

Pesticides are frequently used chemicals that control organisms like insects and fungi. [1] Weeds and bacteria that kill plants, especially those plants which produce food.[2] A pesticide is an chemical used to remove, deter, or decrease any animal, microbial, or plant pest. Pesticides are frequently chemical agents, but they can also be organic or material agents. A lot of individuals erroneously think that insecticides are pesticides. However, there are other insecticides whose calculated pests do not cover insects. Herbicides, fungicides, rodenticides, acaricides, larvacides, etc. are a few cases. An addition, pesticides include attractants, repellents, and growth regulators in addition to toxicants.[3] In the Swat Valley, methyl parathion [4] and Heptachlor [5], Dieldrin, DDT, Malathion, Lindane, glyophosphate, acephate, deet, propoxur, metaldehyde, boric acid and dursban are common pesticides.[6] In addition to being poisonous to aquatic life and natural flora and fauna, pesticides have an impact on public health workplaces, industries, and agriculture. [7] Due to their high

biological toxicity (acute and chronic), pesticides occupy a special place among environmental pollutants. A pesticide naturally has the capability to harm all life forms also the pest classes it is planned to kill. [8] As of this behavior, they are better classified as biocides, which can eradicate all life. [9] The study of environmental toxins' impacts on aquatic organisms, such as how pesticides affect fish or other aquatic organisms' health, is known as aquatic toxicology. [10]. The concentration of pesticide rises with each step in the food chain.[10] Sport fish, such as bass or trout, bio concentrate high quantities in their body fat when they consume contaminated species frequently. Humans can become poisoned by fish..[11] There is ample evidence of both human and animal toxicity. There have been cases of fatal human poisoning from occupational exposure and unintentional oral consumption. [12]. Pesticides including DDT, Dielderin, Dalapon Endrin, and endusolfan are not allowed in Pakistan[13] most widely used technique for removing pesticides from water is adsorption.[14] It entails the adsorption of pesticide molecules to the surface of an adsorbent, a solid substance. This procedure successfully lowers the pesticide concentration in the water, making it safe to drink and reducing the environmental impact.[15] For this function, a variety of adsorbents including activated carbon, clay minerals, zeolites, activated alumina, biochar, and carbon nanotubes can be used. The world still needs new and effective adsorbents to remove these chemicals from the Swat River.[16] Compounds termed sulfones and hydrazones have the potential to be used as adsorbent materials to remove pollutants from water, including pesticides. These compounds are good candidates for adsorption procedures because they include functional groups that enable them to interact with a variety of organic molecules.[17] Organic substances known as sulfones (-SO2-) have a sulfonyl functional group. This group gives the molecule polarity, enabling sulfones to interact with both polar and nonpolar substances. To increase their capacity for adsorption, sulfones can be produced with certain characteristics. They are useful for adsorbing different organic pollutants, including pesticides, since they can offer sites for hydrogen bonding, - interactions, and dipole-dipole interactions.[18] A hydrazine derivative have the -NHN= group, which can take part in interactions for coordination and bonding. As a result of their capacity to create stable complexes with metal ions and other organic molecules, hydrazones have been investigated as possible adsorbents. They may be useful in removing specific types of pesticides from water due to this feature.[19] We are stating that both sulfones and hydrazones can be tailored through structural modifications to enhance their adsorption properties. For example, surface area can be increased, bifunctional groups can be added, or chemical structures can be optimized to target particular contaminants. The chemical makeup of the adsorbate, the characteristics of the target insecticide, and the water environments are basic instances of the variables that capacity affect how well these chemicals adsorb. Objectives to investigate the adsorption potential of selected synthetic sulfonyl hydrazide derivatives, to study the electronic properties of synthetic sulfonyl hydrazide derivatives and to evaluate the mechanism of adsorption of pesticides on selected compounds

1. Materials and Methodology

Natural substances known as sulfonyl hydrazide contain both Sulphone (- SO2-) and hydrazine -NHN= moieties. This gathering gives the atom extremity, empowering sulfones and hydrazide moieties to cooperate with both polar and nonpolar substances. To expand their ability for adsorption, sulfones, and hydrazide can be delivered with specific qualities. They help adsorb different natural poisons, including pesticides, since they can offer locales for hydrogen holding, - connections, and dipole collaborations. For the title concentrate on three sulphonyl hydrazides subordinates SH1-SH2 were chosen for the adsorption reads up for the chosen harmful pesticides Quintozene, Pentachlorophenol (PCP), and Chlorothalonil (CT) given in Figure 1.

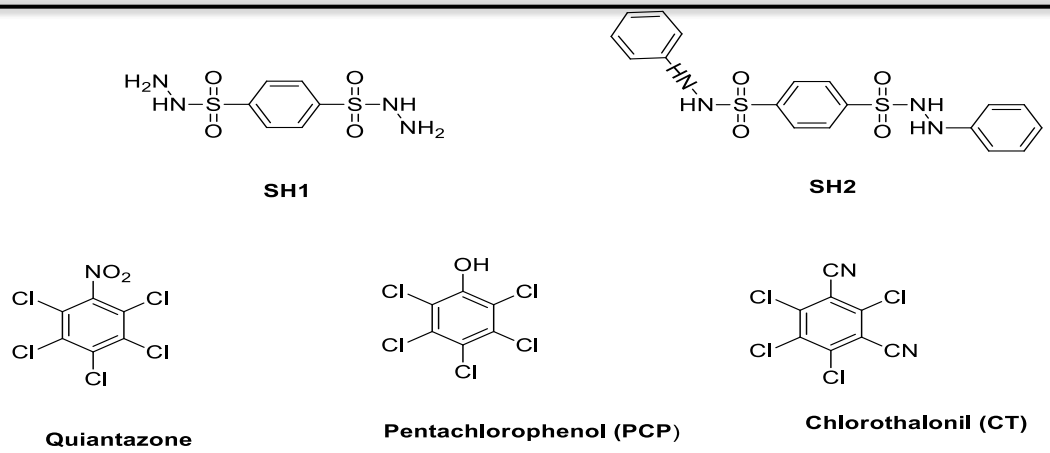

Figure 1. Structural formulae of selected compounds

1.1. Computational Software used in the title study

To make the designs of the title sulphonyl hydrazide subsidiary SH1-SH2 and pesticides, we have labored an assortment of programming bundles of projects, including ChemDraw, Chem3D, Diamond, Avogadro, more computational examinations were accomplished through the most significant computational displaying programming, Gaussian09 bundle with Gaussview06 over Density Functional Theory (DFT). Our title compounds have been all completely advanced through this product, Gaussview06 and Diamond were utilized for an additional examination of the subsequent mixtures[20, 21]

1.2. General Computational Methodology

The recent work regarding the proposed study has been carried out by using chemical modeling, computational simulation, and geometry optimization passing through a set of computational software. The Becke-3-parameter hybrid functional with Lee-Yang correlation functional (B3LYP) level of theory was cast off to fully optimize sulphonyl hydrazide derivatives **(SH1-SH2)** and Pesticides (Quintozene, Pentachlorophenol (PCP) and Chlorothalonil (CT) using 6-311G(d,p) basis set using Density-Functional Theory (DFT) employing the gaussian09 package of software [22]. Initially, all compounds were individually optimized and their optimization energies were calculated. Next, Electronic states of optimized sulphonyl hydrazide derivatives **(SH1-SH2)** and Pesticides (Quintozene, Pentachlorophenol (PCP), and Chlorothalonil (CT) were calculated by following using #n B3LYP/6-31G(d) Opt pop=reg as a route and their frontier molecular orbitals (FMOs) energies were observed [23]. Then different pesticides interacted with sulphonyl hydrazides derivatives and were fully optimized using #n B3LYP/6-31G(d) Opt pop=reg as a route for understanding their interaction pattern and mechanism. The electronic states of all designed systems i.e., Global electrophillicity (ω), Band gap (ΔE), HOMO-LUMO, Electron affinity (EA), Global hardness (η), Chemical potential (μ) and, Ionization potential (IP), were also calculated with same theory and basis sets using DFT calculations using the following formulae. The mentioned parameters are helpful in explaining the structure, mechanism, and reactivity of the systems. From the calculated energies adsorption of the interacting system was also calculated by using the adsorption energy formula given below.

E_{LUMO}

E_{HOMO}

Band gap (ΔE) = E_{HOMO}- E_{LUMO}

Ionization energy (I.E) = -E_{HOMO}

Electron affinity (E.A) =-E_{LUMO}

Global electrophilicity (ω) = $\mu^2/2\eta$)

Chemical potential (μ) = ½(E_{HOMO}+ E_{LUMO})

Global hardness (η) =½(E_{HOMO}- E_{LUMO}) or ½ (ΔE)

$E_{adsorption} = E_{complex} - (E_{pestide} + E_{SH})$

2. Results and Discussion

2.1. Adsorption study of SH1 with Pentachloronitrobenzene (Quintozene)

We present the outcomes of our calculations regarding the adsorption process in the first section of this section. Quintozene to the different sulphonyl hydrazide derivatives (**SH1-SH2**).). The impact of the quantity of Quintozene upon the adsorption energies and designs is researched in the subsequent part. The upgraded fixed designs of the substrates and the adsorption edifices are portrayed schematically in **Figure 2**, and Table 1 with particular key geometry factors (bond lengths). **Figure 2** displays the optimized geometry of Quintozene and the structures of benzene-1,4-disulphonohydrazide. As may be obvious from Figure. 2 and Table 1, the N-O, N-C bond lengths in Quintozene are 1.31 and 1.248 Å, respectively. And N-H and N-N in benzene-1,4-disulphonohydrazide is 1.02 and 1.38 Å. The structures of the adsorption systems with the most appropriate geometry constraints are shown in **Figure 2** and **Table 1**. Inspection of complexes shows that the adsorption cycle frames the new hydrogen-holding in the design of SH1-Quintozene with hydrogen bond distance are 1.02-2.16 Å, The N-H bond lengths in sulphonyl-hydrazide and N-O bond in Quintozene are 1.02 and 1.31 Å, respectively, in SH1-Quintozene complex, the N-O and N-C bond lengths elongated by 0.007 Å and 0.002 Å, respectively, when passing through the Adsorption-systems from the substrates. More stable Adsorption-systems are the result of these changes in bond lengths. The connection energies for the benzene-1,4-disulphonohydrazide to Quintozene are shown in **Table 2.**

This sulphonyl hydrazide N-H and S-O moieties, which could shape a considerable lot of hydrogen-interactions with a Quintozene. Here, we present a nitty resolute computational examination of the sulphonyl hydrazide derivative SH1 by explicitly coordinating one and two molecules, **Figure 2** represents the optimized geometries originate for SH1 to (Quintozene)n (n = 1 and 2), and the crucial geometrical constraints are presented in **Table 1**. In Quintozene2-SH1, the O atom of Quintozene nitro group attack to the H atoms of SH1 on both side through forming hydrogen-interactions having bond distances of 2.15 and 2.165Å on one side and 1.019 and 2.365Å on other side given in **Figure 2**. The new N–H and O–N bond lengths are 1.08 and 1.317 Å in Quintozene2-SH1. Inspection of Table 2 illustrate the two Quintozene molecules interaction over SH1 has contact energy of -6.687 kcal.mol^{-1} comparative to the initial constituents, which is diminished expressively by -6.433 kcal.mol^{-1} associated to the conforming one Quintozene adsorption. The Adsorption-systems becomes more stable as the number of Quintozene goes starting n = 1 to n = 2. Upon overload of the SH1 by adsorption of Quintozene fragments one by one, the coordination energy for adsorption system of species would turn out to be generally consistent.

The Eigen values of frontier molecular orbitals FMOs (E_{HOMO} and E_{LUMO}) were theoretically investigated through DFT calculations. Upon fully optimization of the structures of the title compounds **SH1, Quintozene, SH1-Quintozene** complexes were examined for frontier molecular orbitals, additional electronic properties were also considered via B3LYP/6-311G(d,p) basis set by DFT. Conferring to our computational investigation concerning the title compounds, numerous molecular constraints are given in the following table 3.

Table 1. Selected bond lengths in (Å) of SH1, Quintozene and their complexes

Components	Atoms	Bond length	SH1-Quintozene	SH1-(Quintozene)$_2$
Quintozene	N-O	1.31	1.317	1.315
	N-C	1.31	1.252	1.254
SH1	N-H	1.02	1.026	1.024
	N-N	1.38	1.390	1.391

Table 2. Adsorption energies of Quintozene over SH1 in (kcalmol^{-1})

System	$E_{Complex}$	E_{SH1}	$E_{Quintozene}$	$E_{adsorption}$
SH1- Quintozene	-698858.2	-627757.5	-71093	-6.433
SH1- (Quintozene)$_2$	-698140.8	-627757.5	-71093	-6.687

Table 3. Computed DFT based electronic properties SH1, Quintozene and their complexes

Constraints	Quintozene	SH1	SH1-Quintozene	SH1-(Quintozene)2
E(LUMO)	-0.082	-0.106	-0.134	-0.129
EL(ev)	-2.235	-2.884	-3.646	-3.510
E(HUMO)	-0.189	-0.192	-0.197	-0.182
EH(ev)	-5.149	-5.225	-5.361	-4.952
ΔE=EL(ev)-EH(ev)	2.914	2.340	1.714	1.442
IE= -(EH(ev))	5.149	5.225	5.361	4.952
EA= -EL(ev)	2.235	2.884	3.646	3.510
η= 0.5*ΔE	1.457	1.170	0.857	0.721
μ= 0.5*(EH(ev)+EL(ev))	-3.692	-4.054	-4.503	-4.231
ω= (μ*μ)/(2*η)	4.678	7.025	11.830	12.415

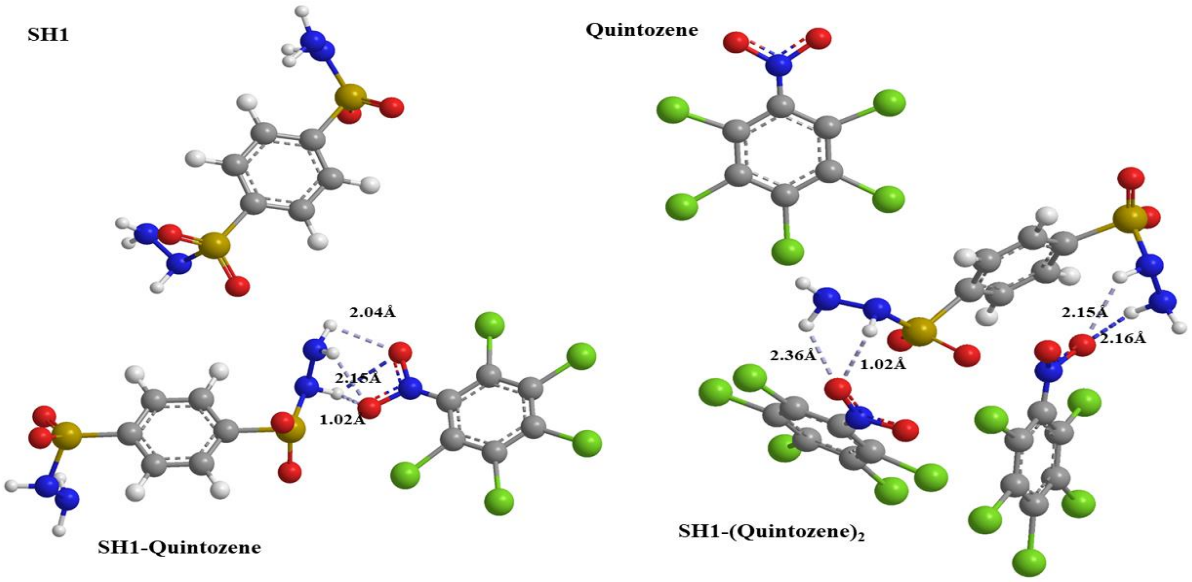

Figure 2. The fully optimized geometries of SH1, Quintozene, SH1- Quintozene and SH1-(Quintozene)$_2$ with hydrogen bond distances in (Å)

Adsorption study of SH1 with Pentachlorophenol (PCP)

In the title investigation, We present the outcomes of our calculations regarding the adsorption process of pentachlorophenol (PCP) to the benzene-1,4-disulphonohydrazide **SH1**. The impact of the quantity of pentachlorophenol (PCP). upon the interaction energies and structures is also investigated. The upgraded fixed designs of the substrates and the adsorption networks are represented schematically in **Figure 3**, and **Table 4** with particular key geometry factors (bond lengths). Figure 3 shows the initially fully optimized geometry of pentachlorophenol (PCP) and the structures of benzene-1,4-disulphonohydrazide.. It is clear from Figure 3 and Table 4, the H-O, O-C bond lengths in pentachlorophenol (PCP) are 0.97 and 1.366 Å, respectively. N-H and N-N in benzene-1,4-

disulphonohydrazide is 1.02 and 1.38 Å. The structures of the adsorption systems with the most appropriate geometry constraints are shown in Figure 3. A review of Figure 3 and Table 4 displays that during physio-sorption progression form new hydrogen-interaction in the structure of SH1-Pentachlorophenol (PCP) with hydrogen bond distance is 2.303 Å, The N-H bond lengths in sulphonyl-hydrazide and H-O bond in (PCP) are 1.023 and 0.981 Å, respectively, in SH1-PCP complex, the N-H, O-H and O-C bond lengths slightly elongated by 0.003 Å, 0.004 and 0.001 Å , respectively, when passing through the Adsorption-systems from the substrates. More stable Adsorption-systems are the result of these changes in bond lengths. The connection energies for the benzene-1,4-disulphonohydrazide with PCP are shown in Table 5

Sulphonyl hydrazide containing N-H and S-O groups, which responsible to form several of hydrogen-interactions with PCP. Upon computational investigation of the sulphonyl hydrazide derivative SH1 by explicitly coordinating one and two molecules of PCP, **Figure 3** represents the fully optimized geometries establish for SH1 with (PCP)n (n = 1 and 2), and the foremost geometrical constraints are presented in Table 4. In PCP2-SH1, the O atom of PCP phenolic group attack to the H-N atoms of SH1 on both side forming hydrogen-interactions having a bond distances of 2.175 and 2.016Å on one side and 2.032 and 2.08 Å on other side given in Figure 3. The innovative N–H and O–H bond lengths are 1.031 and 0.983 Å in SH1-PCP2. Going-over of Table 5 displays the two PCP molecules interacted over SH1 has interface energy of -6.457 kcal mol^{-1} relative to the starting materials, which is decreased significantly by -7.22 kcal mol^{-1} compared to the corresponding one PCP adsorption. The Adsorption-systems becomes more stable as the number of PCP goes from n = 1 to n = 2. Upon overload of the SH1 by coordination of PCP fragments one by one, the cordination energy of syetem would turn out to be generally consistent. The Eigen values of frontier molecular orbitals FMOs (E_{HOMO} and E_{LUMO}) were theoretically investigated through DFT calculations. Upon fully optimization of the structures of the title compounds **SH1, PCP, SH1-PCP** complexes were examined for frontier molecular orbitals, additional electronic properties were also considered via B3LYP/6-311G(d,p) basis set by DFT. Conferring to our computational investigation concerning the title compounds, numerous molecular constraints are given in the following table 6.

Table 4. Selected geometric constraints SH1, PCP and their complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SH1- PCP	Bond length (Å) SH1-$(PCP)_2$
PCP	H-O	0.970	0.981	0.983
	O-C	1.365	1.366	1.366
SH1	N-H	1.02	1.023	1.031
	N-N	1.38	1.382	1.385

Table 5. Adsorption energies of PCP over SH1 in ($kcalmol^{-1}$)

System	$E_{Complex}$	E_{SH1}	E_{PCP}	$E_{adsorption}$
SH1- PCP	-108235.88	-627757.53	-72235	-6.457
SH1- $(PCP)_2$	-649577.83	-627757.53	-72235	-7.22

Table 6. Computed DFT based electronic properties of SH1, PCP and their complexes

Constraints	PCP	SH1	SH1-PCP	SH1-(PCP)2
E(LUMO)	-0.083	-0.106	-0.142	-0.147
EL(ev)	-2.259	-2.884	-3.864	-4.000
E(HUMO)	-0.189	-0.192	-0.232	-0.209
EH(ev)	-5.143	-5.225	-6.313	-5.687
ΔE=EL(ev)-EH(ev)	2.884	2.340	2.449	1.687
IE= -(EH(ev))	5.143	5.225	6.313	5.687
EA= -EL(ev)	2.259	2.884	3.864	4.000
η= 0.5*ΔE	1.442	1.170	1.224	0.844
μ= 0.5*(EH(ev)+EL(ev))	-3.701	-4.054	-5.088	-4.844
ω= (μ*μ)/(2*η)	4.748	7.025	10.573	13.906

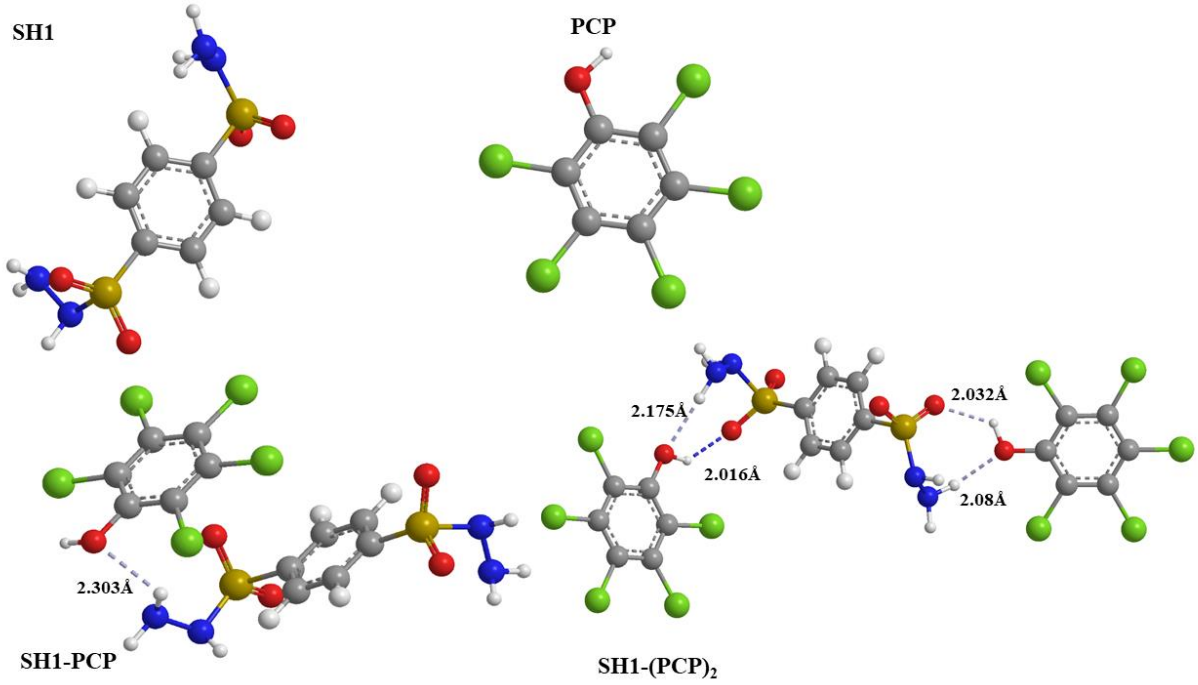

Figure 3. The fully optimized geometries of SH1, PCP, SH1-PCP and SH1-(PCP)$_2$ with hydrogen bond distances in (Å)

Adsorption study of SH1 with Chlorothalonil (CT)

In the recent study, We present the outcomes of our calculations regarding the adsorption process of Chlorothalonil (CT) to the benzene-1,4-disulphonohydrazide **SH1**. The impact of the quantity of Chlorothalonil (CT) upon the interaction energies were also investigated. The optimized geometries of the substrates and the adsorption-systems are illustrated in Figure 4, and Table 7 with selected geometry constraints (bond lengths). Figure 4 shows the optimized geometry of Chlorothalonil (CT) and the structures of benzene-1,4-disulphonohydrazide. The C-N and C-C bond lengths in Chlorothalonil (CT) are 1.160 and 1.322 Å, respectively. N-H and N-N in benzene-1,4-disulphonohydrazide is 1.02 and 1.38 Å. The structures of the adsorption systems with the most appropriate geometry constraints are shown in Figure 4. Examination of Fig. 3 and Table 7 shows that the during physio-sorption process forms hydrogen-interactions in the structure of SH1-Chlorothalonil (CT) with hydrogen bond distance is 1.61 Å C-N...HN and 3.31Å Cl...HN, The N-H

bond lengths in sulphonyl-hydrazide is 1.022 showing slight elongation give conformation to hydrogen bonding. More stable Adsorption-systems are the result of these changes in bond lengths. The interface energies for the 1,4-disulphonohydrazide with CT are shown in Table 8.

Upon computational calculations of the sulphonyl hydrazide derivative SH1 by explicitly coordinating one and two molecules of CT, Figure 4 represents the fully optimized geometries demonstrated for SH1 with (CT)n (n = 1 and 2), and the main geometrical constraints are given in Table 7. In CT2-SH1, the N atom of nitrile group of CT attack to the H-N atoms of SH1 on both side forming two hydrogen-interactions having a bond distances of 1.86 on one side and 1.85 Å on other side given in Figure 4. Analysis of Table 8 shows that two CT molecules adsorbed over SH1 has contact energy of -6.45 kcal mol^{-1} comparative to the starting materials, which is diminished significantly by -6.89 kcal mol^{-1} associated to the consistent one CT adsorption. The adsorption-systems grow into more stable as the number of CT drives from n = 1 to n = 2. Upon inundation of the SH1 by coordination of CT molecules one by one, the interaction energy of species would become relatively constant.

The Eigen values of frontier molecular orbitals FMOs (E_{HOMO} and E_{LUMO}) were theoretically investigated through DFT calculations. Upon fully optimization of the structures of the title compounds **SH1, CT, SH1-CT** complexes were examined for frontier molecular orbitals, additional electronic properties were also considered via B3LYP/6-311G(d,p) basis set by DFT. Conferring to our computational investigation concerning the title compounds, numerous molecular constraints are given in the following table 9.

Table 7. Selected geometric constraints of SH1, CT and their complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SH1-CT	Bond length (Å) SH1-$(CT)_2$
CT	C-N	1.160	1.160	1.160
	C-C	1.322	1.322	1.322
SH1	N-H	1.02	1.022	1.021
	N-N	1.38	1.381	1.381

Table 8. Adsorption energies of CT over SH1 in ($kcalmol^{-1}$)

System	$E_{Complex}$	E_{SH1}	E_{CT}	$E_{adsorption}$
SH1- CT	-602441.81	-627757.53	-69331	-6.45
SH1- $(CT)_2$	-795285.21	-627757.53	-69331	-6.89

Table 9. Computed DFT based electronic properties of SH1, CT and their complexes

Constraints	CT	SH1	SH1-CT	SH1-(CT)2
E(LUMO)	-0.091	-0.106	-0.137	-0.130
EL(ev)	-2.476	-2.884	-3.728	-3.537
E(HUMO)	-0.187	-0.192	-0.222	-0.200
EH(ev)	-5.088	-5.225	-6.041	-5.442
ΔE=EL(ev)-EH(ev)	2.612	2.340	2.313	1.905
IE= -(EH(ev))	5.088	5.225	6.041	5.442
EA= -EL(ev)	2.476	2.884	3.728	3.537
η= 0.5*ΔE	1.306	1.170	1.156	0.952
μ= 0.5*(EH(ev)+EL(ev))	-3.782	-4.054	-4.884	-4.490
ω= (μ*μ)/(2*η)	5.476	7.025	10.315	10.583

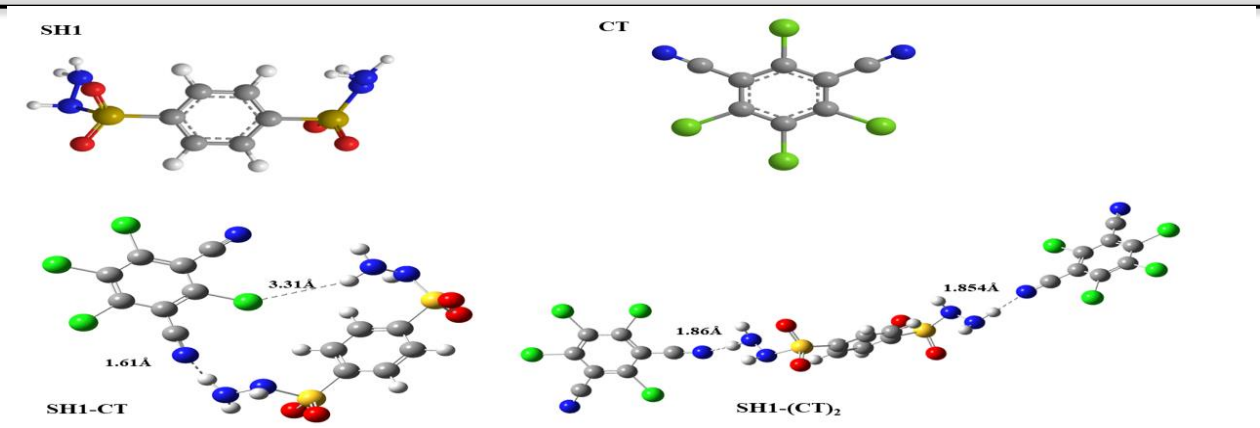

Figure 4. The fully optimized geometries of SH1, CT, SH1-CT and SH1-$(CT)_2$ with hydrogen bond distances in (Å)

Adsorption study of SH2 with Pentachloronitrobenzene (Quintozene)

In this fragment, we illustrate results from our investigation of the adsorption progression of Quintozene to the sulphonyl hydrazide derivatives N^1,N^4-diphenyl-1,4-disulponylhydrazide (**SH2**). The effect of the amount of Quintozene upon the interaction energies and structures were also inspected. The fully optimized geometries of the substrates and the Adsorption-systems are given in Figure 5, and Table 10 with nominated crucial geometry constraints (bond lengths). Figure 5 shows the optimized geometry of Quintozene, the structures of N^1,N^4-diphenyl-1,4-disulponylhydrazide and its Adsorption-systems. The main geometry constraints are shown in Table 10 As one can see from Figure 5 and Table 10, the N-O, N-C bond lengths in Quintozene are 1.31 and 1.248 Å, respectively. And N-H and N-N in N^1,N^4-diphenyl-1,4-disulponylhydrazide is 1.02 and 1.38 Å. The structures of the Adsorption-systems with the most applicable geometry constraints are shown in Figure 5 and Table 10. Inspection of Fig. 5 and Table 10 shows that the adsorption process forms the new hydrogen-interactions in the structure of SH2-Quintozene with hydrogen bond distance are 2.094 and 2.285 Å, The N-H bond lengths in sulphonyl-hydrazide and N-O bond in Quintozene are 1.047 and 1.315 Å, respectively, in SH2-Quintozene complex, the N-O and N-C bond lengths elongated by 0.016 Å and 0.005 Å, correspondingly, upon going from the substrates to the Adsorption-systems. These changes in the bond lengths are endorsed to form the more stable Adsorption-systems. The interaction energies for the N^1,N^4-diphenyl-1,4-disulponylhydrazide with Quintozene are shown in Table 11.

This sulphonyl hydrazide N-H and S-O groups, which might form several of hydrogen-interactions with a Quintozene. Here, we computational investigated of the sulphonyl hydrazide derivative SH2 by explicitly coordinating one and two molecules, Figure 5 represents the optimized geometries found for SH2 with (Quintozene)n (n = 1 and 2), and the selected geometrical constraints are given in Table 10. In Quintozene2-SH2, the O atom of Quintozene nitro group attack to the H atoms of SH2 on both side through forming four hydrogen-interactions having a bond distances of 1.611 and 1.88 Å on one side and 1.95 and 2.32 Å on other side given in Figure 4. The new N–H and O–N bond lengths are 1.201 and 1.343 Å in Quintozene2-SH2. Examination of Table 3.11 displays the two Quintozene molecules adsorbed over SH2 has binding energy of -8.53 kcal mol^{-1} comparative to the initial constituents, which is diminished expressively by -9.38 kcal mol^{-1} associated to the conforming one Quintozene adsorption. The Adsorption-systems becomes more stable as the number of Quintozene goes from n = 1 to n = 2. Upon saturation of the SH2 by coordination of Quintozene molecules one by one, the interaction energy of species would become relatively constant.

The Eigen values of frontier molecular orbitals FMOs (E_{HOMO} and E_{LUMO}) were theoretically

investigated through DFT calculations. Upon fully optimization of the structures of the title compounds **SH2, Quintozene, SH2-Quintozene** complexes were examined for frontier molecular orbitals, additional electronic properties were also considered via B3LYP/6-311G(d,p) basis set by DFT. Conferring to our computational investigation concerning the title compounds, numerous molecular constraints are given in the following table 12.

Table 10. Selected geometric constraints of SH2, Quintozene, SH2-Quintozene complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SH1-Quintozene	Bond length (Å) SH1-(Quintozene)$_2$
Quintozene	N-O	1.31	1.315	1.326
	N-C	1.31	1.270	1.271
SH2	N-H	1.02	1.047	1.022
	N-N	1.38	1.352	1.353

Table 11. Adsorption energies of Quintozene over SH2 in (kcalmol^{-1})

System	$E_{Complex}$	E_{SH2}	$E_{Quintozene}$	$E_{adsorption}$
SH2-Quintozene	-700993	-581308.47	-71093	-8.53
SH2-(Quintozene)$_2$	-701001.40	-581308.47	-71093	-9.38

Table 12. Computed DFT based electronic properties of SH2, Quintozene and their complexes

Constraints	Quintozene	SH2	SH2-Quintozene	SH2-(Quintozene)2
E(LUMO)	-0.082	-0.104	-0.132	-0.135
EL(ev)	-2.235	-2.830	-3.592	-3.673
E(HUMO)	-0.189	-0.191	-0.191	-0.182
EH(ev)	-5.149	-5.197	-5.197	-4.952
ΔE=EL(ev)-EH(ev)	2.914	2.367	1.605	1.279
IE= -(EH(ev))	5.149	5.197	5.197	4.952
EA= -EL(ev)	2.235	2.830	3.592	3.673
η= 0.5*ΔE	1.457	1.184	0.803	0.639
μ= 0.5*(EH(ev)+EL(ev))	-3.692	-4.014	-4.395	-4.313
ω= (μ*μ)/(2*η)	4.678	6.805	12.029	14.545

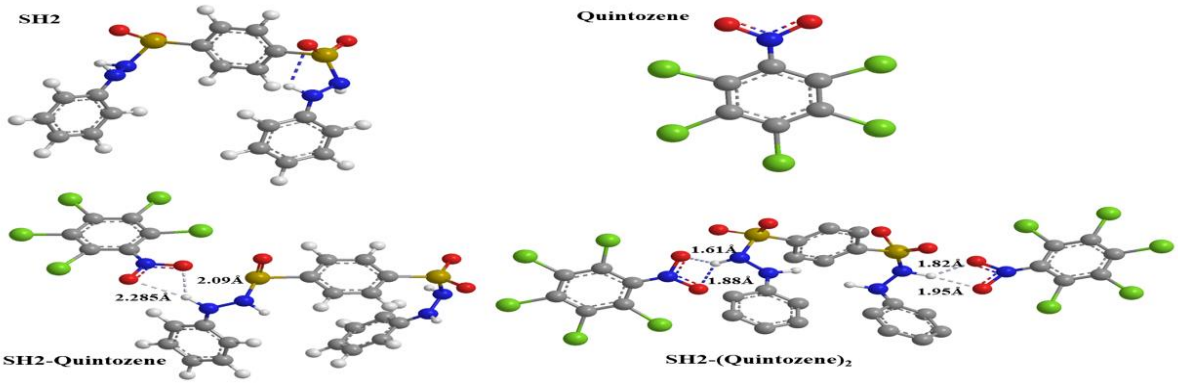

Figure 5. The fully optimized geometries of SH2, Quintozene, SH2-Quintozene and SH2-(Quintozene)$_2$ with hydrogen bond distances in (Å)

Adsorption study of SH2 with Pentachlorophenol (PCP)

In the title investigation, we present results from our calculations on the adsorption process of pentachlorophenol (PCP) to the N^1,N^4-diphenyl-1,4-disulponylhydrazide **SH2**. The effect of the number of pentachlorophenol (PCP) upon the adsorption energies and structures is also investigated. The optimized stationary structures of the substrates and the Adsorption-systems are given schematically in Figure 6, and Table 13 with selected key geometry constraints (bond lengths). Figure 6 shows the optimized geometry of pentachlorophenol (PCP) and the structures of N^1,N^4-diphenyl-1,4-disulponylhydrazide and its interacting complexes.. It is clear from Figure 6 and Table 13, the H-O, O-C bond lengths in pentachlorophenol (PCP) are 0.97 and 1.366 Å, respectively. N-H and N-N in N^1,N^4-diphenyl-1,4-disulponylhydrazide is 1.02 and 1.38 Å. The structures of the Adsorption-systems with the most relevant geometry constraints are shown in Figure 6. Inspection of Fig 3.5 and Table 13 shows that the during physio-sorption process forms the two hydrogen-interactions in the structure of SH2-Pentachlorophenol (PCP) with hydrogen bond distance is 2.097 and 2.313 Å, The N-H bond lengths in sulphonyl-hydrazide and H-O bond in (PCP) are 1.019 and 0.971 Å, respectively, in SH2-PCP complex, the N-H, O-H and O-C bond lengths slightly changed upon going from the substrates to the Adsorption-systems. These changes in the bond lengths are responsible to form the more stable Adsorption-systems. The interaction energies for the 1,4-disulphonohydrazide with PCP are shown in Table 14.

SH2 containing N-H and S-O groups, which responsible to form many of hydrogen-interactions with PCP. Upon computational investigation of the sulphonyl hydrazide derivative SH2 by clearly coordinating one and two molecules of PCP, Figure 6 represents the optimized geometries found for SH2 with (PCP)n (n = 1 and 2), and the main geometrical constraints are given in Table 13. In PCP2-SH2, the O-H group of PCP phenolic group are involved in hydrogen bonding through O...HN and H...OS on both side forming hydrogen-interactions having a bond distances of 2.03 and 2.04Å on one side and 2.077 and 2.162 Å on other side given in Figure 6. The new N–H and O–H bond lengths are 1.08 and 0.971 Å in SH2-PCP2. Examination of Table 3.14 shows the two PCP molecules adsorption over SH2 has interaction energy of -7.61 kcal mol^{-1} relative to the starting materials, which is decreased significantly by -8.14 kcal mol^{-1} compared to the corresponding one PCP adsorption. The adsorption-systems becomes more stable as the number of PCP goes from n = 1 to n = 2. Upon saturation of the SH1 by coordination of PCP molecules one by one, the interaction energy of species would become relatively constant. The Eigen values of frontier molecular orbitals FMOs (E_{HOMO} and E_{LUMO}) were theoretically investigated through DFT calculations. Upon fully optimization of the structures of the title compounds **SH2, PCP, SH2-PCP** complexes were examined for frontier molecular orbitals, additional electronic properties were also considered via B3LYP/6-311G(d,p) basis set by DFT. Conferring to our computational investigation concerning the title compounds, numerous molecular constraints are given in the following table 15

Table Error! No text of specified style in document.**.13. Selected geometric constraints of SH2, PCP, and their complexes**

Components	Atoms	Bond length (Å)	Bond length (Å) SH1- PCP	Bond length (Å) SH1-$(PCP)_2$
PCP	H-O	0.970	0.971	0.97
	O-C	1.365	1.365	1.365
SH1	N-H	1.02	1.019	1.018
	N-N	1.38	1.381	1.382

Table Error! No text of specified style in document.**.14. Adsorption energies of PCP over SH2 in (kcalmol^{-1})**

System	$E_{Complex}$	E_{SH2}	E_{PCP}	$E_{adsorption}$
SH2-PCP	-47056.85	-581308.47	-72235	-7.61
SH2-$(PCP)_2$	-652409.60	-581308.47	-72235	-8.14

Table Error! No text of specified style in document.**.15. Computed DFT based electronic properties of SH2, PCP, and their complexes**

Constraints	PCP	SH2	SH2-PCP	SH2-(PCP)2
E(LUMO)	-0.083	-0.104	-0.136	-0.139
EL(ev)	-2.259	-2.830	-3.701	-3.782
E(HUMO)	-0.189	-0.191	-0.197	-0.199
EH(ev)	-5.143	-5.197	-5.361	-5.415
ΔE=EL(ev)-EH(ev)	2.884	2.367	1.660	1.633
IE= -(EH(ev))	5.143	5.197	5.361	5.415
EA= -EL(ev)	2.259	2.830	3.701	3.782
η= 0.5*ΔE	1.442	1.184	0.830	0.816
μ= 0.5*(EH(ev)+EL(ev))	-3.701	-4.014	-4.531	-4.599
ω= (μ*μ)/(2*η)	4.748	6.805	12.366	12.953

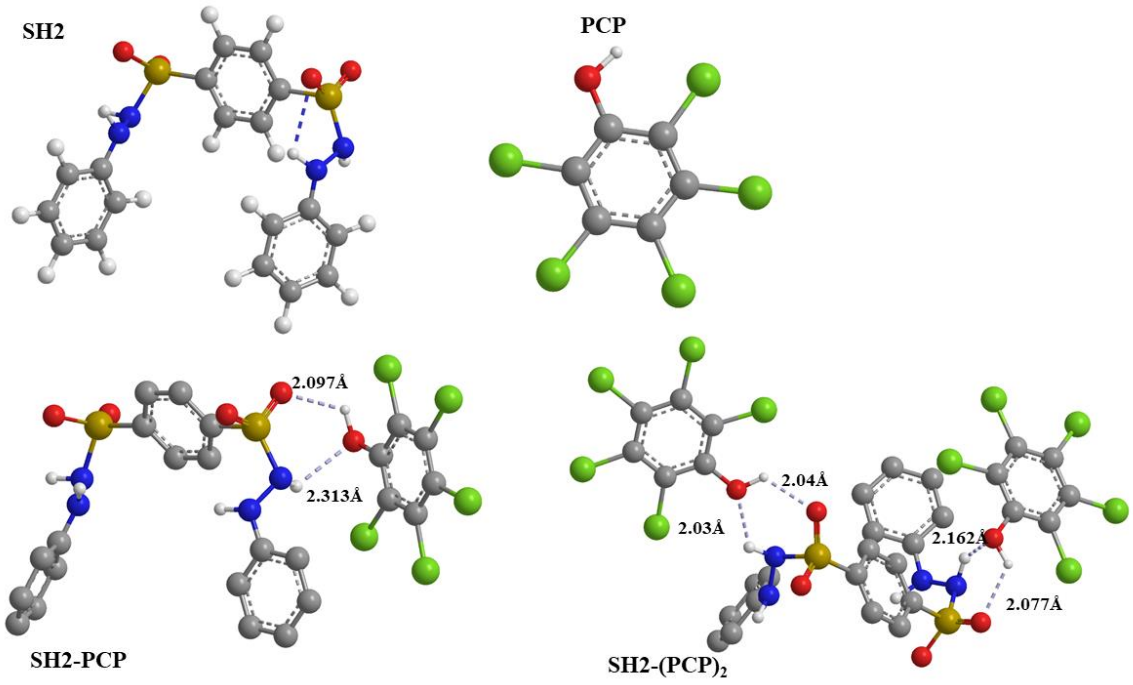

Figure 6 The fully optimized geometries of SH2, PCP, SH2-PCP and SH2-$(PCP)_2$ with hydrogen bond distances in (Å)

Adsorption study of SH2 with Chlorothalonil (CT)

In the recent study, our calculations on the adsorption process of Chlorothalonil (CT) to the N^1,N^4-diphenyl-1,4-disulponylhydrazide **SH2**. The impression of the number of Chlorothalonil (CT) upon the interaction energies and structures were also investigated. The optimized geometries of the substrates and the adsorption-systems are illustrated in **Figure 7**, and **Table 16** with selected geometry

constraints (bond lengths). Figure 7 shows the optimized geometry of Chlorothalonil (CT) and the structures of N^1,N^4-diphenyl-1,4-disulponylhydrazide. The C-N and C-C bond lengths in Chlorothalonil (CT) are 1.160 and 1.322 Å, respectively. N-H and N-N in N^1,N^4-diphenyl-1,4-disulponylhydrazide is 1.018 and 1.38 Å. The structures of the Adsorption-systems with the most relevant geometry constraints are shown in Figure 7. Examination of Fig. 7 and Table 16 shows that the during physio-sorption process forms hydrogen-interactions in the structure of SH2-Chlorothalonil (CT) with hydrogen bond distance is 1.69 Å C-N...HN, The N-H bond lengths in sulphonyl-hydrazide is 1.021 showing slight elongation give conformation to hydrogen bonding. These changes in the bond lengths are responsible to form the more stable Adsorption-systems. The interaction energies for the N^1, N^4-diphenyl-1,4-disulponylhydrazide with CT are shown in Table 17 Upon computational calculations of the sulphonyl hydrazide derivative SH2 by explicitly coordinating one and two molecules of CT, Figure 7 represents the optimized geometries found for SH2 with (CT)n (n = 1 and 2), and the main geometrical constraints are given in Table 16. In CT2-SH2, the N atom of nitrile group of CT attack to the H-N atoms of SH2 on both side forming two hydrogen-interactions having a bond distances of 1.74 on one side and 1.71 Å on other side given in Figure 7. Examination of Table 16 shows the two CT molecules adsorption over SH2 has interaction energy of -7.61 kcal mol^{-1} relative to the starting materials, which is decreased significantly by -7.92 kcal mol^{-1} compared to the corresponding one CT adsorption. The adsorption-systems becomes more stable as the number of CT goes from n = 1 to n = 2. Upon saturation of the SH1 by coordination of CT molecules one by one, the interaction energy of species would become relatively constant. The Eigen values of frontier molecular orbitals FMOs (E_{HOMO} and E_{LUMO}) were theoretically investigated through DFT calculations. Upon fully optimization of the structures of the title compounds **SH2, CT, SH2-CT** complexes were examined for frontier molecular orbitals, additional electronic properties were also considered via B3LYP/6-311G(d,p) basis set by DFT. Conferring to our computational investigation concerning the title compounds, numerous molecular constraints are given in the following table 18

Table Error! No text of specified style in document.**.16. Selected geometric constraints of SH2, CT, and their complexes**

Components	Atoms	Bond length (Å)	Bond length (Å) SH1-CT	Bond length (Å) SH1-$(CT)_2$
CT	C-N	1.160	1.161	1.161
	C-C	1.322	1.322	1.322
SH2	N-H	1.018	1.019	1.018
	N-N	1.38	1.381	1.38

Table Error! No text of specified style in document.**.17. Adsorption energies of CT over SH2 in (kcalmol^{-1})**

System	$E_{Complex}$	E_{SH2}	E_{CT}	$E_{adsorption}$
SH2-CT	-604592.61	-581308.47	-69331	-7.61
SH2-$(CT)_2$	-798123.43	-581308.47	-69331	-7.92

Table Error! No text of specified style in document.**.18. Computed DFT based electronic properties of SH2, CT, and their complexes**

Constraints	CT	SH2	SH2-CT	SH2-(CT)2
E(LUMO)	-0.091	-0.104	-0.133	-0.132
EL(ev)	-2.476	-2.830	-3.619	-3.592
E(HUMO)	-0.187	-0.191	-0.221	-0.201

EH(ev)	-5.088	-5.197	-6.014	-5.469
ΔE=EL(ev)-EH(ev)	2.612	2.367	2.395	1.878
IE= -(EH(ev))	5.088	5.197	6.014	5.469
EA= -EL(ev)	2.476	2.830	3.619	3.592
η= 0.5*ΔE	1.306	1.184	1.197	0.939
μ= 0.5*(EH(ev)+EL(ev))	-3.782	-4.014	-4.816	-4.531
ω= (μ*μ)/(2*η)	5.476	6.805	9.687	10.933

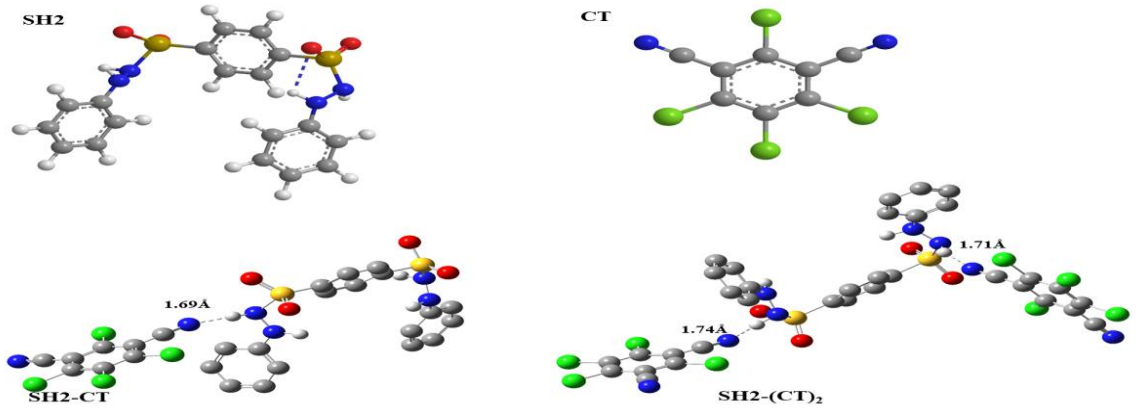

Figure 7. The fully optimized geometries of SH2, CT, SH2-CT and SH2-$(CT)_2$ with hydrogen bond distances in (Å)

Conclusion

Pesticides are frequently used chemicals that control organisms like insects and fungi. A pesticide is a chemical used to remove, deter, or decrease any animal, microbial, or plant pest. Pesticides are frequently chemical agents, but they can also be organic or material agents. A lot of individuals erroneously think that insecticides are pesticides. However, there are other insecticides whose calculated pests do not cover insects. In this work we have investigated the adsorption potential of three selected sulphonyl hydrazides derivatives SH1-SH2 against some selected pesticides i.e. Quintozene, pentachlorophenol (PCP) and Chlorothalonil (CT) which are commonly used in swat region of KP, Pakistan. The title study were carried out through computational chemistry and modeling via Density Functional Theory (DFT) by using B3LYP level of theory with 6-311G(d,p) basis sets. According to our investigation the adsorption mechanism were based on hydrogen bonding and weak Vander Waal forces. The adsorption energies are 5-10 $kcal.mol^{-1}$.

The DFT investigation shows that the complexes with two pesticides coordinated to sulphonyl hydrazide derivatives are more stable than their corresponding substrates and the complex with one molecule of pesticide. Our theoretical findings are good explanation for experimental researchers and we believe that these derivatives will be best adsorbents in future

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Conflict of Interest
The authors declare no conflict of interest

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