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Selectivity of Salicylaldoxime and its Derivatives

Burak Tüzün (btuzun@cumhuriyet.edu.tr)

Chemistry Department, Faculty of Science, Cumhuriyet University, 58100 Sivas, TURKEY

Abstract – Salicylaldoxime and its derivatives have been investigated by the DFT (Density Functional Theory) Method. All calculations were made using the Gaussian 09, Revision B.01 program. The initial molecular modelings of all molecules were optimized by b3lyp methods. The obtained geometries were further optimized at the B3LYP/ 6-311++g (d,p) level using Gaussian package. Density functional theory (DFT) offered an effective tool in the study of properties and energies of various collectors. Thus, the structural information, relative energies, atomic charges, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and compositions about salicylaldoxime containing different substituent groupings were obtained by DFT. The calculated properties of the free molecules are the useful information for better understanding the interaction and bond formation between the chelating molecule and the mineral surface.

Keywords – *Flotation, collector, salicylaldoxime, DFT, HSAB.*

1. Introduction

Flotation, which cannot be enriched by gravimetry, a physico-chemical separation method used for enriching the ore very fine. In this method, different surface properties of particles and air bubbles generated in the pulp is utilized. The separation of particles in the air bubbles come in contact with the particles (hydrophobes) upwards, unable particles (hydrophilic) with the downward movement takes place.

Flotation method, the physical events are: a finely ground ore is mixed with water and pulp that occur with air bubbles (foam) is potted, the air bubbles attach themselves to some of the mineral grains, and other minerals in the water as they remain in the show this feature. The air bubbles in the pulp upward above minerals produce a self-adhesive. This foam layer is collected and gathered with a suitable vehicle is called the foam flotation concentrate. According to one or more of the ore concentrate can be obtained. Common features of flotation and concentrate on only one similar case of minerals at the same time as the collection of liquor "collective flotation", with properties similar to the flotation of minerals in the flotation process for the separation of "selective flotation" is called.

As a result of increased mechanization in mining and depletion of high-grade ore deposits, ore processing is a very fine grain size requirement with a great momentum to the development of flotation technology has been the front foot. In addition, the food, chemical and environmental engineering for the various fields in areas such as the spread of different types of flotation technology has enabled the development of flotation devices. At present, wastewater treatment (removal of suspended solids and oils), the removal of ink from recycled paper, heavy metals, cleaning of industrial wastes, pollutants, and oils to eliminate meat and dairy industries are widely utilized in flotation technology. In the field of mineral processing has been enriched with more than 100 known fact that the mineral flotation process (copper, zinc, nickel, silver, manganese, chromite, cobalt, tungsten, boron and sulfur minerals, etc.).

Flotation is commonly employed process for the separation of minerals from their ores. Collectors either chemically bond (chemisorption) on a hydrophobic mineral surface, or adsorb onto the surface in the case of, for example, coal flotation through physisorption. Valuable minerals are separated from the crude ore with the help of organic chemicals known as collectors. Owing to the limitation of sources and supplies of minerals raw materials and the need to treat ores of lower grades, increasingly fineness and mineralogical complexity new flotation technologies have been developed.

In recent years, water pollution caused by heavy metals is one of the major economic and environmental problems all over the world. Heavy metal ions are considered to be a non-biodegrade like organic pollutant in water and attracted more attention due to its toxicity, persistent in nature particularly, even at low concentrations [1-3]. Consequently, the development of reliable methods for the removal and determination of lead in environmental and biological samples is of particular significance [4].

Froth flotation is single most important process for enriching low grade ores. A variety of surface-active reagents are used in the process, depending on their function which may be as collectors, frothers, depressants and activators. These flotation reagents affect the flotation chemistry in terms of the chemical and electrochemical control of the system. Without the reagents, controlling the wettability of solid surfaces by water, chemistry and electrochemistry of the solution, the dispersing and aggregation of solid particles, and the generation and stability of the forth would not be possible. There are many recent publications in the literature reviewing the development and use of these chemical agents in froth flotation for better understanding of flotation chemistry [7-11].

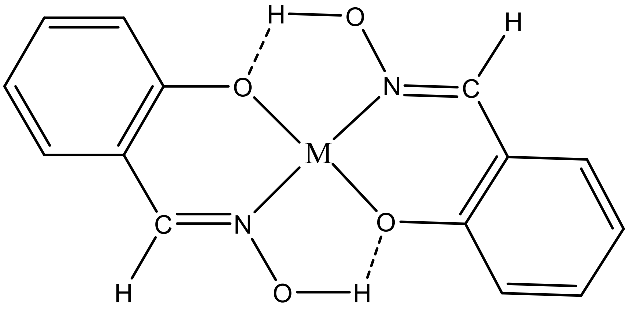
Collector is the crucial technology in the flotation process, and success of the separation process mainly depends on the selective adsorption of the collector on the objective mineral [13-14]. The choice of collector type is a very important step in the flotation performance of minerals. In the search for new chemical reagents with strong affinity for certain metal ions, many researchers have indicate that chelating reagents have the advantage of offering better selectivity and specificity as flotation collectors. Therefore, the use of chelating reagents in the flotation process has been paid much attention for many years. Chelating reagents-type collector molecules contain donor atoms such as S, N and O in the functional group, and they are capable of bonding via two or more atoms with metal ions in a given mineral to form heterocyclic rings in which the metal atom is one of the members . Since metal-chelates are more stable than ionic or covalently bonded metal salts, chelating-agents are important for the flotation of minerals. The formation of metal complexes with varying stability allows selectivity for the separation of minerals.

Quantum chemical methods and molecular modeling techniques enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule as well as of molecular fragments and substituents. The use of theoretical parameters presents two main advantages: firstly, the compounds and their various fragments and substituents can be directly characterized on the basis of their molecular structure only; and secondly, the proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study [19].

Quantum chemically derived parameters are fundamentally different from experimentally measured quantities, although there is some natural overlap. Unlike experimental measurements there is no statistical error in quantum chemical calculations. There is inherent error however, associated with the assumptions required to facilitate the calculations. In most cases the direction but not the magnitude of the error is known [19]. In using quantum chemistry-based parameters with a series of related compounds, the computational error is considered to be approximately constant throughout the series.

The mechanism of interaction of collector on mineral surfaces can be described by various reactions, physically and chemically. The principal forms of adsorption are by hydrophobic association [23-24], hydrogen bonding [25], electrostatic attraction and chemical interaction [26]. Physical adsorption results from electrostatic interaction between the charged centers of molecules and the charged metal surface which results in a dipole interaction of molecules and metal surface, whereas chemical adsorption results from charge sharing or charge transfer from the collector to the metal surface, Also, we will try to explain which adsorption site is favored to bind the inhibitor to the metal surface, the sulphur atom or the nitrogen atom [62].

The theoretical and practical aspects of the use of salicylaldoxime ($SALO_xH_2$) in chemical analysis have been discussed in several papers. Those papers also dealt with the structure and changes taking place on chelation by different metallic ion. The oximes, through a rigorous stable coloured chelate compounds with nickel (II), palladium (II) and copper (II) ions. The bis-salicylaldoximates studied by us correspond to formula:



where M=Ni(II), Pd (II), Cu (II), Cd (II), Zn (II) Ca (II), Mg (II).

Determinations of the structure have pointed out that in bis-salicylaldoximates the hydrogen bonds are very short and probably asymmetry may be explained through the interpolation of the hydrogen between the oxygen atom of the oximic group and the oxygen atom of the phenolic group [32]. Some of the characteristic reactions of the functional groups of the free collectors are masked or diminished through coordination. The lack of reactivity of the OH groups in the coordinated oximes was caused by the $O-H\cdots O$ intramolecular hydrogen bonds existing in these compounds [36-44]. Oxy-imines >C=N-OH, more commonly abbreviated as oximes, constitute an important class of chelating agents. They have found extensive applications as highly selective reagents for the separation and/or spectrophotometric determination of a diversity of metal ions [51].

Several experimental and commercial oxime containing chelating polymers have been described in the literature. The incorporation of oxime groups in chelate forming polymers has been achieved by a variety of reaction schemes. The relative selectivity and capacity of the resulting chelate-forming polymer, however, is largely influenced by the nature of the polymer backbone. Walsh and co-workers have described the incorporation of hydroxyoxime groups in substituted phenyl acrylate polymers via the Fries rearrangement. Extensive work has been reported by Warshawsky et al. on the impregnation of many 2-hydroxyaryloximes in polymeric matrices where the oxime collectors are physically or chemically bound to the otherwise unreactive polymeric backbone [51].

Chelating collectors are compounds which form multidentate complexes by ring closure with a metal ion [50]. A majority of chelating collectors contain the three most important donors, e.g. N, O and S [55]. Based on the knowledge of well-known analytical reagents and their metal ion specificity, modified chelating collectors have been used for the extraction of metals, e.g. dimethyl glyoxime for nickel minerals and salicylaldoxime (SALO) for copper minerals [56]. Among the various N, O type chelating collectors, hydroxy oximes are very efficient solvent extraction reagents for purification and concentration of copper leach liquors.

The remarkable inhibitory effect is reinforced by the presence of heteroatom such as sulphur, nitrogen and oxygen in the ring which facilitates its adsorption on the metal surface following the sequence O < N < S [59-61]. It has been reported that N-containing inhibitors exert their best efficiencies in hydrochloric acid [62].

2. Method

DFT (density functional theory) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods in less time and are cheaper from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT.

All calculations were made using the Gaussian 09, Revision B.01. The initial molecular modeling of salicylaldoxime and its derivates were optimized by B3LYP methods. The obtained geometries were further optimized at b3lyp/ 6-311++g (d,p) level and calculated with ab initio methods. Atomic charge values were determined to describe the reactivity of the molecules and calculated according to scheme of Mulliken (1955).

3. Result and Discussion

The computed geometrical parameters of all structures in the gas have been given as supporting Information with this text (Table S1, Supporting Information).

Glembotskii [84] suggested that the collecting power of collectors is directly proportional to the electron density of the reactive center of the molecule (i.e., sulfur). The use of Mulliken population analysis to estimate center of collector of flotation has been widely reported and is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule [20,64,65,66]. The calculated Mulliken charges show that there are more than one active center and it was confirmed that the more negative the atomic partial charges of the adsorbed center are, the more easily the atoms donate its electrons to the unoccupied d-orbital of the metal [66-68]. There is a general consensus by several authors that the more negatively charged heteroatom is, the more is its ability to adsorb on the metal surface through a donor–acceptor type reaction [64,77]. Variation in the flotation efficiency of the collector depends on the presence of electronegative O- and N-atoms as substituents in their molecular structure. The calculated Mulliken charges of selected atoms are presented in [78].

The structure and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The geometry of the collector in its ground state, as well as the nature of their molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the properties of activity of collector. The relationships between the structural parameters and collector of those compounds have not been studied yet. The objective of this work is to calculate the most relevant molecular properties on its action as collector of the flotation of compounds. These properties are the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), and the total energy (TE) [70].

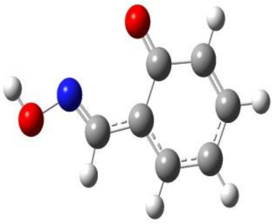
The energy of HOMO is often associated with the electron donating ability of a molecule; high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Therefore, the energy of LUMO indicates the ability of the molecule to accept electrons [71]. So, the lower the value of E_{LUMO}, the more probable that the molecule accepts electrons. The binding ability of the collector to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values.

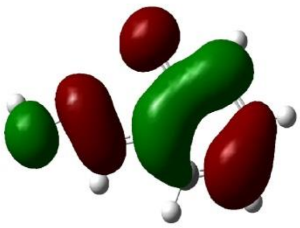
According to the frontier molecular orbital theory, FMO, the chemical reactivity is a function of interaction between HOMO and LUMO levels of the reacting species [80]. The E_{HOMO} indicates the ability of the molecule to donate electrons to an appropriated acceptor with empty molecular orbitals and E_{LUMO} indicates its ability to accept electrons. The lower the value of E_{LUMO}, the more ability of the molecule is to accept electrons [20]. While, the higher is the value of E_{HOMO} of the collector, the easer is its offering electrons to the unoccupied d-orbital of metal surface and the greater is its collector efficiency. The calculations showed that the lowest energy E_{HOMO} is assigned for the parent compound which is expected to have the lowest collector among the investigated compounds.

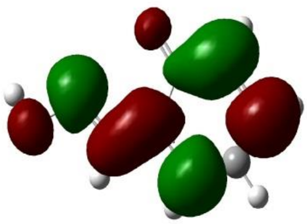
Table 1. The calculated frontier orbital eigenvalues for collector of salicylaldoxime (au).

	HOMO	LUMO
SSA	-0,23438	-0,06619
SSA-1-CH_3	-0,22986	-0,05556
SSA-3-CH_3	-0,22793	-0,06089
SSA-1/3-CH_3	-0,22380	-0,04984
SSA-1-OCH3	-0,22941	-0,05507
SSA-3-OCH3	-0,21787	-0,05740
SSA-1/3-OCH3	-0,21357	-0,04685
SSA-1-NO_2	-0,25440	-0,10215
SSA-3- NO_2	-0,25563	-0,10156
SSA-1/3- NO_2	-0,27509	-0,11680
SSA-1-F	-0,24227	-0,06935
SSA-3-F	-0,23936	-0,07211
SSA-1/3-F	-0,24677	-0,07500
SSA-1- NH_2	-0,22806	-0,05116
SSA-3- NH_2	-0,20403	-0,05077
SSA-1/3- NH_2	-0,20737	-0,04069

The eigenvalues of HOMO and LUMO and their energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, whereas HOMO as an electron donor represents the ability donates an electron. The smaller, the energy gap of LUMO and HOMO, the easier, it is for the electrons of HOMO to be excited; the higher, the energies of HOMO, the easier, it is for HOMO to donate electrons; the lower energy of LUMO, the easier, it is for LUMO to accepted electrons [82].


SSA


HOMO OF SSA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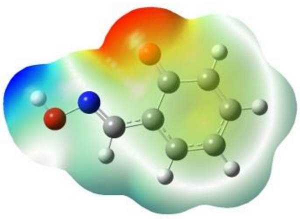
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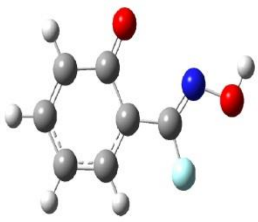
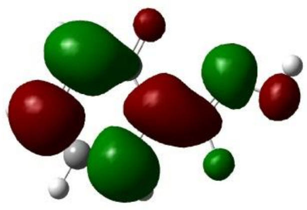

SSA-1-F


HOMO OF SSA-1-F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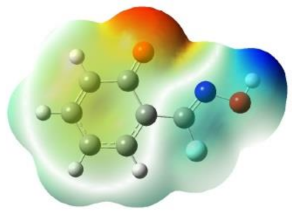
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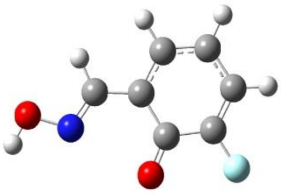

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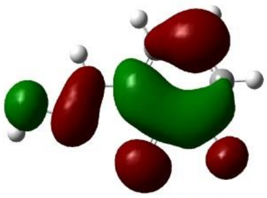

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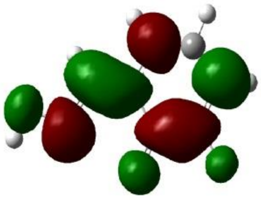

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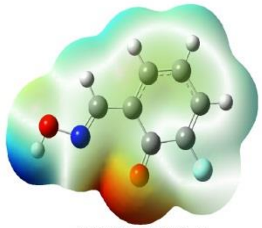

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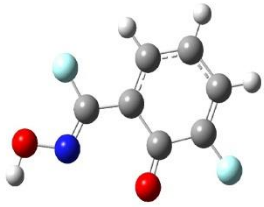

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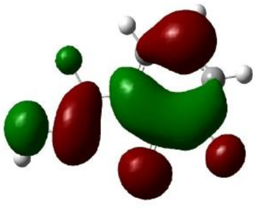

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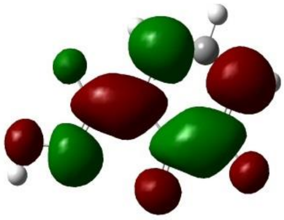

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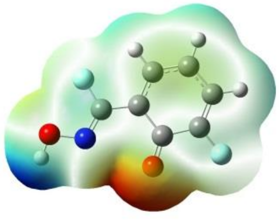

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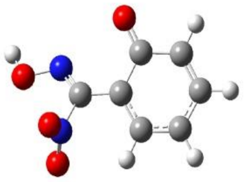

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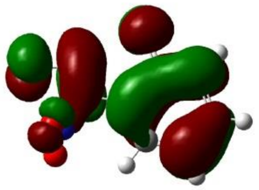

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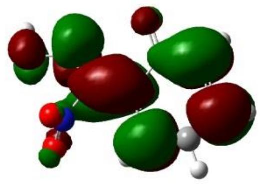

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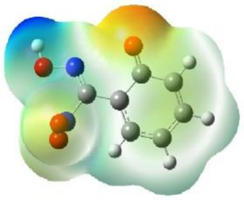

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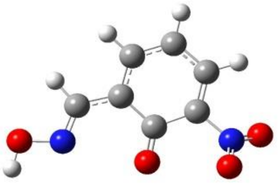

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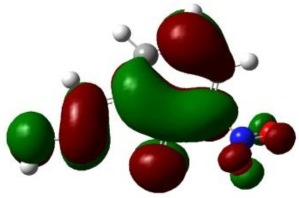

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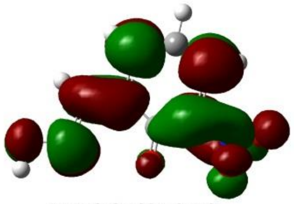

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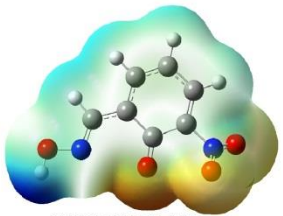

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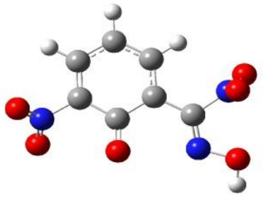

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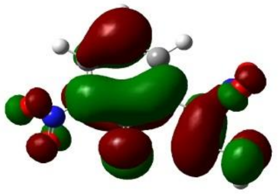

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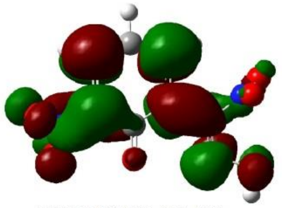

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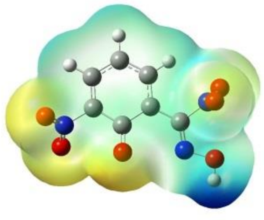

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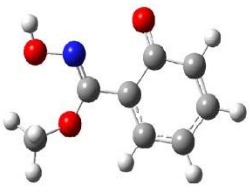

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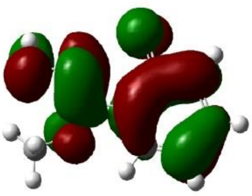

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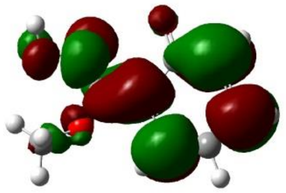

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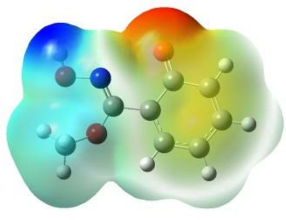

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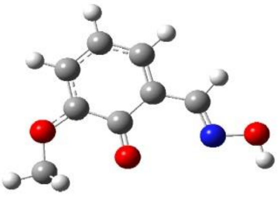

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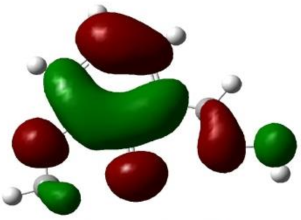

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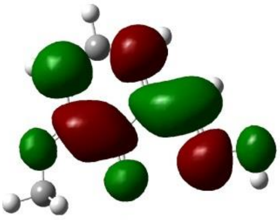

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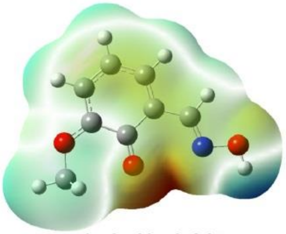

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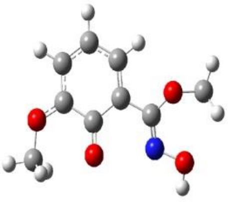

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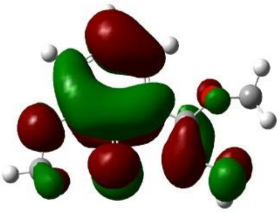

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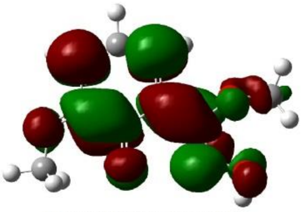

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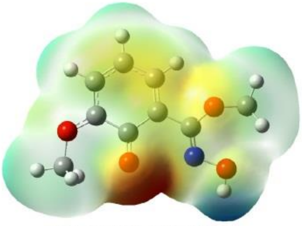

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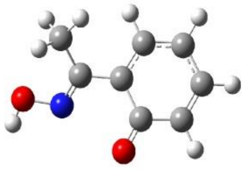

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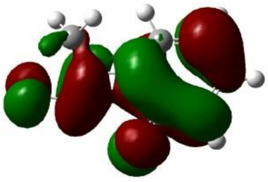

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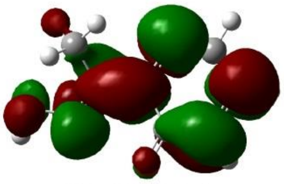

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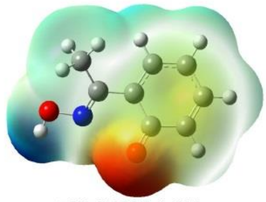

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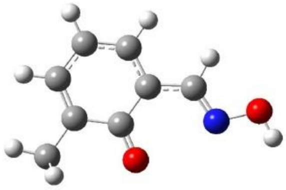

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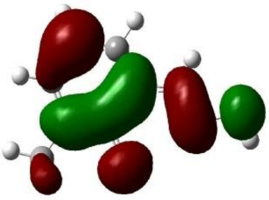

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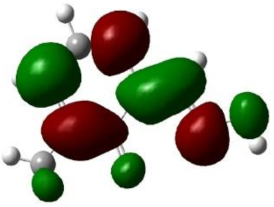

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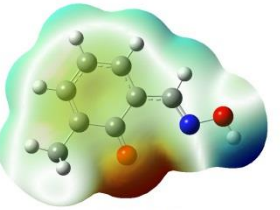

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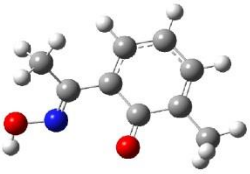

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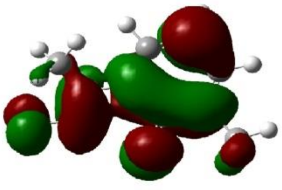

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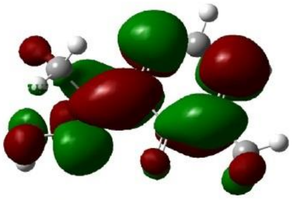

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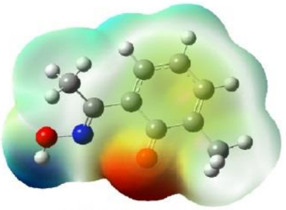

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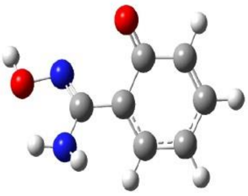
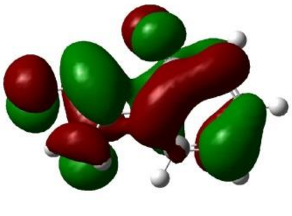


SSA-1-NH$_2$



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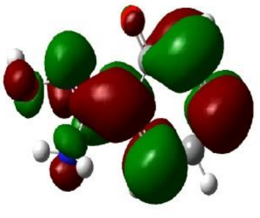

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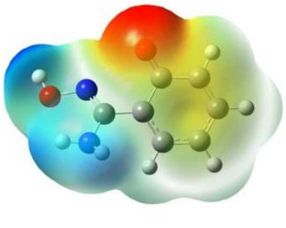

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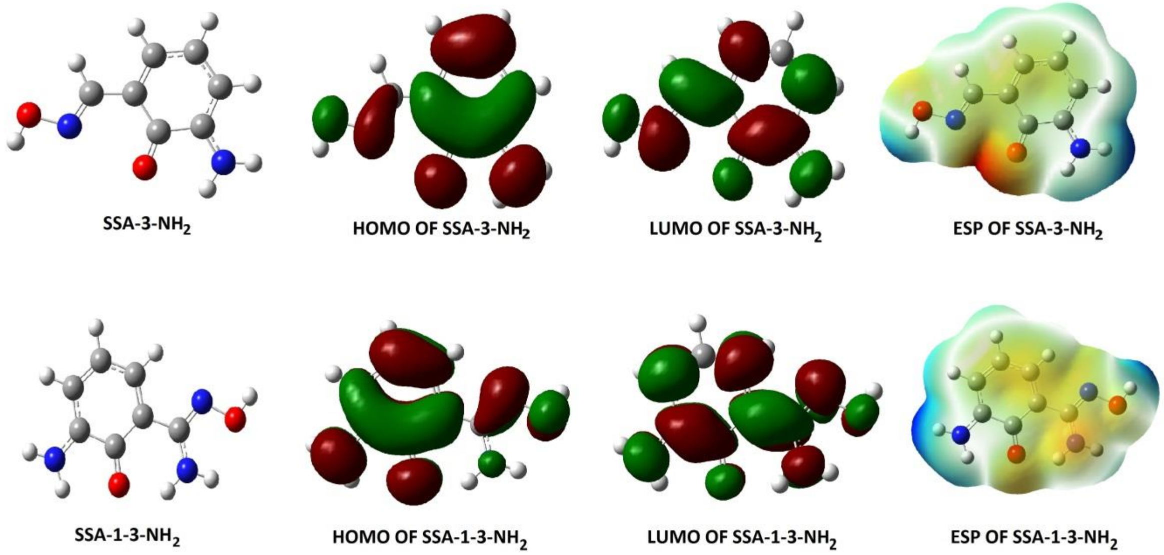

Figure 1. Densities of the HOMO-LUMO and ESP of Salicylaldoxime and its derivatives.

Stability of the complex energy values as predicted by the HOMO-LUMO predictable with the concepts of hard-soft. According to Koopman's theorem [72], the energies of the HOMO and the LUMO orbitals of the inhibitor molecule are related to the ionization potential, I, and the electron affinity, A, respectively, by the following relations: $I = -E_{HOMO}$ and $A = -E_{LUMO}$. Absolute electronegativity, v, and absolute hardness, g, of the inhibitor molecule are given by [73]. $\chi = I + A/2$ and $\eta = I - A/2$. Softness is the inverse of hardness: $\sigma = 1/\eta$.

Absolute hardness, η and softness, σ are important properties to measure the molecular stability and reactivity. Hard and soft acids and bases were originally defined only in general term:

Soft base-donor atom is of high polarizability, low electronegativity, easily oxidized and associated with empty, low lying orbitals.

Hard base-donor atom is of low polarizability, high electronegativity, hard to reduce, and associated with empty orbitals of high energy and hence inaccessible.

Soft acids-the acceptor atom is of low positive charge, large size, and has several easily excited outer electrons, polarizable.

Hard acids-acceptor atom is of high positive charge, small size, and does not have easily excited outer electrons, not polarizable [86].

Hard and soft acid-base approach (HSAB) benefiting comments can be made on the stability of complexes formed. As is known, according to the principle of HSAB, hard acids prefer hard bases, soft acids prefer soft bases. A hard molecule has a large HOMO-LUMO energy gap and a soft molecule has a small HOMO-LUMO energy gap. Soft molecules are more reactive than hard ones because they could easily offer electrons to an acceptor. According to molecular orbital theory, between soft acids and soft base interaction is strong. Because energy value of HOMO of acid are close to energy value of

LUMO of base. The energy value of the HOMO and LUMO orbitals are close to each other as a means to be more covalent interaction. So knowledge of the acid-base complex is more covalent interaction will be more stable.

Any transition metal is constant the LUMO energy value. collector-metal HOMO-LUMO energy gap is decreases when collector has high HOMO energy value. When collector-metal HOMO-LUMO energy gap decreased, covalent interaction increases. This will enhance the stability of the complexes.

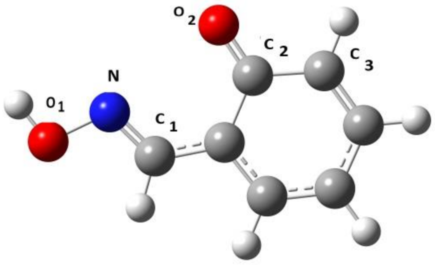

Figure 2. Structures of SSA molecule

In this study, electron donor and electron acceptor groups were connected to positions near of electron donor atoms of collector of salicylaldoxime. Electron donor groups increased the HOMO energy value of collector thus softness is increased. Electron acceptor groups decreased the HOMO energy value of collector thus hardness is increased. This study was showed that stability of complexes is depending on softness. Therefore, stability of complexes is increased when softness is increased. Concepts of hardness and softness mustn't have ignored in synthesis of complex and experimental study.

Table 2. Selected Mulliken atomic charges of compounds have been calculated (atomic units).

	O_1	N	C_1	C_2	C_3	O_2
SSA	0,056	-0,351	-0,128	-0,944	0,398	-0,206
SSA-1-CH_3	-0,029	-0,234	0,255	-1,153	0,402	0,194
SSA-3-CH_3	0,076	-0,391	0,023	-1,272	1,316	-0,194
SSA-1/3-CH_3	-0,013	-0,261	0,165	-1,810	1,538	-0,195
SSA-1-OCH3	-0,049	-0,250	0,031	-0,912	0,311	-0,192
SSA-3-OCH3	0,075	-0,411	-0,070	-0,643	-0,246	-0,217
SSA-1/3-OCH3	-0,039	-0,281	0,276	-0,188	-0,177	-0,219
SSA-1-NO_2	-0,007	-0,224	-0,235	-1,126	0,361	-0,178
SSA-3- NO_2	0,066	-0,329	-0,091	-0,632	-0,502	-0,164
SSA-1/3- NO_2	0,042	-0,266	-0,158	-0,622	-0,384	-0,150
SSA-1-F	0,093	-0,461	0,067	-1,116	0,428	-0,201
SSA-3-F	0,062	-0,359	-0,124	-0,592	-0,141	-0,208
SSA-1/3-F	0,099	-0,467	0,087	-0,765	-0,124	-0,203
SSA-1- NH_2	-0,103	-0,266	0,068	-1,132	0,364	-0,196
SSA-3- NH_2	0,060	-0,399	-0,075	-0,895	0,087	-0,275
SSA-1/3- NH_2	-0,066	-0,401	-0,258	-1,244	0,060	-0,360

Molecular electrostatic potential (ESP) at a point in the space around a molecule givens an indication of the total charge distribution (electron + nuclei) of the molecule and correlates with dipole moments, electronegativity, partial charges and chemical reactivity of molecules. It provides a visual method to understand the relative polarity of the molecules. An electron density isosurface mapped with electrostatic potential surface the size, shape, charge density and site of chemical reactivity of molecules.

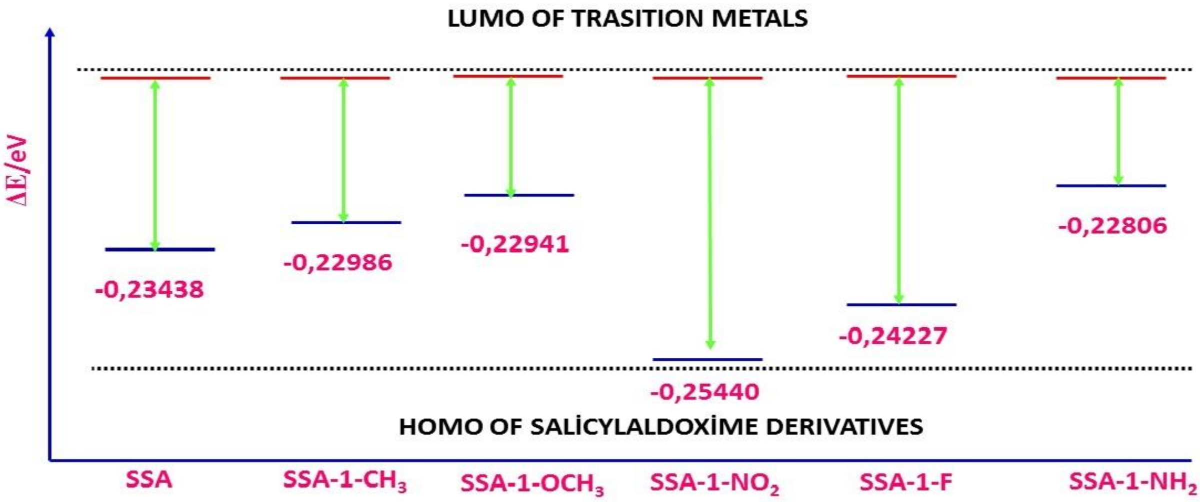

Figure 3. The energy gap for location 1 of Salicylaldoxime and its derivatives.

The different value of the electrostatic potential represented by different colors: red represents the region of the most negative electrostatic potential, blue represent the regions of the most positive electrostatic potential and green represents the region of zero potential. Potential increases in the order red < orange < yellow < green < blue. Such mapped have been plotted for title molecules in 6-311++G** basis set using the computer software gauss view.

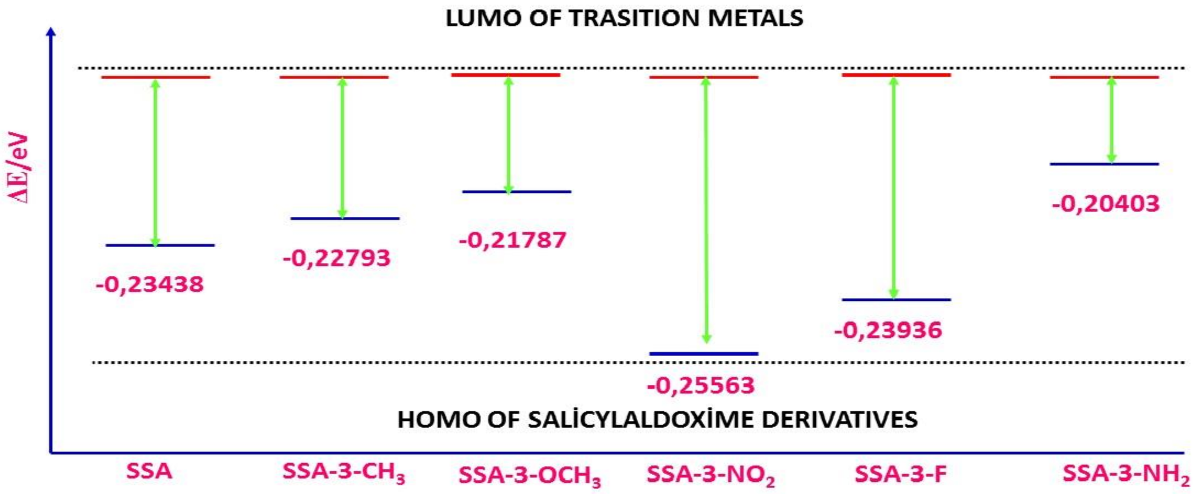

Figure 4. The energy gap for location 3 of Salicylaldoxime and its derivatives.

It may see that, all of the molecules, a region of zero potential envelopes the π-system of the aromatic rings, leaving a more electrophilic region in the plane of hydrogen atoms. The shapes of electrostatic potential at sites close to the polar group in two molecules. The halogen group in molecules is influenced by the stereo structure and the charge density distribution. These sites show region of most negative electrostatic potential and high activity of the halogen groups. In contrast, region close to the other polar atom-oxygen of the aromatic rings show regions of mildly negative and zero potential, respectively [90].

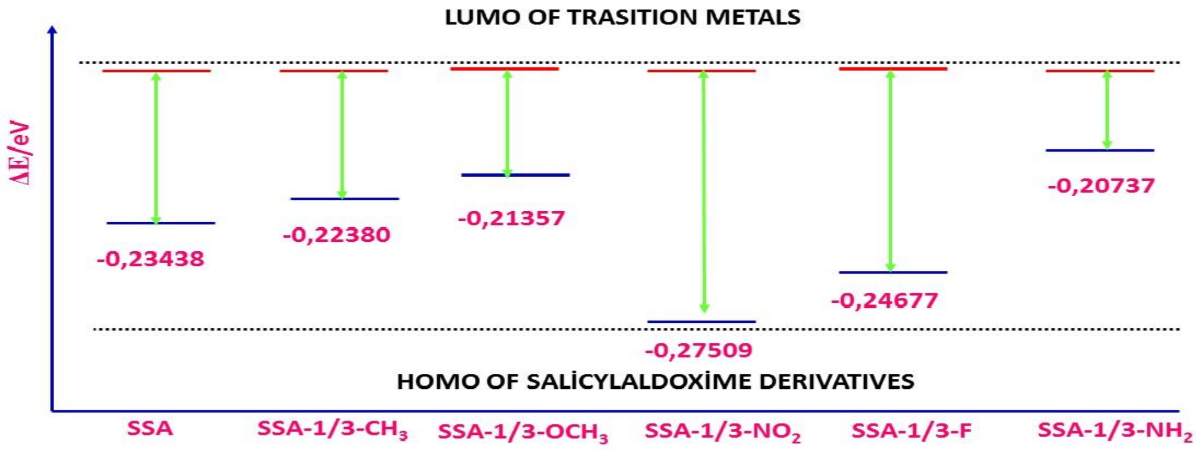

Figure 5. The energy gap for location 1/3 of Salicylaldoxime and its derivatives.

The separation energy, ΔE = (E_{LUMO} – E_{HOMO}) is an important parameter as a function of reactivity of the collector molecule towards the adsorption on metallic surface [66]. The HOMO–LUMO energy gap, ΔE approach, which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems [78]. Fig. 3 summarizes a schematic of diagrams of frontier molecular orbitals for the investigated collectors to their estimated energy gap ΔE. Collector of flotation is generally interpreted by adsorption of collector molecules onto the metal surface. Two modes of adsorption can be envisaged. The physical adsorption requires the interaction of electrically charged metal surface and charged species in the bulk of the solution. Chemisorption mode implies charge sharing or charge transfer from the inhibitor molecule to the vacant orbitals of the metal having low energy. The effect of temperature on the efficacy of quinoxalines and adsorption parameters showed that physisorption phenomenon is more favored [74-76].

Collectors of flotation examined under three major groups. The first group is included to bonded group of the three position of collector of salicylaldoxime. The second group is included to bonded group of the carbon atom of oxime groups. The third and last group of them, including to bonded group in both position.

The HOMO energies (Table 1) of the first group compounds increased in the following order: SSA-1-NO_2< SSA-1-F« SSA< SSA-1-CH_3< SSA-1-OCH_3< SSA-1-NH_2. The HOMO energies (Table 1) of the second group compounds increased in the following order: SSA-3-NO_2« SSA-3-F< SSA< SSA-3-CH_3< SSA-3-OCH_3< SSA-3-NH_2. The HOMO energies (Table 1) of the second group compounds increased in the following order: SSA-1/3-NO_2« SSA-1/3-F< SSA< SSA-1/3-CH_3< SSA-1/3-OCH_3< SSA-1/3-NH_2.

The higher HOMO energy level means that the molecule easily releases the electrons to the unoccupied orbitals of the metal atom, and it has better activity used as collector. Accordingly, based on the normal covalent bond (denominator term), the selectivity of these collectors against transition metals would be followed as: SSA-1/3-NO_2< SSA-3-NO_2< SSA-1-NO_2< SSA-1/3-F< SSA-1-F< SSA-3-F< SSA< SSA-1-CH_3< SSA-1-OCH_3< SSA-1-NH_2< SSA-3-CH_3< SSA-1/3-CH_3< SSA-3-OCH_3< SSA-1/3-OCH_3< SSA-3-NH_2< SSA-1/3-NH_2 and their collecting power for transition metals was followed as: SSA-1/3-NO_2> SSA-3-NO_2> SSA-1-NO_2> SSA-1/3-F> SSA-1-F> SSA-3-F> SSA> SSA-1-CH_3> SSA-1-OCH_3> SSA-1-NH_2> SSA-3-CH_3> SSA-1/3-CH_3> SSA-3-OCH_3> SSA-1/3-OCH_3> SSA-3-NH_2> SSA-1/3-NH_2.

Acknowledge

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