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Density Functional Theory Based Investigation of Adsorption Mechanism of an Endocrine Disruptors Pesticides over Benzene-1,4-Disulfinohydrazide

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Abstract

Substances that are synthetically alluded to as endocrine disruptors restrain the endocrine framework from executing its unexpected capabilities by cooperating with chemical amalgamation, discharge, transport, digestion, restricting, activity, and evacuation inside the body. Endocrine disruptors have various adverse consequences on human wellbeing, including hormonal awkwardness, anomalies in multiplication, irregularities being developed, expanded chance of malignant growth, issues of the thyroid and digestion, irregularities of the safe framework, and different irregularities of the sensory system. Neonicotinoids are engineered synthetic substances intended to impersonate the activity of nicotine, a characteristic insect spray found in plants containing, Clothianidin (CA), Dinotefuran (DF), Imidacloprid (IC) and nitenpyram (NP). In title work we have examined the adsorption perspective of benzene-1,4-disulfinohydrazide SA1 against some selected pesticides i.e. Clothianidin (CA), Dinotefuran (DF), Imidacloprid (IC) and nitenpyram (NP) which are commonly used in swat region of KP, Pakistan. In this study, we carried out our desired investigation over computational chemistry and modeling through Density Functional Theory (DFT) by using the B3LYP level of model with 6-311G(d,p) basis sets. Giving to our exploration the adsorption mechanism were based on hydrogen bonding and weak Vander Waal forces. The adsorption energies are -6.68 to -12.45 kcal.mol-1. The theoritcial examination demonstrate that the adsorption complexes with two pesticides interacted to sulfinamides derivativ benzene-1,4-disulfinohydrazide are more stable than their corresponding substrates and

the complex with one molecule of pesticide. Our theoretical results are respectable clarification for experimental researchers and we believe that these derivative will be best adsorbents in future

1.Introduction

Substances that are chemically referred to as endocrine disruptors inhibit the endocrine system from executing its normal functions by interacting with hormone synthesis, release, transport, metabolism, binding, action, and removal inside the body [1]. These disruptors have the potential to significantly affect the environment and human health. Endocrine disruptors have a variety of negative effects on human health, including hormonal imbalance, abnormalities in reproduction, abnormalities in development, increased risk of cancer, problems of the thyroid and metabolism, abnormalities of the immune system, and other abnormalities of the nervous system [2-4]. In addition to having negative effects on human health, it has significant negative effects on the environment, disrupting ecosystems and causing biodiversity and bioaccumulation [5]. Regulatory agencies in multiple countries have put in place measures to lessen exposure to endocrine disruptors in response to the growing awareness of their effects [6]. These actions include limiting the amount of specific endocrine-disrupting substances allowed in consumer items, banning or limiting their usage, and undertaking studies to better comprehend their negative impacts on human health and the environment. Campaigns for public awareness and education are also crucial for limiting exposure to these disruptors and lessening their impacts [7]. The endocrine system is a complex network of hormones and glands that controls a number of physiological functions, such as metabolism, growth, and reproduction. Pesticides that disturb the endocrine system impede this system by imitating or obstructing the effects of natural hormones. They can disrupt hormonal balance in the body, even at low exposure levels, leading to a range of health problems [8]. Organochlorine pesticides (OCPs), a class of chemical compounds which comprises chlorinated pesticides (Chlothalonil, hexaconazone, chloropyrifos, acetamiprid, difenoconazole, pyraclostrobin and propiconazole), have been identified to be significant endocrine disruptors. These pesticides have caused worry because of how persistent they are in the environment and since they can mess with both human and animal endocrine systems [9]. Here, we examine the precise mechanisms by which chlorinated pesticides function as endocrine disruptors, as well as the resulting effects on human health and the environment. Adsorption is an effective method for removing chlorinated pesticides, which are endocrine disruptors, from water and soil, reducing their effects on human health and the environment. Contaminants cling to the surface of an adsorbent material through the process of adsorption. Here's how this technique can be employed for the removal of chlorinated pesticides [10]. Adsorption is the technique that is most frequently employed to remove pesticides from water. Pesticide molecules must be adsorbed to the surface of an adsorbent, a solid material. By successfully lowering the pesticide concentration in the water, this process both makes it safe to drink and has less of an influence on the environment. Activated carbon, clay minerals, zeolites, activated alumina, charcoal, and carbon nanotubes are just a few examples of the adsorbents that may be employed for this purpose. The Swat River still needs to have these pollutants removed, and the world needs new, powerful adsorbents [11, 12]. It is feasible to utilize chemicals known as sulfinamides as adsorbent materials to remove contaminants from water, including pesticides. These substances have functional groups that allow them to interact with a range of organic molecules, making them excellent candidates for adsorption methods [4, 13]. Sulfones can interact with both polar and nonpolar molecules thanks to organic compounds with the functional groups (-SO2-) sulfonyl and (-NR2) amide. Sulfones can be created with specific characteristics to boost their ability for adsorption. Which can participate in interactions for bonding and coordination. Hydrazones have been studied as potential adsorbents due to their ability to form stable complexes with metal ions and other organic compounds. Since they can provide sites for

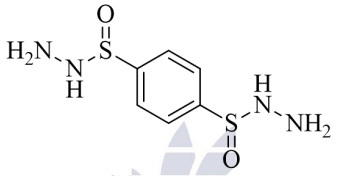
hydrogen bonding, -interactions, and dipole-dipole interactions, they are helpful for adsorbing many organic contaminants, including pesticides [14]. The objectives the title study to explore the adsorption prospective of selected sulfonyl hydrazide derivatives and to assess the mechanism of adsorption of pesticides on selected compounds

We claim that structural alterations may be made to sulfones and hydrazones to improve their adsorption capabilities. To target certain pollutants, for instance, chemical structures can be improved, surface area can be raised, bifunctional groups can be added, etc. Basic examples of the factors that can influence how successfully these compounds adsorb include the chemical composition of the adsorbate, the properties of the target pesticide, and the water conditions.

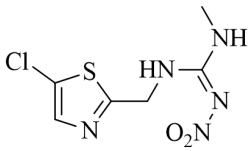
2.Methodology

2.1. Selected Compound and Pesticides

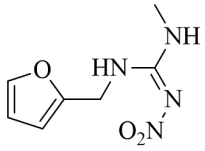
Sulfinamides, a class of substance compounds containing the sulfinamide practical gathering (-S(=O)- N-), have shown guarantee as viable adsorbents in different applications. The remarkable properties of sulfinamides make them reasonable for adsorption processes, especially in the expulsion of poisons and impurities from various conditions. This paper investigates the attributes of sulfinamides, their adsorption capacities, and their possible applications as adsorbents. They support adsorb different natural toxins, including pesticides, since they can deal sites for hydrogen interactions, - connections, and weak Vander Waal interactions. For the title investigations benzene-1,4-disulfinohydrazide subordinates SA1 was selected for the adsorption process for the chosen harmful pesticides Clothianidin (CA), Dinotefuran (DF), Imidacloprid (IC) and Nitenpyram (NP) given in Figure 1.



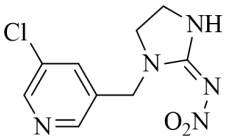
SA1



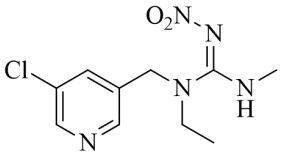
Clothianidin



Dinotefuran



Imidaclopride



Nitenpyram

Figure 1. Structural Formulae of Selected Compounds

2.2.Computational Software used in the Title Study

For the title investigation, the designing of the title sulfinamide subsidiary SA1, and pesticides, we have involved a collection of programming packages of projects, containing Chem-Draw, Chem-3D, Diamond, Murcury, Avogadro, [15] for detail computational considerations were skilled over the most noteworthy computational displaying programming, Gaussian-09 bundle with Gauss view-06 over Density Functional theory (DFT). Our subjected compounds have been all completely optimized through this product, Gauss view-06 and Diamond were utilized for a supplementary inspection of the adsorption mixtures [16].

2.3.General Computational Methodology

The topical work concerning the projected study has been carried out employing theoretical modeling, geometry optimization, and computational simulation, passing via a set of computational software. benzene-1,4-disulfinohydrazide SA1 and pesticides Clothianidin (CA), Dinotefuran (DF), Imidacloprid (AC) and nitenpyram (NP) were completely optimized by (B3LYP) Becke-3-parameter hybrid functional with Lee-Yang correlation functional level of theory using 6-311G(d,p) basis set with Density-Functional Theory

(DFT) employing the Gaussian-09 package of software [17, 18]. Primarily, all substrates were separately optimized and their stable conformation energies were considered. Next, Electronic states of optimized Sulfinamide and Pesticides Clothianidin (CA), Dinotefuran (DF), Imidacloprid (AC) and nitenpyram (NP) were calculated by subsequent path using #n B3LYP/6-31G(d) opt Pop=Reg as a route and their frontier molecular orbitals (FMOs) energies were noted. Then different toxins coordinated with Sulfinamide derivatives were completely optimized using #n B3LYP/6-311g(d,p) opt Pop=Reg as a route section for understanding their coordination configuration and mechanism. The electronic states of all theoretical designed schemes i.e., HOMO-LUMO, Global electrophillicity (ω), Band gap (ΔE), Global hardness (η), Electron affinity (EA), Ionization potential (IP) and Chemical potential (μ) were also calculated with SA1me theory and basis sets through DFT calculations using the following formulations. The stated constraints are helpful in exploring the structure, mechanism, stability, and reactivity of the systems. From the considered energies adsorption of the interacting mixture was also calculated by using the adsorption energy formula given below [19].

ELUMO

EHOMO

Band gap (ΔE) = EHOMO- ELUMO

Ionization energy (I.E) = -EHOMO

Electron affinity (E.A) =-ELUMO

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

Chemical potential (μ) = ½(EHOMO+ ELUMO)

Global hardness (η) =½(EHOMO- ELUMO) or ½ (ΔE)

Eadsorption = Ecomplex – (Epestide + ESA1)

Results and Discussion

Adsorption study of benzene-1,4-disulfinohydrazide (SA1) with Clothianidin (CA)

To approve trial discoveries and furthermore to comprehend the interactions among pesticides and adsorbent Sulfinamides with sulphonyl and amide containing moieties, computational estimations were performed inside DFT system in the water phase. Advanced calculations of benzene-1,4-disulfinohydrazide (SA1) with sulphonyl and sulfinamide containing functionalities and picked with destructive pesticides Clothianidin (CA) were carried out in this portion of study. Further we consider various designs of pesticides concerning adsorbents by setting pesticide at shifted distance over benzene-1,4-disulfinohydrazide (SA1) adsorbent.

To study the interaction pattern of SA1 with CA, the respected geometries of both substrates are completely optimized given in Figure.1 and their optimized structural constraints (bond lengths) are given in Table.1 inside Clothianidin (CA), the N-O, N-N, N-C, and N-H bond lengths are 1.31, 1.355, 1.267 and 1.05 Å respectively, while the N-H, N-N and S-O bond lengths values for sulfinamide SA1 are 1.02, 1.38 and 1.46 Å, respectively before interaction. Upon interaction of one CA molecules to SA1 the N-H, N-N and S-O bond lengths of SA1 slightly changed. New N-H and N-N bond lengths are 1.022 and 1.383 Å at the SA1me time N-O and N-N bond lengths of CA also changed having bond lengths of 1.312 and 1.357 Å. shifts in bond lengths during the adsorption interaction, in SA1-Clothianidin (CA) demonstrate of evidence of arising hydrogen bonding. The coordinating complex SA1-Clothianidin (CA) are stabilized by two hydrogen bonds through NH...O and N...NH with separation distances of 2.34 and 2.5 Å given in Figure 2.

Similarly upon the Saturation of Clothianidin (CA) molecules to SA1 was also investigated for their adsorption behavior. The completely optimized structure of SA1-(CA)2 is given in Figure.1 and their optimized structural constraints (bond lengths) are given in Table.1. After the interaction investigations of CA to SA1 the new N-O and N-N bond lengths of CA are 1.312 and 1.357 Å respectively, which shows a slight variations in bond lengths corresponds to initial structures responsible for hydrogen bonding. SA1-(CA)2 complex are stabilized by four hydrogen bonds NH...ON, on both sides, mean on both side of NO of nitro interact with two NH moieties of SA1 having bond distance of 2.23 and 2.52 Å and on other side two hydrogen bonds with two NH groups of CA having interaction distances of 2.19 and 2.26 Å respectively.

Due to coordination of CA to SA1 their adsorption energies were also calculated. The adsorption energies of SA1-CA and SA1-(CA)2 are -8.53 and -11.99 kcal.mol-1, given in Table.2. It is clear form Table.2 that SA1-(CA)2 adsorption complex are more stable than SA1-(CA). So upon overload of SA1 with

number of CA molecules the adsorption-complex become more stabilize.

To check the stability and electronic properties of all system, theoretical computational investigation of frontier molecular orbitals (EHOMO and ELUMO) were carried out through DFT computations. All electronic properties of SA1, Clothianidin (CA), and their complexes were also investigated. Electronic and molecular properties of all molecules are demonstrated in Table.3

Table.1. Selected geometric constraints of SA1, Clothianidin and their Complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SA1-CA	Bond length (Å) SA1-$(CA)_2$
CA	N-O	1.31	1.312	1.312
	N-N	1.355	1.357	1.356
	N-C	1.267	1.267	1.267
	N-H	1.05	1.05	1.05
SA1	N-H	1.02	1.022	1.021
	N-N	1.38	1.383	1.383
	S-O	1.46	1.46	1.46

Table.2. Adsorption Energies of Clothianidin over SA1 in ($kcalmol^{-1}$)

System	$E_{Complex}$	E_{SA1}	E_{CA}	$E_{adsorption}$
SA1-CA	-700993.33	-629890.82	-71094	-8.53
SA1-(CA)2	-604575.55	-629890.82	-71094	-11.99

Table.3. Computed DFT based Electronic Properties SA1, Clothianidin and their Complexes

Parameters	CA	SA1	SA1-CA	SA1-(CA)2
EL(ev)	-2.503	-2.912	-3.755	-3.565
EH(ev)	-5.116	-5.252	-6.068	-5.469
ΔE=EL(ev)-EH(ev)	2.612	2.340	2.313	1.905
IE= -(EH(ev))	5.116	5.252	6.068	5.469
EA= -EL(ev)	2.503	2.912	3.755	3.565
η= 0.5*ΔE	1.306	1.170	1.156	0.952
μ= 0.5*(EH(ev)+EL(ev))	-3.810	-4.082	-4.912	-4.517
ω= (μ*μ)/(2*η)	5.556	7.119	10.430	10.712

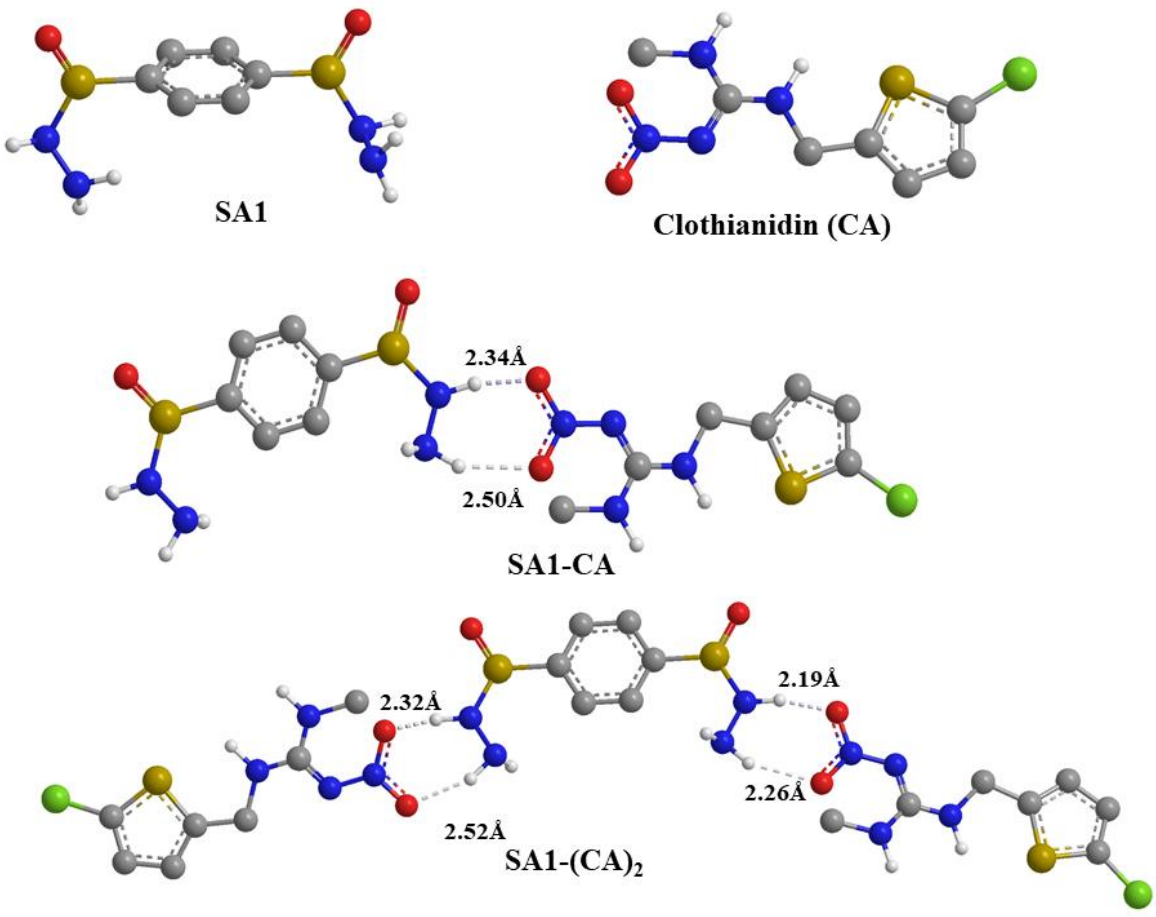


Figure 2. The Fully Optimized Geometries Of Sa1, Clothianidin (Ca), Sa1-Clothianidin And Sa1-(Clothianidin)$_2$ With Hydrogen Bond Distances In (å). Only Polar Hydrogens Are Represented For Clarity.

Adsorption study of SA1 with Dinotefuran (DF)

To approve trial discoveries and furthermore to comprehend the interactions among pesticides and adsorbent sulfinamides with sulphonyl and amide containing moieties, computational estimations were performed inside DFT system in the water phase. Advanced calculations of benzene-1,4-disulfinohydrazide **(SA1)** with sulphonyl and sulfinamide containing functionalities and picked with destructive pesticides Dinotefuran (DF) were carried out in this portion of study. Further we consider various designs of pesticides concerning adsorbents by setting pesticide at shifted distance over benzene-1,4-disulfinohydrazide **(SA1)** adsorbent.

To study the interaction pattern of **SA1** with DF, the respected geometries of both substrates are completely optimized given in Figure.2 and their optimized structural constraints (bond lengths) are given in Table.4. Inside Dinotefuran (DF), the N-O, N-N, N-C, and N-H bond lengths are 1.31, 1.35, 1.260 and 1.05 Å respectively, while the N-H, N-N and S-O bond lengths values for sulfinamide **SA1** are 1.02, 1.38 and 1.46 Å, respectively before interaction. Upon interaction of one DF molecules to **SA1** the N-H, N-N and S-O bond lengths of **SA1** slightly changed. New N-H and N-N bond lengths are 1.021 and 1.382 Å at the **SA1**me time N-O and N-N bond lengths of DF also changed having bond lengths of 1.311 and 1.353 Å, shifts in bond lengths during the adsorption interaction, in **SA1**- Dinotefuran (DF), demonstrate of evidence of rising hydrogen bonding. The coordinating complex **SA1**- Dinotefuran (DF), are stabilized by two hydrogen bonds by nitro group Dinotefuran (DF) and NH moieties of **SA1** through NH...O with separation distances of 2.06 and 1.90 Å given in Figure 3.

Similarly upon the Saturation of Dinotefuran (DF), molecules to **SA1** was also inspected for their

adsorption performance. The completely optimized structure of **SA1**-(DF)2 is given in Figure.2 and their optimized structural constraints (bond lengths) are given in Table.4. After the interaction investigations of DF to **SA1** the new N-O, N-N and N-C bond lengths of DF are 1.312, 1.351 and 1.262 Å respectively, which shows a slight variations in bond lengths corresponds to initial structures responsible for hydrogen bonding. **SA1**-(DF)2 complex are stabilized by four hydrogen bonds NH...ON, on both sides, on one side both NO of nitro group of DF interact with two NH moieties of **SA1** having bond distance of 1.85 and 2.20 Å and on other side **SA1**me groups are involved in two hydrogen bonds with two NH groups of **SA1** having interaction distances of 2.12 and 2.03 Å forming one dimensional interaction.

Due to coordination of CA to **SA1** their adsorption energies were also calculated. The adsorption energies of SA1-DF and SA1-(DF)2 are -8.07 and -10.60 kcal.mol$^{-1,}$ given in Table.5. It is clear form Table.5 that SA1-(DF)2 adsorption complex are more stable than SA1-(DF). So upon Saturation of **SA1** with number of DF molecules the adsorption-complex become more stabilize.

To check the stability and electronic properties of all system, theoretical computational investigation of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) were carried out through DFT computations. All electronic properties of **SA1**, Dinotefuran (DF), and their complexes were also investigated. Electronic and molecular properties of all molecules are demonstrated in Table.6

Table.4. Selected Geometric Constraints of SA1, Dinotefuran and their Complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SA1-DF	Bond length (Å) SA1-(DF)2
DF	N-O	1.31	1.311	1.312
	N-N	1.355	1.353	1.351
	N-C	1.267	1.267	1.262
	N-H	1.05	1.05	1.05
SA1	N-H	1.02	1.021	1.021
	N-N	1.38	1.382	1.382
	S-O	1.46	1.46	1.46

Table.5. Adsorption Energies of Dinotefuran over SA1 in (kcalmol-1)

System	EComplex	ESA1	EDF	Eadsorption
SA1-DF	-701001.401	-629890.82	-71347.6	-8.07
SA1-(DF)2	-1085130.96	-629890.82	-71347.6	-10.60

Table.6. Computed DFT based electronic properties SA1, Dinotefuran and their complexes

Parameters	DF	SA1	SA1-DF	SA1-(DF)2
EL(ev)	-2.237	-2.912	-3.673	-3.537
EH(ev)	-5.176	-5.252	-5.388	-4.980
ΔE=EL(ev)-EH(ev)	2.939	2.340	1.714	1.442
IE= -(EH(ev))	5.176	5.252	5.388	4.980
EA= -EL(ev)	2.237	2.912	3.673	3.537
η= 0.5*ΔE	1.470	1.170	0.857	0.721
μ= 0.5*(EH(ev)+EL(ev))	-3.706	-4.082	-4.531	-4.259
ω= (μ*μ)/(2*η)	4.674	7.119	11.974	12.575

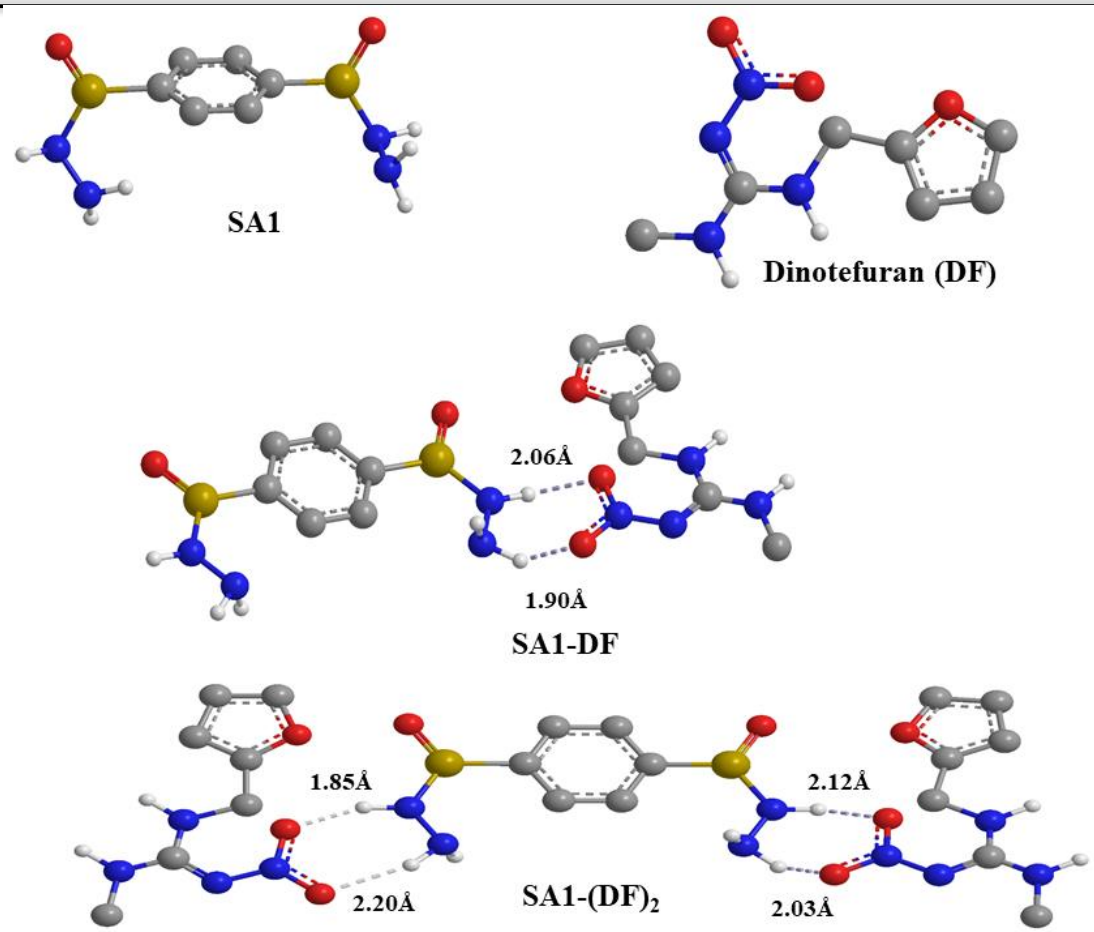


Figure 3. The fully optimized geometries of SA1, Dinotefuran (DF), SA1-Dinotefuran and SA1-(Dinotefuran)2 with hydrogen bond distances in (Å). Only polar hydrogens are represented for clarity.

Adsorption Study of SA1 with Imidacloprid (IC)

To approve trial discoveries and furthermore to comprehend the interactions among pesticides and adsorbent sulfinamides with sulphonyl and amide containing moieties, computational estimations were performed inside DFT system in the water phase. Advanced calculations of benzene-1,4-disulfinohydrazide **(SA1)** with sulphonyl and sulfinamide containing functionalities and picked with destructive pesticides Imidacloprid (IC)were carried out in this portion of study. Further we consider various designs of pesticides concerning adsorbents by setting pesticide at shifted distance over benzene-1,4-disulfinohydrazide **(SA1)** adsorbent.

To study the interaction pattern of **SA1** with Imidacloprid (IC), the respected geometries of both substrates are completely optimized given in Figure.3 and their optimized structural constraints (bond lengths) are given in Table.7. Inside Imidacloprid (IC), due to **SA1** structural similarities the N-O, N-N, N-C, and N-H bond lengths are 1.31, 1.35, 1.260 and 1.05 Å respectively, while the N-H, N-N and S-O bond lengths values for sulfinamide **SA1** are 1.02, 1.38 and 1.46 Å, respectively before interaction. Upon interaction of one Imidacloprid (IC) molecules to **SA1** the N-H, N-N and S-O bond lengths of **SA1** slightly changed. New N-H and N-N bond lengths of SA1 are 1.022 and 1.381 Å at the **SA1**me time N-O and N-N bond lengths of Imidacloprid (IC), also changed having bond lengths of 1.312 and 1.352 Å, shifts in bond lengths during the adsorption interaction, in **SA1**-Imidacloprid (IC), demonstrate of indication of rising hydrogen bonding. The coordinating complex **SA1**-Imidacloprid (IC), are stabilized by two hydrogen bonds by nitro group Imidacloprid (IC) and NH moieties of **SA1** through NH...O with separation distances of 2.01 and 2.30 Å given in Figure.4.

Similarly upon the Saturation of Imidacloprid (IC), molecules to **SA1** was also reviewed for their adsorption interaction. The completely optimized structure of **SA1**-(IC)2 is given in Figure.3 and their optimized structural constraints (bond lengths) are given in Table.7. After the interaction investigations of Imidacloprid (IC) to **SA1** the new N-O, N-N and N-C bond lengths of IC are 1.311, 1.352 and 1.261 Å respectively, which shows a slight variations in bond lengths corresponds to initial structures responsible for hydrogen interaction. **SA1**-(IC)2 complex are stabilized by four hydrogen bonds NH...ON, on both sides, on one side both NO of nitro group of Imidacloprid (IC) interact with two NH moieties of **SA1** having bond distance of 2.01 and 2.30 Å and on other side **SA1**me groups are involved in two hydrogen bonds with two NH groups of **SA1** having interaction distances of 1.96 and 2.30 Å forming one dimensional interaction.

Due to coordination of IC to **SA1** their adsorption energies were also calculated. The adsorption energies of SA1-IC and SA1-(IC)2 are -7.14 and -9.45 kcal.mol$^{-1,}$ given in Table.8. It is clear form Table.8 that SA1-(IC)2 adsorption complex are more stable than SA1-(IC). So upon **sa**turation of **SA1** with number of IC molecules the adsorption complex become more stabilize.

To check the stability and electronic properties of all system, theoretical computational investigation of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) were carried out through DFT computations. All electronic properties of **SA1**, Imidacloprid (IC), and their complexes were also investigated. Electronic and molecular properties of all molecules are demonstrated in Table.9

Table.7. Selected geometric constraints of SA1, Imidacloprid and their Complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SA1-IC	Bond length (Å) SA1-$(IC)_2$
IC	N-O	1.31	1.312	1.311
	N-N	1.35	1.352	1.352
	N-C	1.260	1.261	1.261
	N-H	1.05	1.05	1.05
SA1	N-H	1.02	1.022	1.021
	N-N	1.38	1.381	1.383
	S-O	1.46	1.46	1.46

Table.8. Adsorption Energies of Imidacloprid over SA1 in (kcalmol^{-1})

System	$E_{Complex}$	E_{SA1}	E_{IC}	$E_{adsorption}$
SA1-IC	-652409.6	-629890.82	-70840.3	-7.14
SA1-(IC)2	-604592.6	-629890.82	-70840.3	-9.45

Table.9. Computed DFT based Electronic Properties SA1, Imidacloprid and their Complexes

Parameters	IC	SA1	SA1-IC	SA1-(IC)2
EL(ev)	-2.286	-2.912	-3.891	-4.027
EH(ev)	-5.197	-5.252	-6.340	-5.714
ΔE=EL(ev)-EH(ev)	2.912	2.340	2.449	1.687
IE= -(EH(ev))	5.197	5.252	6.340	5.714
EA= -EL(ev)	2.286	2.912	3.891	4.027
η= 0.5*ΔE	1.456	1.170	1.224	0.844
μ= 0.5*(EH(ev)+EL(ev))	-3.742	-4.082	-5.116	-4.871
ω= (μ*μ)/(2*η)	4.808	7.119	10.686	14.062

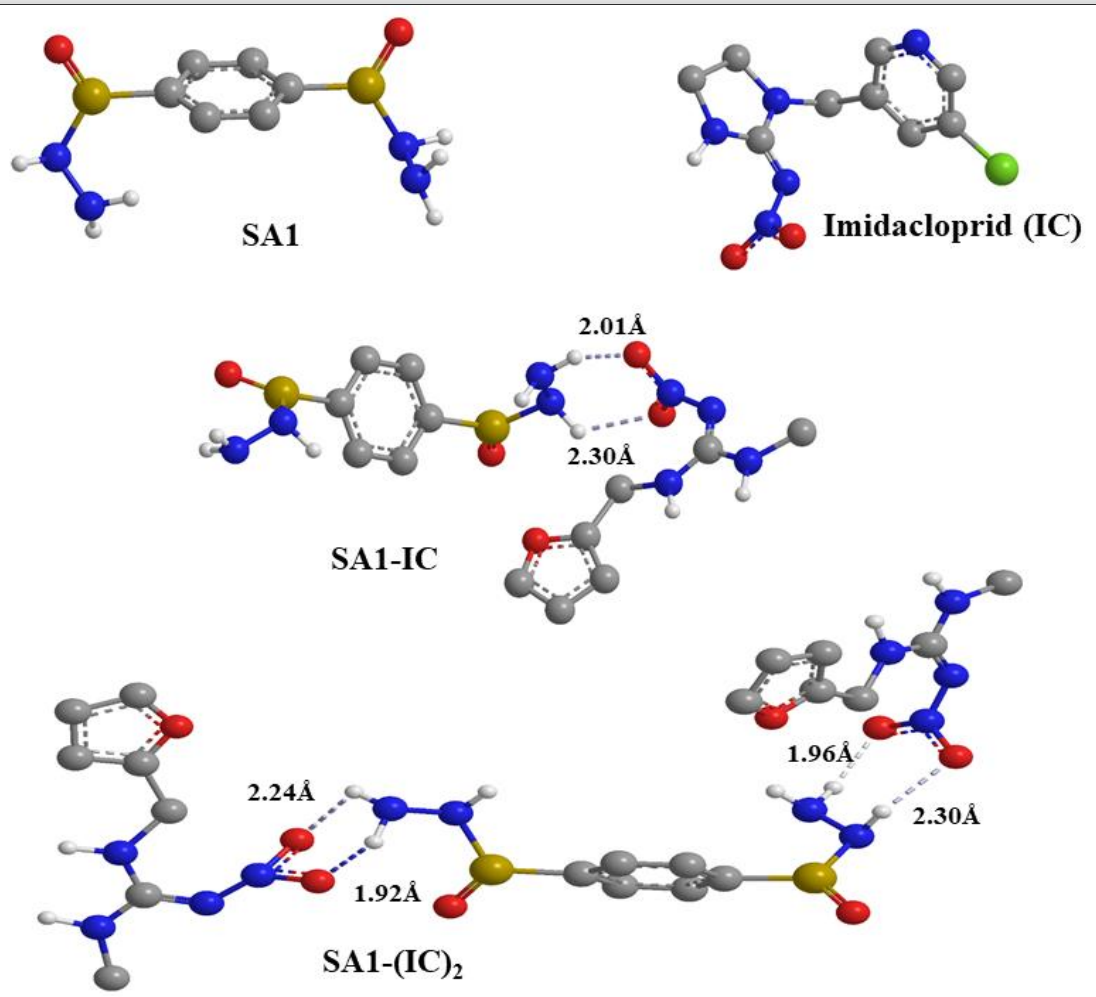


Figure 4. The fully optimized geometries of SA1, Imidacloprid (IC), SA1-Imidacloprid (IC) and SA1-(Imidacloprid)$_2$ with hydrogen bond distances in (Å). Only polar hydrogens are represented for clarity.

Adsorption study of SA1 with Nitenpyram (NP)

To approve trial discoveries and furthermore to comprehend the interactions among pesticides and adsorbent sulfinamides with sulphonyl and amide containing moieties, computational estimations were performed inside DFT system in the water phase. Advanced calculations of benzene-1,4-disulfinohydrazide **(SA1)** with sulphonyl and sulfinamide containing functionalities and picked with destructive pesticides Nitenpyram (NP) were carried out in this portion of study. Further we consider various designs of pesticides concerning adsorbents by setting pesticide at shifted distance over benzene-1,4-disulfinohydrazide **(SA1)** adsorbent.

To study the interaction pattern of **SA1** with Nitenpyram (NP) the respected geometries of both substrates are completely optimized given in Figure.4 and their optimized structural constraints (bond lengths) are given in Table.10. Inside Nitenpyram (NP) due to **SA1**me structural similarities no clear change observed in the selected N-O, N-N, N-C, and N-H bond lengths are 1.31, 1.35, 1.260 and 1.05 Å respectively, while the N-H, N-N and S-O bond lengths values for sulfinamide **SA1** are 1.02, 1.38 and 1.46 Å, respectively before interaction. Upon interaction of one Nitenpyram (NP) molecules to **SA1** the N-H, N-N and S-O bond lengths of **SA1** slightly changed. New N-H and N-N bond lengths are 1.021 and 1.380 Å at the **SA1**me time N-O and N-N bond lengths of Nitenpyram (NP) also changed having bond lengths of 1.311 and 1.351 Å, shifts in bond lengths during the adsorption interaction, in **SA1**- Nitenpyram (NP) demonstrate of indication of rising hydrogen bonding. The coordinating complex **SA1**- Nitenpyram (NP), are stabilized by two hydrogen bonds by nitro group Nitenpyram (NP) and NH moieties of **SA1** through

NH...O with separation distances of 1.80 and 2.21 Å given in Figure.5.

Similarly upon the Saturation of Nitenpyram (NP), molecules to **SA1** was also studied for their adsorption behavior. The completely optimized structure of **SA1**-(NP)2 is given in Figure.4 and their optimized structural constraints (bond lengths) are given in Table.10. After the interaction investigations of Nitenpyram (NP) to **SA1** the new N-O, N-N and N-C bond lengths of IC are 1.312, 1.354 and 1.262 Å respectively, which shows a slight variations in bond lengths corresponds to initial structures responsible for hydrogen interaction. **SA1**-(NP)2 complex are stabilized by four hydrogen bonds NH...ON, on both sides, on one side both NO of nitro group of Nitenpyram (NP) interact with two NH moieties of **SA1** having bond distance of 1.80 and 2.18 Å and on other side **SA1**me groups are involved in two hydrogen bonds with two NH groups of **SA1** having interaction distances of 1.75 and 2.20Å forming one dimensional interaction.

Due to coordination of NP to **SA1** their adsorption energies were also calculated. The adsorption energies of SA1-NP and SA1-(NP)2 are -8.30 and -12.45 kcal.mol$^{-1,}$ given in Table.11. It is clear form Table.11 that SA1-(NP)2 adsorption complex are more stable than SA1-(NP). So upon Saturation of **SA1** with number of NP molecules the adsorption complex become more stabilize.

To check the stability and electronic properties of all system, theoretical computational investigation of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) were carried out through DFT computations. All electronic properties of **SA1**, Nitenpyram (NP), and their complexes were also investigated. Electronic and molecular properties of all molecules are demonstrated in Table.12

Table.10. Selected Geometric Constraints of SA1, Nitenpyram and their Complexes

Components	Atoms	Bond length (Å)	Bond length (Å) SA1-NP	Bond length (Å) SA1-$(NP)_2$
NP	N-O	1.31	1.311	1.312
	N-N	1.35	1.351	1.354
	N-C	1.267	1.267	1.262
	N-H	1.05	1.05	1.05
SA1	N-H	1.02	1.021	1.021
	N-N	1.38	1.38	1.38
	S-O	1.46	1.46	1.46

Table.11. Adsorption Energies of Nitenpyram over SA1 in (kcalmol^{-1})

System	$E_{Complex}$	E_{SA1}	E_{NP}	$E_{adsorption}$
SA1-NP	-798123.434	-629890.82	-70978.7	-8.30
SA1-(NP)2	-821183.434	-629890.82	-70978.7	-12.45

Table.12. Computed DFT based Electronic Properties SA1, Nitenpyram and their Complexes

Parameters	NP	SA1	SA1-NP	SA1-(NP)2
EL(ev)	-2.286	-2.912	-3.891	-4.027
EH(ev)	-5.116	-5.252	-6.340	-5.714
ΔE=EL(ev)-EH(ev)	2.830	2.340	2.449	1.687
IE= -(EH(ev))	5.116	5.252	6.340	5.714
EA= -EL(ev)	2.286	2.912	3.891	4.027
η= 0.5*ΔE	1.415	1.170	1.224	0.844
μ= 0.5*(EH(ev)+EL(ev))	-3.701	-4.082	-5.116	-4.871
ω= (μ*μ)/(2*η)	4.839	7.119	10.686	14.062

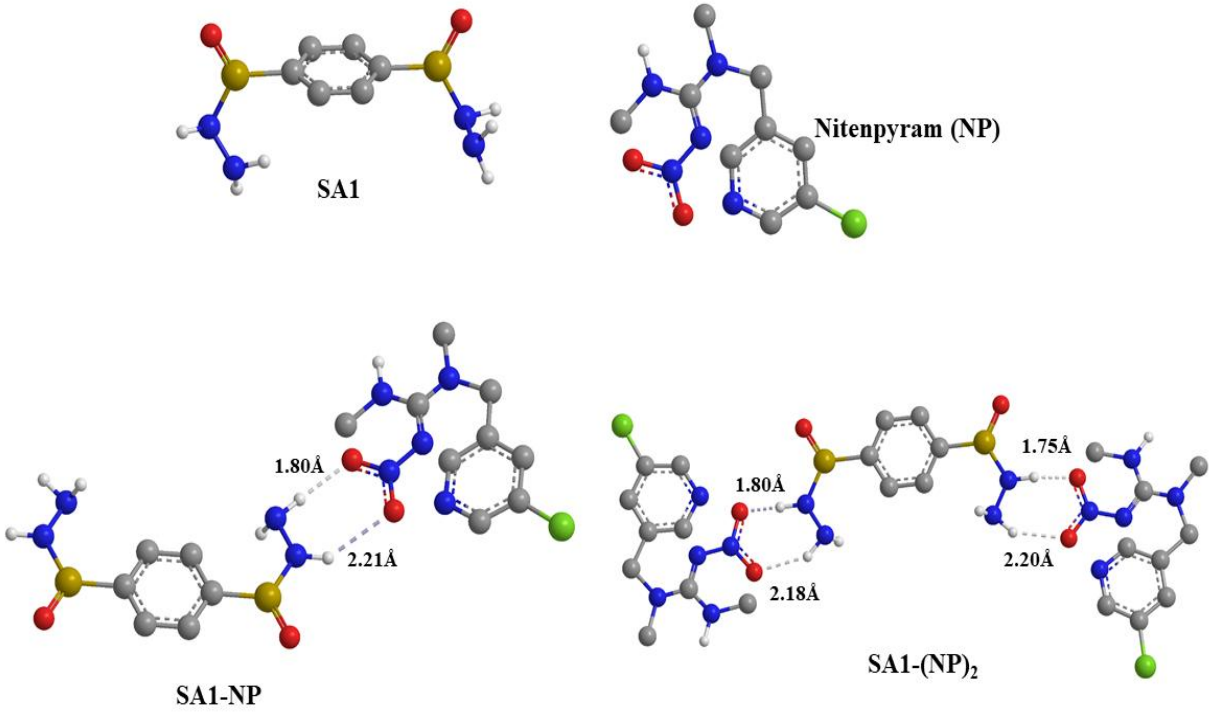


Figure 5. The fully optimized geometries of SA1, Nitenpyram (NP) SA1-Nitenpyram (NP) and SA1-(Nitenpyram)$_2$ with hydrogen bond distances in (Å). Only polar hydrogens are represented for clarity.

Conclusion

Substances that are synthetically alluded to as endocrine disruptors restrain the endocrine framework from executing its unexpected capabilities by cooperating with chemical amalgamation, discharge, transport, digestion, restricting, activity, and evacuation inside the body. Endocrine disruptors have various adverse consequences on human wellbeing, including hormonal awkwardness, anomalies in multiplication, irregularities being developed, expanded chance of malignant growth, issues of the thyroid and digestion, irregularities of the **SA1**fe framework, and different irregularities of the sensory system. Neonicotinoids are engineered synthetic substances intended to impersonate the activity of nicotine, a characteristic insect spray found in plants containing, Clothianidin (CA), Dinotefuran (DF), Imidacloprid (AC) and nitenpyram (NP)

In title work we have examined the adsorption perspective of two selected Sulfinamide derivatives **SA1** and **SA12** against some selected pesticides i.e. Clothianidin (CA), Dinotefuran (DF), Imidacloprid (AC) and nitenpyram (NP) which are commonly used in swat region of KP, Pakistan. In this study, we carried out our desired investigation over computational chemistry and modeling through Density Functional Theory (DFT) by using the B3LYP level of model with 6-311G(d,p) basis sets. Giving to our exploration the adsorption mechanism were based on hydrogen bonding and weak Vander Waal forces. The adsorption energies are -6.68 to -12.45 kcal.mol^{-1}. The theoretical examination demonstrate that the adsorption complexes with two pesticides interacted to sulfinamides derivatives are more stable than their corresponding substrates and the complex with one molecule of pesticide. Our theoretical results are respectable clarification for experimental researchers and we believe that these derivatives will be best adsorbents in future

Future Plan

Our future plan on the basis of these theoretical investigation, we are planning that supramolecular compounds having large hydrophobic and these active sulfonamides moieties can act as best adsorbent, which

will be supported by Magnetic iron oxide Fe3O4. The large hydrophobic portion will give insoluble nature and sulfonamide moieties will give slight soluble potion. These pesticide will easily adsorbed on these supramolecular compounds and will easily be separated by magnet from water for water purification.

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Conflict of Interest

The authors declare no conflict of interest

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