Chemistry Research Journal, 2021, 6(1):49-76

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

A Theoretical Approach to the Study of Some Plant Extracts of *Striga hermonthica* as Eco-Friendly Corrosion Inhibitor for Aluminium Alloy

B. El-yaqub

Department of Chemistry, Faculty of Science, Nigerian Defence Academy Kaduna, Nigeria.
Corresponding author email address: balarabeelyaqub@gmail.com

Abstract Theoretical studies on the performance of corrosion inhibition of some plant extracts of *striga hermonthica* have been carried out using DND basis set and Perdew Wang local correlation density functional theory. The effect of electron donor groups and electron withdrawing groups was also studied. Quantum chemical parameters such as HOMO, LUMO, ionization energy, electron affinity, electronegativity, chemical potential, global hardness and global softness were calculated and interpreted. The Fukui indices indicated sites for nucleophilic and electrophilic attack.

Keywords Aluminium Alloy, corrosion Inhibition, HOMO, LUMO, DFT, quantum chemical calculations

Introduction

Corrosion is an electrochemical process which affects less noble metals and alloys. It generally destroys structures when metals or alloys interact with a aggressive environment such as hydrochloric acid or sodium hydroxide [1]. Corrosion may lead to large economic losses since it has no prevention but can be slowed down. Therefore, a lot of efforts have been geared towards producing high efficiency corrosion inhibitors. Moreover, searching for less toxic and more eco-friendly corrosion inhibitors becomes very paramount due to the increased awareness of the importance of the green chemistry applications. A variety of organic compounds has been used as green corrosion inhibitors [2-4]. The electronegativity nature of some functional groups such as heteroatomic oxygen, sulfur, nitrogen and π-electron are some of the conditions for inhibitors to have high efficiency [5-7]. This functional groups help molecules to adsorb on the surfaces of metals to inhibit corrosion by chemical adsorption or physical adsorption [8-9]. The uniform films of organic molecules formed on the surface of the meals prevent the metals from interacting with the corrosive medium [10].

The active phytochemicals in plants that are effective for corrosion inhibition can be regarded as those with heteroatom in their aromatic or long chain, possession of π-electrons or suitable groups may also facilitate the transfer of charge from the inhibitor molecules to the charge metal surface (physical adsorption) or the transfer of electron from the inhibitor molecule to vacant d-orbital of the metal (chemical adsorption). Therefore in order to identify the active constituent of plant extract involved in corrosion inhibition, more knowledge of the chemical structures and phytochemicals is required.

Experimental

The electronic structure of compounds from the extracts, including the distribution of frontier molecular orbital E_{HOMO} and E_{LUMO}, Fukui indices were assessed with a view to establishing the active sites as well as local reactivity

of the molecule. The simulation were performed by means of density functional theory (DFT) electronic program $Dmol^3$ using Mulliken and Hirshfeld population analysis of the electronic structures and energetic of the molecules using DFT. Electronic parameters for the simulation include restricted spin polarization using the DND basis set and perdewwang local correlation density functional theory. Local reactivity of the studied compounds was analyzed by means of the Fukui indices (FI) to assess site of nucleophilic and electrophilic attack [11-13]. The HOMO energy is related to the ionization potential (IE) whereas the LUMO energy is linked to the electron affinity (EA), as follows:

$$IE = -E_{HOMO} \quad (1)$$

$$EA = -E_{LUMO} \quad (2)$$

Then, the electronegativity (χ), the chemical potential (μ) and the global hardness (η) were evaluated, based on the finite difference approximation, as linear combinations of the calculated IE and EA [14]:

$$\chi = -\mu = IE + EA/2 \quad (3)$$

$$\eta = IE - EA/2 \quad (4)$$

The softness (σ) is the inverse of the global hardness [16].

$$\sigma = 1/\eta \quad (5)$$

The chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [15]. The global electrophilicity (ω) index was introduced by [16] as a measure of energy lowering due to maximal electron flow between donor and acceptor and is given by

$$\omega = \mu^2/2.\ \sigma \quad (6)$$

The fraction of transferred electrons (ΔN), evaluating the electronic flow in a reaction of two systems with different electronegativities, in particular case; a metallic surface and an inhibitor molecule was calculated according to Pearson theory [17] as:

$$\Delta N = \chi_{Fe} + \chi_{inh}/2(\eta_{Fe} + \eta_{inh}) \quad (7)$$

Where χFe and χinh denote the absolute electronegativity of iron and inhibitor molecule respectively, ηFe and ηinh denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χFe= 7.0eV and ηFe= 0.0eV for the computation of number of transferred electrons [14]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [18].

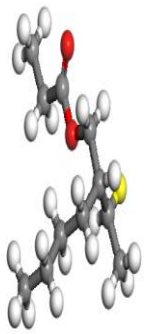
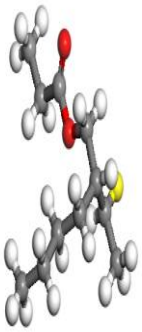
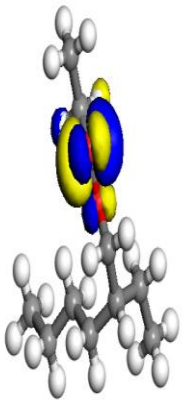
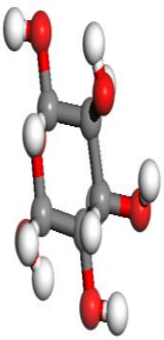
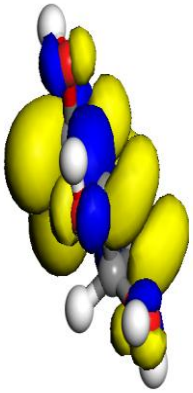
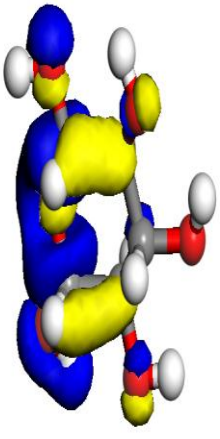
Result and discussion

Quantum chemical calculations gives an insight to the molecular level, electron distribution of the different organic constituents present in the plant extracts as well as to study the nature of their interactions with the Aluminium alloy surface. Geometric optimization of the compounds from the extracts was established including the distribution of frontier molecular orbitals, with a view to establish the active sites as well as local reactivity of the molecules. The simulations were performed by means of density functional theory (DFT) electronic structure program $Dmol^3$ available in material studio 8.0 (Accrelys Inc., San Diego, CA, USA). [19-20]. Electronic structures parameters for the simulation include spin unrestricted polarization using DND basis set and the Perdew-Wang local-correlation density functional theory. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular (LUMO) of various selected constituent in the plant extract with a view of establishing their inhibitive capacity respectively. The corresponding quantum chemical parameters are presented in table 1. High values of E_{HOMO} indicate the disposition of the molecule to donate electrons to an appropriate acceptor with vacant molecular orbitals, whereas low values of ΔE would enhance inhibition efficiencies because the energy to remove an electron from the last occupied orbital will be minimized [21]. This indicates that the compounds effect is the same. Values of IE and EA were calculated using the values of E_{HOMO} and E_{LUMO} respectively. The fraction of electrons transferred from inhibitor to the aluminium Alloy surface (ΔN) was calculated. According to other reports [22], values of ΔN showed inhibition effect resulted from electrons donation. The local reactivity of each molecule was analyzed by means of Fukui indices (FI) to assess reactive regions in terms of nucleophilic, electrophilic and radical attack. The regions of the highest electron densities are generally the potential sites for electrophiles attack [23]. The

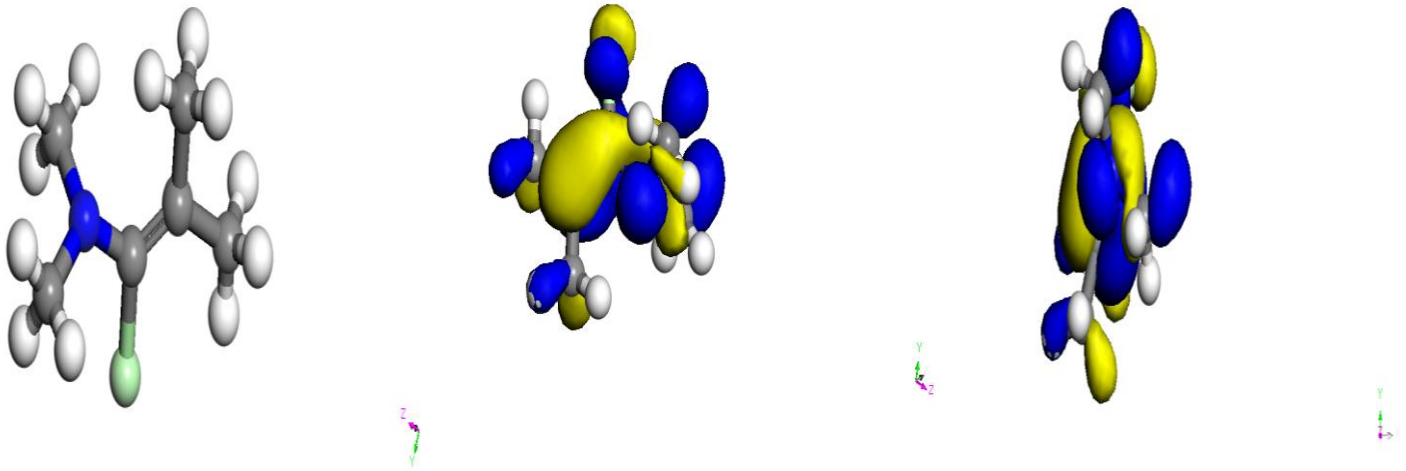
use of Mulliken and Hirshfeld population analysis to prove adsorption center of inhibitors has earlier been reported [24].

Table 1: Active constituents of *striga hermonthica*

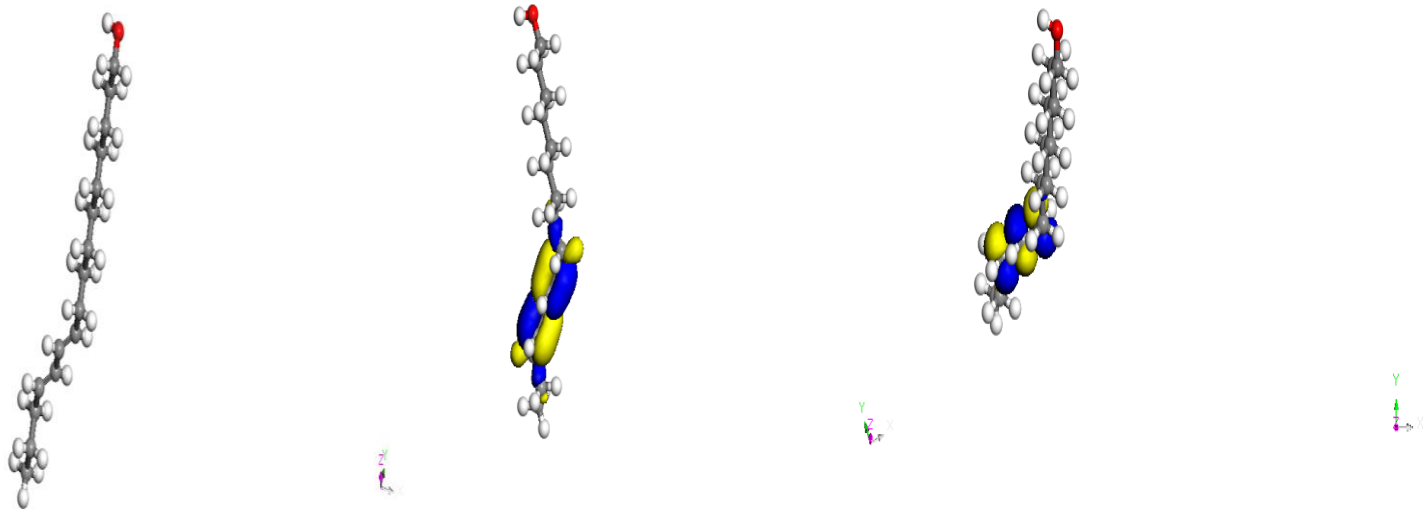
SH1	1-ethyl-2-heptyl-2-propenoic acid
SH2	D-glucopyranose
SH3	2-(2-propenyl)-chloro-methyl-methoxy-amine
SH4	9,12,15-octadecatrienoic acid
SH5	E,E-10,12-hexadecadien-1-ol
SH6	9,12-octadecadienyl chloride
SH7	2-(2-methylene cyclopropyl)propyl ester
SH8	3-docosenamide
SH9	8-methyl-N-vanillyl-trans-nonenamide
SH10	4-methoxy-4-methylbiphenyl

Comp	Optimized	HOMO	LUMO
SH1			
SH2			

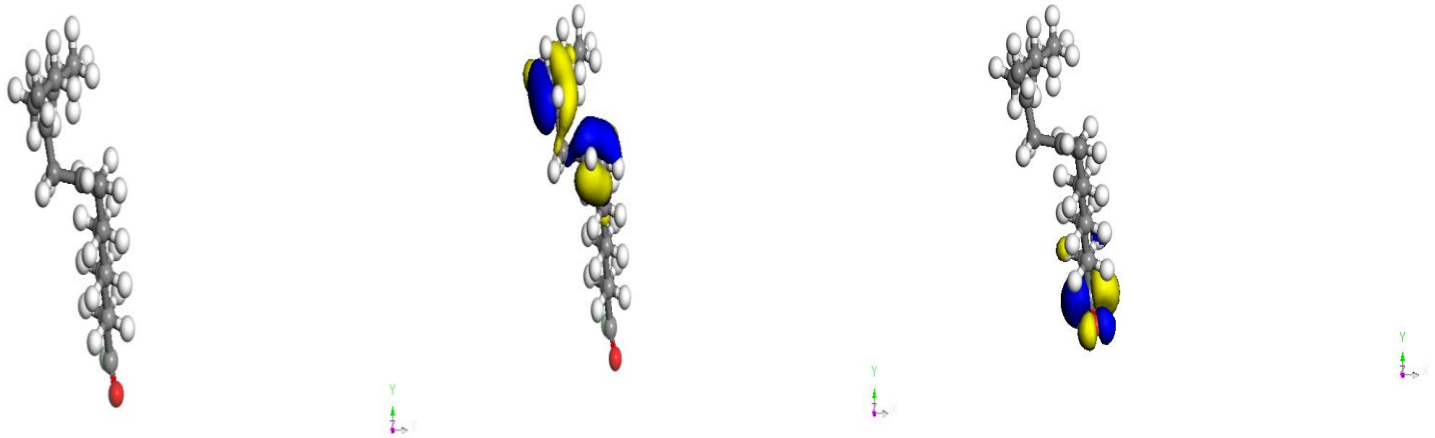
SH3



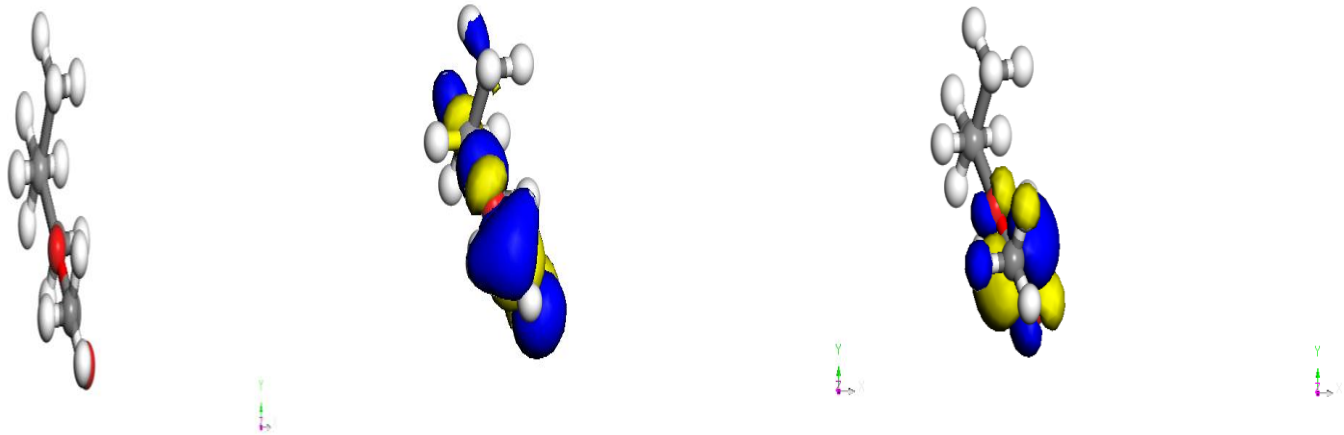
SH4



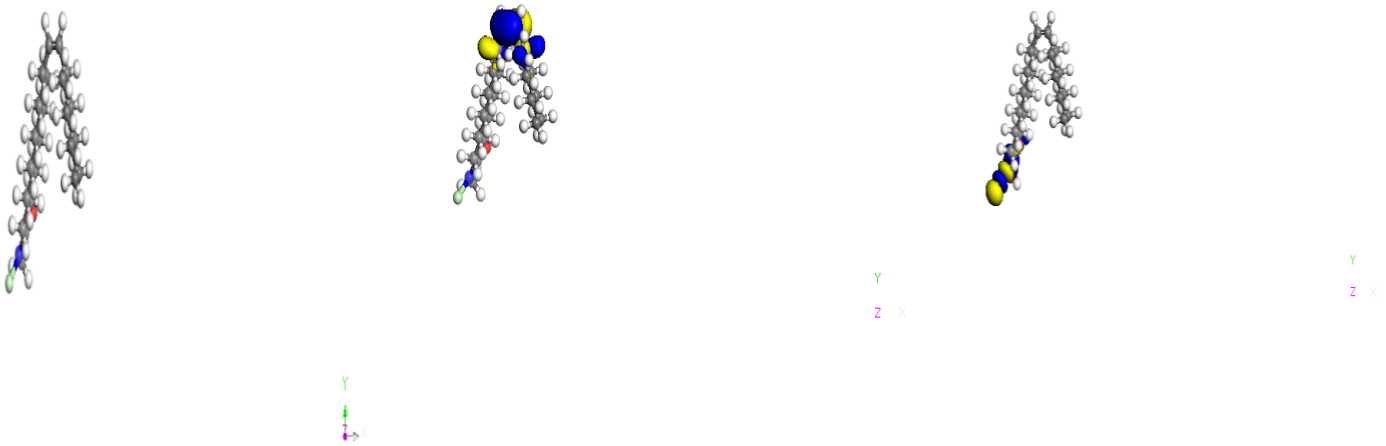
SH5



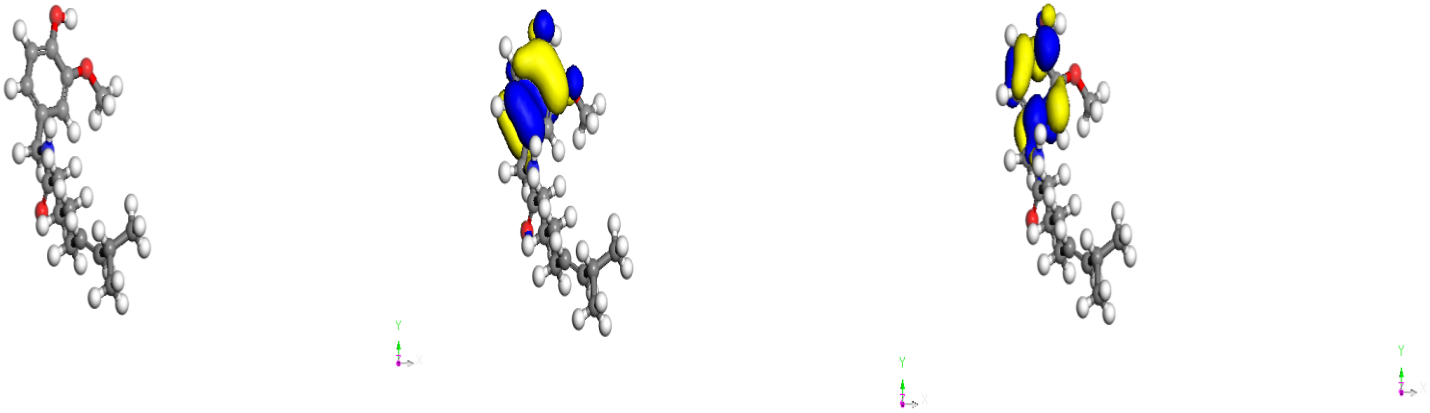
SH6



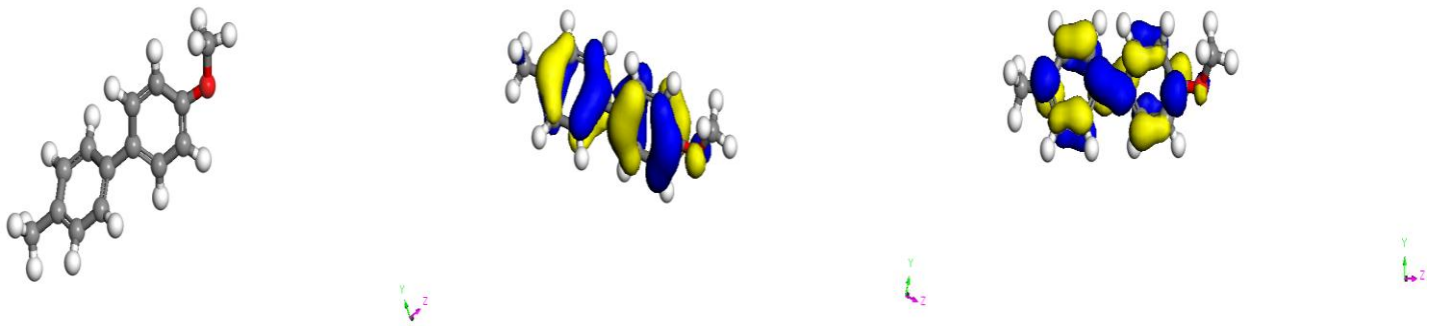
SH7



SH8



SH9



SH10

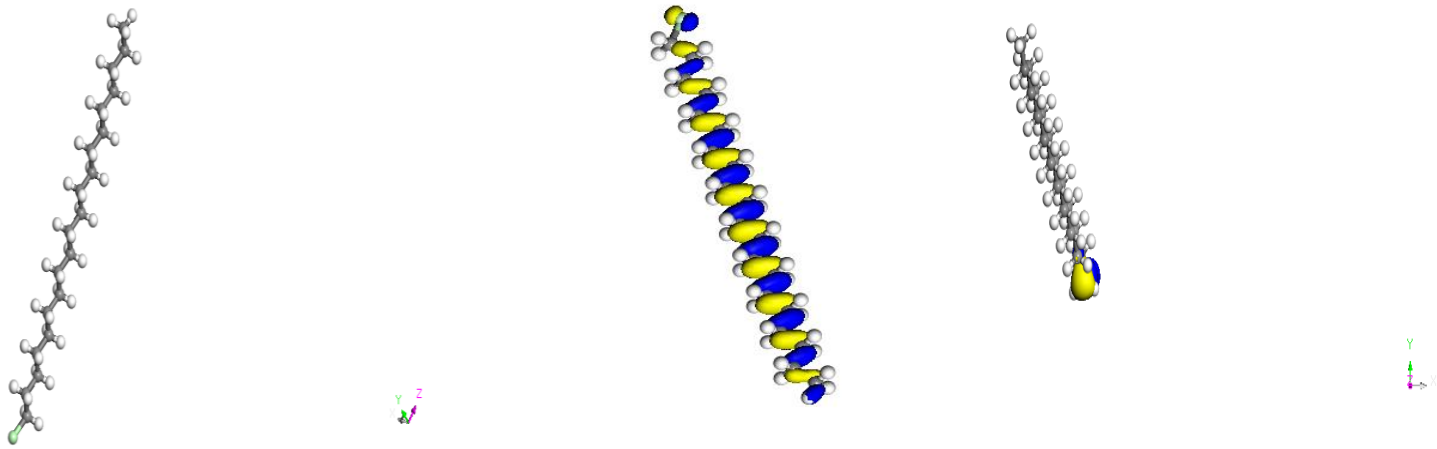


Figure 1: Optimized structure, HOMO and LUMO for some constituent of striga hermonthica

Table 2: Computed quantum chemical parameters of the studied compound of *striga hermonthica*

S/no	Molecule	E_{homo}	E_{lumo}	ΔE	X	μ	η	σ	ω	ΔN	EA	IE
1	SH1	-11.0440	1.2210	12.2650	4.9115	-4.9115	6.1325	0.1631	1.9672	0.1703	-1.2210	11.0440
2	SH2	-10.9470	-1.6250	9.3220	6.2860	-6.2860	4.6610	0.2145	4.2379	0.0766	1.6250	10.9470
3	SH3	-8.6910	0.8150	9.5060	3.9380	-3.9380	4.7530	0.2104	1.6314	0.3220	-0.8150	8.6910
4	SH4	-9.6270	1.0240	10.6510	4.3015	-4.3015	5.3255	0.1877	1.7365	0.2533	-1.0240	9.6270
5	SH5	-8.8870	0.3620	9.2490	4.2625	-4.2625	4.6245	0.2162	1.9641	0.2959	-0.3620	8.8870
6	SH6	-9.6800	0.2480	9.9280	4.7160	-4.7160	4.9640	0.2015	2.2407	0.2300	-0.2480	9.6800
7	SH7	-11.3000	1.1710	12.4710	5.0645	-5.0645	6.2355	0.1604	2.0583	0.1552	-1.1710	11.3000
8	SH8	-9.6640	-0.6130	9.0510	5.1385	-5.1385	4.5255	0.2209	2.9163	0.2057	0.6130	9.6640
9	SH9	-8.9630	0.1140	9.0770	4.4245	-4.4245	4.5385	0.2203	2.1563	0.2837	-0.1140	8.9630
10	SH10	-8.6850	0.0900	8.7750	4.2975	-4.2975	4.3875	0.2279	2.1045	0.3079	-0.0900	8.6850

Table 3: Fukui function calculated with $Dmol^3$ for some compounds of *striga hermonthica*

Molecule: SH1

Fukui Indices for Electrophilic Attack (Fukui(-))

atom MullikenHirshfeld

C (1)	-0.005	0.004
C (2)	-0.007	0.005
C (3)	-0.011	-0.000
C (4)	-0.010	0.002
C (5)	-0.018	0.007
C (6)	-0.075	0.013
O (7)	0.095	0.102
H (8)	0.044	0.022
C (9)	-0.017	0.001
C (10)	-0.009	0.009
C (11)	0.090	0.096
O (12)	0.370	0.356
C (13)	-0.007	0.053
C (14)	-0.051	0.016
H (15)	0.011	0.005
H (16)	0.026	0.013
H (17)	-0.005	-0.002
H (18)	0.025	0.012
H (19)	0.013	0.006
H (20)	0.017	0.004
H (21)	-0.031	-0.009
H (22)	0.037	0.019
H (23)	0.016	0.006
H (24)	0.050	0.022
H (25)	0.046	0.021
H (26)	0.015	0.004
H (27)	-0.000	0.000
H (28)	0.027	0.015
H (29)	0.017	0.009
H (30)	0.022	0.011
H (31)	0.087	0.049
H (32)	0.088	0.049
H (33)	0.073	0.040
H (34)	0.038	0.019
H (35)	0.038	0.019

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	-0.005	0.004
C (2)	-0.006	0.005
C (3)	-0.009	-0.002
C (4)	-0.011	0.001
C (5)	-0.016	0.004
C (6)	-0.068	0.014
O (7)	0.090	0.096
H (8)	0.042	0.020
C (9)	-0.017	-0.000
C (10)	-0.008	0.009
C (11)	0.242	0.225
O (12)	0.216	0.222
C (13)	-0.064	0.043
C (14)	-0.031	0.016
H (15)	0.010	0.005
H (16)	0.026	0.013
H (17)	-0.008	-0.003
H (18)	0.024	0.012

H (19)	0.013	0.006
H (20)	0.016	0.004
H (21)	-0.041	-0.012
H (22)	0.036	0.017
H (23)	0.015	0.006
H (24)	0.056	0.026
H (25)	0.053	0.025
H (26)	0.013	0.003
H (27)	-0.004	-0.001
H (28)	0.026	0.014
H (29)	0.016	0.009
H (30)	0.022	0.012
H (31)	0.112	0.067
H (32)	0.114	0.067
H (33)	0.068	0.037
H (34)	0.038	0.020
H (35)	0.038	0.020

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
C (1)	-0.005	0.004
C (2)	-0.007	0.005
C (3)	-0.010	-0.001
C (4)	-0.011	0.002
C (5)	-0.017	0.005
C (6)	-0.072	0.013
O (7)	0.093	0.099
H (8)	0.043	0.021
C (9)	-0.017	0.000
C (10)	-0.008	0.009
C (11)	0.166	0.160
O (12)	0.293	0.289
C (13)	-0.035	0.048
C (14)	-0.041	0.016
H (15)	0.011	0.005
H (16)	0.026	0.013
H (17)	-0.007	-0.002
H (18)	0.025	0.012
H (19)	0.013	0.006
H (20)	0.017	0.004
H (21)	-0.036	-0.011
H (22)	0.036	0.018
H (23)	0.015	0.006
H (24)	0.053	0.024
H (25)	0.050	0.023
H (26)	0.014	0.004
H (27)	-0.002	-0.001
H (28)	0.026	0.014
H (29)	0.016	0.009
H (30)	0.022	0.011
H (31)	0.099	0.058
H (32)	0.101	0.058
H (33)	0.071	0.038
H (34)	0.038	0.019
H (35)	0.038	0.019

Molecule: SH2
Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	0.008	0.019
C (2)	-0.002	0.029
C (3)	0.026	0.023
C (4)	-0.004	0.030
O (5)	0.012	0.034
C (6)	0.004	0.025
O (7)	0.034	0.040
O (8)	-0.006	0.064
O (9)	-0.047	0.080
O (10)	-0.056	0.073
O (11)	-0.011	0.039
H (12)	0.054	0.027
H (13)	0.051	0.027
H (14)	0.047	0.026
H (15)	0.056	0.027
H (16)	0.047	0.024
H (17)	0.027	0.020
H (18)	0.159	0.081
H (19)	0.261	0.130
H (20)	0.247	0.125
H (21)	0.093	0.058

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
C (1)	-0.012	0.028
C (2)	-0.010	0.022
C (3)	-0.004	0.027
C (4)	-0.008	0.027
O (5)	0.082	0.084
C (6)	-0.003	0.024
O (7)	0.084	0.082
O (8)	0.016	0.050
O (9)	0.028	0.089
O (10)	0.010	0.073
O (11)	0.021	0.046
H (12)	0.081	0.046
H (13)	0.052	0.027
H (14)	0.069	0.038
H (15)	0.057	0.027
H (16)	0.051	0.024
H (17)	0.036	0.030
H (18)	0.095	0.053
H (19)	0.149	0.083
H (20)	0.141	0.078
H (21)	0.064	0.044

Fukui Indices for Electrophilic Attack (Fukui(-))

atom	Mulliken	Hirshfeld
C (1)	-0.033	0.038
C (2)	-0.017	0.015
C (3)	-0.033	0.032
C (4)	-0.012	0.024
O (5)	0.153	0.134
C (6)	-0.011	0.022

O (7) 0.134 0.123
O (8) 0.037 0.036
O (9) 0.104 0.098
O (10) 0.076 0.072
O (11) 0.054 0.052
H (12) 0.108 0.065
H (13) 0.054 0.026
H (14) 0.091 0.050
H (15) 0.059 0.027
H (16) 0.055 0.023
H (17) 0.045 0.041
H (18) 0.031 0.026
H (19) 0.037 0.035
H (20) 0.035 0.030
H (21) 0.035 0.029

Molecule: SH3

Fukui Indices for Electrophilic Attack (Fukui(-))

atom	Mulliken	Hirshfeld
C (1)	-0.020	0.029
C (2)	0.069	0.100
C (3)	0.016	0.050
Cl(4)	0.175	0.149
N (5)	0.114	0.139
C (6)	-0.043	0.037
C (7)	-0.041	0.034
C (8)	-0.027	0.024
H (9)	0.042	0.022
H (10)	0.063	0.037
H (11)	0.067	0.041
H (12)	0.092	0.058
H (13)	0.070	0.038
H (14)	0.051	0.028
H (15)	0.083	0.050
H (16)	0.070	0.040
H (17)	0.056	0.030
H (18)	0.065	0.037
H (19)	0.027	0.017
H (20)	0.070	0.040

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	-0.031	0.036
C (2)	0.106	0.133
C (3)	0.122	0.131
Cl(4)	0.183	0.166
N (5)	-0.012	0.027
C (6)	-0.031	0.028
C (7)	-0.035	0.021
C (8)	-0.033	0.034
H (9)	0.053	0.027
H (10)	0.086	0.055
H (11)	0.082	0.052
H (12)	0.061	0.032
H (13)	0.065	0.035
H (14)	0.023	0.015

H (15) 0.050 0.026
H (16) 0.060 0.033
H (17) 0.035 0.019
H (18) 0.084 0.055
H (19) 0.053 0.026
H (20) 0.080 0.050
Fukui Indices for Radical Attack (Fukui(0))
atom MullikenHirshfeld
C (1) -0.025 0.032
C (2) 0.087 0.116
C (3) 0.069 0.090
Cl(4) 0.179 0.158
N (5) 0.051 0.083
C (6) -0.037 0.032
C (7) -0.038 0.027
C (8) -0.030 0.029
H (9) 0.047 0.025
H (10) 0.075 0.046
H (11) 0.075 0.046
H (12) 0.076 0.045
H (13) 0.068 0.036
H (14) 0.037 0.021
H (15) 0.067 0.038
H (16) 0.065 0.037
H (17) 0.046 0.025
H (18) 0.075 0.046
H (19) 0.040 0.022
H (20) 0.075 0.045
Molecule: SH5
Fukui Indices for Electrophilic Attack (Fukui(-))
atom MullikenHirshfeld
C (1) -0.012 0.014
C (2) -0.025 0.015
C (3) -0.034 0.022
C (4) 0.105 0.139
C (5) 0.034 0.086
C (6) 0.034 0.087
C (7) 0.106 0.139
C (8) -0.032 0.022
C (9) -0.021 0.014
C (10) -0.010 0.008
C (11) -0.009 0.004
C (12) -0.006 0.004
C (13) -0.004 0.002
C (14) -0.003 0.002
C (15) -0.003 0.001
C (16) -0.000 0.002
O (17) 0.006 0.006
H (18) 0.086 0.047
H (19) 0.081 0.038
H (20) 0.081 0.038
H (21) 0.086 0.047
H (22) 0.038 0.022
H (23) 0.026 0.014
H (24) 0.023 0.012

H (25)	0.027	0.012
H (26)	0.034	0.014
H (27)	0.044	0.020
H (28)	0.066	0.038
H (29)	0.065	0.038
H (30)	0.044	0.020
H (31)	0.031	0.013
H (32)	0.023	0.010
H (33)	0.021	0.010
H (34)	0.018	0.008
H (35)	0.013	0.005
H (36)	0.010	0.004
H (37)	0.010	0.004
H (38)	0.009	0.004
H (39)	0.006	0.003
H (40)	0.005	0.002
H (41)	0.005	0.002
H (42)	0.005	0.002
H (43)	0.004	0.002
H (44)	0.003	0.001
H (45)	0.004	0.002
H (46)	0.004	0.002
H (47)	0.003	0.002

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	-0.011	0.014
C (2)	-0.031	0.013
C (3)	-0.037	0.022
C (4)	0.117	0.139
C (5)	0.039	0.087
C (6)	0.038	0.086
C (7)	0.119	0.140
C (8)	-0.035	0.022
C (9)	-0.026	0.011
C (10)	-0.010	0.008
C (11)	-0.008	0.003
C (12)	-0.006	0.003
C (13)	-0.004	0.002
C (14)	-0.003	0.001
C (15)	-0.003	0.001
C (16)	-0.000	0.002
O (17)	0.005	0.005
H (18)	0.087	0.052
H (19)	0.081	0.040
H (20)	0.081	0.040
H (21)	0.087	0.052
H (22)	0.038	0.021
H (23)	0.026	0.014
H (24)	0.023	0.012
H (25)	0.026	0.011
H (26)	0.032	0.013
H (27)	0.045	0.021
H (28)	0.063	0.038
H (29)	0.062	0.037

H (30)	0.044	0.020
H (31)	0.029	0.012
H (32)	0.022	0.010
H (33)	0.021	0.010
H (34)	0.018	0.008
H (35)	0.012	0.005
H (36)	0.010	0.004
H (37)	0.009	0.004
H (38)	0.008	0.003
H (39)	0.006	0.002
H (40)	0.005	0.002
H (41)	0.005	0.002
H (42)	0.004	0.002
H (43)	0.004	0.002
H (44)	0.003	0.001
H (45)	0.004	0.002
H (46)	0.004	0.002
H (47)	0.002	0.002

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
C (1)	-0.012	0.014
C (2)	-0.028	0.014
C (3)	-0.036	0.022
C (4)	0.111	0.139
C (5)	0.036	0.086
C (6)	0.036	0.086
C (7)	0.113	0.140
C (8)	-0.034	0.022
C (9)	-0.023	0.012
C (10)	-0.010	0.008
C (11)	-0.008	0.004
C (12)	-0.006	0.003
C (13)	-0.004	0.002
C (14)	-0.003	0.002
C (15)	-0.003	0.001
C (16)	-0.000	0.002
O (17)	0.006	0.006
H (18)	0.086	0.049
H (19)	0.081	0.039
H (20)	0.081	0.039
H (21)	0.086	0.049
H (22)	0.038	0.021
H (23)	0.026	0.014
H (24)	0.023	0.012
H (25)	0.026	0.012
H (26)	0.033	0.014
H (27)	0.045	0.020
H (28)	0.064	0.038
H (29)	0.063	0.037
H (30)	0.044	0.020
H (31)	0.030	0.012
H (32)	0.023	0.010
H (33)	0.021	0.010
H (34)	0.018	0.008
H (35)	0.012	0.005

H (36)	0.010	0.004
H (37)	0.010	0.004
H (38)	0.008	0.004
H (39)	0.006	0.003
H (40)	0.005	0.002
H (41)	0.005	0.002
H (42)	0.004	0.002
H (43)	0.004	0.002
H (44)	0.003	0.001
H (45)	0.004	0.002
H (46)	0.004	0.002
H (47)	0.002	0.002

Molecule: SH6

Fukui Indices for Electrophilic Attack (Fukui(-))

atom	Mulliken	Hirshfeld
Cl(1)	0.018	0.015
C (2)	0.000	0.001
C (3)	-0.002	0.001
C (4)	-0.005	0.002
C (5)	-0.005	0.003
C (6)	-0.008	0.004
C (7)	-0.008	0.006
C (8)	-0.015	0.012
C (9)	-0.025	0.014
C (10)	0.079	0.110
C (11)	0.034	0.090
C (12)	-0.024	0.020
C (13)	0.048	0.107
C (14)	0.089	0.126
C (15)	-0.028	0.018
C (16)	-0.016	0.013
C (17)	-0.010	0.007
C (18)	-0.010	0.005
C (19)	-0.007	0.007
O (20)	0.004	0.004
H (21)	0.004	0.001
H (22)	0.002	0.000
H (23)	0.008	0.003
H (24)	0.006	0.002
H (25)	0.008	0.003
H (26)	0.004	0.002
H (27)	0.015	0.006
H (28)	0.011	0.005
H (29)	0.017	0.007
H (30)	0.007	0.003
H (31)	0.033	0.014
H (32)	0.020	0.009
H (33)	0.050	0.027
H (34)	0.011	0.005
H (35)	0.085	0.047
H (36)	0.080	0.040
H (37)	0.047	0.019
H (38)	0.066	0.033
H (39)	0.086	0.043

H (40)	0.090	0.049
H (41)	0.032	0.014
H (42)	0.063	0.034
H (43)	0.001	0.002
H (44)	0.038	0.016
H (45)	0.010	0.004
H (46)	0.028	0.012
H (47)	0.004	0.002
H (48)	0.020	0.009
H (49)	0.007	0.004
H (50)	0.024	0.013
H (51)	0.017	0.009

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
Cl(1)	0.280	0.258
C (2)	0.215	0.228
C (3)	-0.063	0.037
C (4)	-0.026	0.004
C (5)	-0.018	0.007
C (6)	-0.011	0.004
C (7)	-0.008	0.003
C (8)	-0.005	0.002
C (9)	-0.003	0.001
C (10)	-0.008	-0.002
C (11)	0.006	0.007
C (12)	-0.002	0.001
C (13)	-0.002	0.002
C (14)	0.001	0.003
C (15)	-0.001	0.000
C (16)	-0.001	0.001
C (17)	0.001	-0.001
C (18)	0.000	0.000
C (19)	0.002	-0.001
O (20)	0.232	0.237
H (21)	0.098	0.058
H (22)	0.098	0.058
H (23)	0.031	0.013
H (24)	0.031	0.013
H (25)	0.024	0.011
H (26)	0.024	0.011
H (27)	0.015	0.006
H (28)	0.015	0.006
H (29)	0.011	0.004
H (30)	0.011	0.004
H (31)	0.006	0.003
H (32)	0.006	0.003
H (33)	0.005	0.002
H (34)	0.005	0.001
H (35)	0.005	0.002
H (36)	0.012	0.006
H (37)	-0.007	-0.002
H (38)	0.007	0.003
H (39)	0.009	0.004
H (40)	0.009	0.004
H (41)	-0.007	-0.003

H (42)	0.006	0.002
H (43)	-0.002	-0.001
H (44)	0.009	0.004
H (45)	-0.014	-0.005
H (46)	0.006	0.002
H (47)	-0.004	-0.001
H (48)	0.011	0.005
H (49)	-0.020	-0.008
H (50)	0.004	0.001
H (51)	0.006	0.002

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
Cl(1)	0.149	0.137
C (2)	0.108	0.114
C (3)	-0.033	0.019
C (4)	-0.016	0.003
C (5)	-0.011	0.005
C (6)	-0.009	0.004
C (7)	-0.008	0.005
C (8)	-0.010	0.007
C (9)	-0.014	0.007
C (10)	0.036	0.054
C (11)	0.020	0.048
C (12)	-0.013	0.010
C (13)	0.023	0.054
C (14)	0.045	0.064
C (15)	-0.014	0.009
C (16)	-0.009	0.007
C (17)	-0.004	0.003
C (18)	-0.005	0.003
C (19)	-0.002	0.003
O (20)	0.118	0.120
H (21)	0.051	0.030
H (22)	0.050	0.029
H (23)	0.019	0.008
H (24)	0.018	0.007
H (25)	0.016	0.007
H (26)	0.014	0.006
H (27)	0.015	0.006
H (28)	0.013	0.005
H (29)	0.014	0.006
H (30)	0.009	0.004
H (31)	0.020	0.008
H (32)	0.013	0.006
H (33)	0.028	0.014
H (34)	0.008	0.003
H (35)	0.045	0.024
H (36)	0.046	0.023
H (37)	0.020	0.008
H (38)	0.036	0.018
H (39)	0.047	0.023
H (40)	0.050	0.027

H (41)	0.013	0.006
H (42)	0.034	0.018
H (43)	-0.000	0.001
H (44)	0.024	0.010
H (45)	-0.002	-0.001
H (46)	0.017	0.007
H (47)	-0.000	0.000
H (48)	0.015	0.007
H (49)	-0.007	-0.002
H (50)	0.014	0.007
H (51)	0.012	0.005

Molecule: SH7

Fukui Indices for Electrophilic Attack (Fukui(-))

atom	Mulliken	Hirshfeld
C (1)	-0.013	0.012
C (2)	-0.026	0.007
C (3)	-0.015	0.006
C (4)	-0.077	0.013
O (5)	0.100	0.109
C (6)	0.093	0.105
C (7)	-0.005	0.067
O (8)	0.396	0.386
H (9)	0.022	0.011
H (10)	0.041	0.023
H (11)	0.021	0.011
H (12)	0.034	0.014
H (13)	0.022	0.010
H (14)	-0.000	0.002
H (15)	0.046	0.024
H (16)	0.048	0.022
H (17)	0.051	0.023
H (18)	0.069	0.041
H (19)	0.097	0.058
H (20)	0.097	0.058

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	-0.014	0.011
C (2)	-0.024	0.004
C (3)	-0.015	0.005
C (4)	-0.068	0.015
O (5)	0.096	0.103
C (6)	0.236	0.230
C (7)	-0.045	0.059
O (8)	0.229	0.236
H (9)	0.022	0.011
H (10)	0.040	0.022
H (11)	0.021	0.011
H (12)	0.031	0.012
H (13)	0.022	0.010
H (14)	-0.004	0.001
H (15)	0.047	0.024
H (16)	0.055	0.026
H (17)	0.057	0.027
H (18)	0.082	0.043
H (19)	0.116	0.075

H (20) 0.117 0.076
Fukui Indices for Radical Attack (Fukui(0))
atom Mulliken Hirshfeld
C (1) -0.013 0.011
C (2) -0.025 0.006
C (3) -0.015 0.006
C (4) -0.073 0.014
O (5) 0.098 0.106
C (6) 0.165 0.168
C (7) -0.025 0.063
O (8) 0.312 0.311
H (9) 0.022 0.011
H (10) 0.041 0.022
H (11) 0.021 0.011
H (12) 0.032 0.013
H (13) 0.022 0.010
H (14) -0.002 0.001
H (15) 0.046 0.024
H (16) 0.051 0.024
H (17) 0.054 0.025
H (18) 0.075 0.042
H (19) 0.106 0.067
H (20) 0.107 0.060
Molecule: SH8
Fukui Indices for Electrophilic Attack (Fukui(-))
atom Mulliken Hirshfeld
C (1) -0.007 0.008
N (2) 0.042 0.025
C (3) 0.009 0.011
C (4) -0.004 0.003
C (5) -0.006 0.002
C (6) -0.004 0.002
C (7) -0.004 0.002
C (8) -0.005 0.003
C (9) -0.006 0.004
C (10) -0.007 0.005
C (11) -0.011 0.007
C (12) -0.011 0.011
C (13) -0.024 0.018
C (14) -0.030 0.022
C (15) 0.072 0.144
C (16) 0.074 0.145
H (17) 0.094 0.051
C (18) -0.030 0.022
C (19) -0.024 0.018
C (20) -0.011 0.010
C (21) -0.010 0.006
C (22) -0.007 0.005
C (23) -0.006 0.003
C (24) -0.005 0.003
C (25) -0.004 0.004
H (26) 0.093 0.051
Cl(27) 0.066 0.048
O (28) 0.056 0.035

H (29)	0.020	0.011
H (30)	0.018	0.010
H (31)	0.012	0.007
H (32)	0.009	0.004
H (33)	0.010	0.005
H (34)	0.007	0.003
H (35)	0.007	0.003
H (36)	0.006	0.002
H (37)	0.006	0.003
H (38)	0.006	0.002
H (39)	0.006	0.003
H (40)	0.007	0.003
H (41)	0.007	0.003
H (42)	0.008	0.003
H (43)	0.009	0.004
H (44)	0.011	0.005
H (45)	0.012	0.005
H (46)	0.014	0.006
H (47)	0.016	0.007
H (48)	0.020	0.009
H (49)	0.024	0.011
H (50)	0.026	0.012
H (51)	0.035	0.015
H (52)	0.043	0.019
H (53)	0.062	0.035
H (54)	0.062	0.035
H (55)	0.042	0.018
H (56)	0.035	0.015
H (57)	0.026	0.011
H (58)	0.024	0.011
H (59)	0.019	0.008
H (60)	0.016	0.007
H (61)	0.013	0.005
H (62)	0.012	0.005
H (63)	0.010	0.004
H (64)	0.008	0.004
H (65)	0.007	0.003
H (66)	0.007	0.003
H (67)	0.006	0.003
H (68)	0.012	0.007
H (69)	0.005	0.003
H (70)	0.006	0.003

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	-0.034	0.036
N (2)	0.025	0.108
C (3)	0.052	0.046
C (4)	-0.039	0.006
C (5)	-0.015	0.007
C (6)	-0.011	0.004
C (7)	-0.008	0.003
C (8)	-0.005	0.002
C (9)	-0.004	0.002
C (10)	-0.003	0.001
C (11)	-0.002	0.001

C (12)	-0.002	0.001
C (13)	-0.001	0.000
C (14)	-0.000	0.000
C (15)	-0.003	-0.001
C (16)	0.003	0.003
H (17)	0.005	0.002
C (18)	-0.001	0.000
C (19)	-0.000	0.000
C (20)	0.000	-0.000
C (21)	-0.000	0.000
C (22)	-0.000	-0.000
C (23)	-0.000	0.000
C (24)	-0.000	0.000
C (25)	-0.000	0.000
H (26)	0.002	0.000
Cl(27)	0.507	0.448
O (28)	0.122	0.122
H (29)	0.064	0.032
H (30)	0.066	0.036
H (31)	0.077	0.048
H (32)	0.029	0.014
H (33)	0.029	0.013
H (34)	0.024	0.011
H (35)	0.025	0.011
H (36)	0.013	0.005
H (37)	0.013	0.005
H (38)	0.011	0.005
H (39)	0.011	0.005
H (40)	0.006	0.003
H (41)	0.006	0.003
H (42)	0.006	0.002
H (43)	0.006	0.002
H (44)	0.004	0.001
H (45)	0.003	0.001
H (46)	0.003	0.001
H (47)	0.003	0.001
H (48)	0.002	0.001
H (49)	0.002	0.001
H (50)	0.002	0.001
H (51)	0.002	0.001
H (52)	0.001	0.000
H (53)	0.001	0.000
H (54)	0.002	0.001
H (55)	-0.004	-0.001
H (56)	0.003	0.002
H (57)	-0.000	-0.000
H (58)	0.001	0.000
H (59)	-0.003	-0.001
H (60)	0.003	0.001
H (61)	-0.000	-0.000
H (62)	0.001	0.000
H (63)	-0.002	-0.001
H (64)	0.002	0.001
H (65)	-0.000	0.000

H (66)	0.001	0.000
H (67)	-0.001	-0.001
H (68)	0.002	0.001
H (69)	0.000	0.000
H (70)	0.002	0.001

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
C (1)	-0.020	0.022
N (2)	0.033	0.066
C (3)	0.030	0.029
C (4)	-0.021	0.005
C (5)	-0.010	0.004
C (6)	-0.007	0.003
C (7)	-0.006	0.003
C (8)	-0.005	0.002
C (9)	-0.005	0.003
C (10)	-0.005	0.003
C (11)	-0.006	0.004
C (12)	-0.006	0.006
C (13)	-0.012	0.009
C (14)	-0.015	0.011
C (15)	0.035	0.071
C (16)	0.038	0.074
H (17)	0.049	0.027
C (18)	-0.015	0.011
C (19)	-0.012	0.009
C (20)	-0.005	0.005
C (21)	-0.005	0.003
C (22)	-0.004	0.002
C (23)	-0.003	0.002
C (24)	-0.003	0.001
C (25)	-0.002	0.002
H (26)	0.048	0.026
Cl(27)	0.287	0.248
O (28)	0.089	0.079
H (29)	0.042	0.022
H (30)	0.042	0.023
H (31)	0.045	0.028
H (32)	0.019	0.009
H (33)	0.019	0.009
H (34)	0.016	0.007
H (35)	0.016	0.007
H (36)	0.009	0.004
H (37)	0.010	0.004
H (38)	0.009	0.004
H (39)	0.009	0.004
H (40)	0.007	0.003
H (41)	0.007	0.003
H (42)	0.007	0.003
H (43)	0.007	0.003
H (44)	0.007	0.003
H (45)	0.008	0.003
H (46)	0.008	0.004
H (47)	0.009	0.004
H (48)	0.011	0.005

H (49)	0.013	0.006
H (50)	0.014	0.006
H (51)	0.018	0.008
H (52)	0.022	0.009
H (53)	0.032	0.018
H (54)	0.032	0.018
H (55)	0.019	0.008
H (56)	0.019	0.008
H (57)	0.013	0.006
H (58)	0.012	0.006
H (59)	0.008	0.004
H (60)	0.009	0.004
H (61)	0.006	0.003
H (62)	0.006	0.003
H (63)	0.004	0.002
H (64)	0.005	0.002
H (65)	0.003	0.001
H (66)	0.004	0.002
H (67)	0.002	0.001
H (68)	0.007	0.004
H (69)	0.003	0.002
H (70)	0.004	0.002

Molecule: SH9

Fukui Indices for Electrophilic Attack (Fukui(-))

atom	Mulliken	Hirshfeld
C (1)	0.048	0.050
C (2)	0.037	0.057
C (3)	0.039	0.065
C (4)	0.026	0.030
C (5)	0.028	0.064
C (6)	0.037	0.050
O (7)	0.107	0.102
O (8)	0.044	0.049
C (9)	-0.031	0.017
C (10)	-0.013	0.012
N (11)	-0.000	0.018
C (12)	0.021	0.028
C (13)	-0.004	0.014
H (14)	0.024	0.013
O (15)	0.103	0.099
C (16)	-0.014	0.003
C (17)	-0.007	0.004
C (18)	-0.005	0.003
C (19)	-0.004	0.003
C (20)	0.011	0.014
C (21)	-0.006	0.002
C (22)	-0.002	0.002
C (23)	-0.003	0.003
H (24)	0.008	0.004
H (25)	0.009	0.004
H (26)	0.063	0.033
H (27)	0.048	0.023
H (28)	0.065	0.033
H (29)	0.034	0.032

H (30)	0.030	0.017
H (31)	0.033	0.018
H (32)	0.044	0.023
H (33)	0.037	0.020
H (34)	0.038	0.018
H (35)	0.023	0.012
H (36)	0.026	0.013
H (37)	0.012	0.005
H (38)	0.015	0.006
H (39)	0.009	0.004
H (40)	0.011	0.005
H (41)	0.007	0.003
H (42)	0.010	0.004
H (43)	0.006	0.002
H (44)	0.004	0.002
H (45)	-0.003	-0.001
H (46)	0.012	0.006
H (47)	0.011	0.006
H (48)	0.004	0.002
H (49)	0.005	0.003

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	0.047	0.061
C (2)	0.024	0.059
C (3)	0.041	0.064
C (4)	0.126	0.117
C (5)	0.012	0.060
C (6)	0.118	0.119
O (7)	0.057	0.058
O (8)	0.030	0.036
C (9)	-0.036	0.016
C (10)	-0.002	0.013
N (11)	-0.024	-0.001
C (12)	0.020	0.021
C (13)	-0.009	0.005
H (14)	0.018	0.008
O (15)	0.041	0.039
C (16)	-0.006	0.002
C (17)	-0.004	0.001
C (18)	-0.003	0.001
C (19)	-0.006	-0.003
C (20)	0.005	0.006
C (21)	-0.003	0.001
C (22)	-0.001	0.001
C (23)	-0.002	0.002
H (24)	0.003	0.002
H (25)	0.004	0.001
H (26)	0.078	0.040
H (27)	0.080	0.052
H (28)	0.089	0.058
H (29)	0.031	0.025
H (30)	0.028	0.016
H (31)	0.029	0.016
H (32)	0.051	0.027
H (33)	0.041	0.021

H (34)	0.039	0.019
H (35)	0.009	0.005
H (36)	0.015	0.007
H (37)	0.008	0.003
H (38)	0.010	0.004
H (39)	0.004	0.002
H (40)	0.006	0.002
H (41)	0.004	0.002
H (42)	0.006	0.002
H (43)	0.003	0.001
H (44)	0.002	0.001
H (45)	-0.004	-0.002
H (46)	0.008	0.004
H (47)	0.008	0.004
H (48)	0.003	0.002
H (49)	0.003	0.002

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
C (1)	0.048	0.056
C (2)	0.031	0.058
C (3)	0.040	0.065
C (4)	0.076	0.073
C (5)	0.020	0.062
C (6)	0.077	0.085
O (7)	0.082	0.080
O (8)	0.037	0.042
C (9)	-0.034	0.016
C (10)	-0.007	0.013
N (11)	-0.012	0.008
C (12)	0.021	0.024
C (13)	-0.006	0.009
H (14)	0.021	0.010
O (15)	0.072	0.069
C (16)	-0.010	0.003
C (17)	-0.006	0.002
C (18)	-0.004	0.002
C (19)	-0.005	0.000
C (20)	0.008	0.010
C (21)	-0.005	0.001
C (22)	-0.002	0.002
C (23)	-0.003	0.002
H (24)	0.006	0.003
H (25)	0.007	0.002
H (26)	0.071	0.036
H (27)	0.064	0.037
H (28)	0.077	0.045
H (29)	0.032	0.029
H (30)	0.029	0.017
H (31)	0.031	0.017
H (32)	0.047	0.025
H (33)	0.039	0.020
H (34)	0.039	0.019
H (35)	0.016	0.009
H (36)	0.020	0.010

H (37)	0.010	0.004
H (38)	0.012	0.005
H (39)	0.006	0.003
H (40)	0.008	0.004
H (41)	0.006	0.002
H (42)	0.008	0.003
H (43)	0.005	0.002
H (44)	0.003	0.002
H (45)	-0.004	-0.001
H (46)	0.010	0.005
H (47)	0.009	0.005
H (48)	0.003	0.002
H (49)	0.004	0.002

Molecule: SH10

Fukui Indices for Electrophilic Attack (Fukui(-))

atom	Mulliken	Hirshfeld
C (1)	0.022	0.051
C (2)	-0.001	0.021
C (3)	0.020	0.034
C (4)	0.020	0.034
C (5)	0.021	0.030
C (6)	0.020	0.030
C (7)	0.033	0.065
C (8)	0.031	0.059
C (9)	0.036	0.051
C (10)	0.024	0.041
C (11)	0.043	0.058
C (12)	0.036	0.051
O (13)	0.089	0.089
C (14)	-0.042	0.023
C (15)	-0.011	0.016
H (16)	0.050	0.025
H (17)	0.050	0.025
H (18)	0.038	0.019
H (19)	0.037	0.018
H (20)	0.059	0.030
H (21)	0.057	0.029
H (22)	0.066	0.034
H (23)	0.059	0.030
H (24)	0.045	0.026
H (25)	0.052	0.027
H (26)	0.045	0.026
H (27)	0.032	0.018
H (28)	0.038	0.023
H (29)	0.032	0.018

Fukui Indices for Nucleophilic Attack (Fukui(+))

atom	Mulliken	Hirshfeld
C (1)	0.047	0.070
C (2)	0.034	0.049
C (3)	0.030	0.050
C (4)	0.016	0.042
C (5)	0.036	0.051
C (6)	0.017	0.039
C (7)	0.014	0.036
C (8)	0.052	0.057

C (9)	0.059	0.064
C (10)	0.007	0.028
C (11)	0.043	0.054
C (12)	0.006	0.036
O (13)	0.030	0.035
C (14)	-0.030	0.014
C (15)	-0.017	0.021
H (16)	0.061	0.032
H (17)	0.060	0.030
H (18)	0.054	0.029
H (19)	0.050	0.025
H (20)	0.053	0.031
H (21)	0.045	0.022
H (22)	0.059	0.033
H (23)	0.054	0.026
H (24)	0.027	0.015
H (25)	0.039	0.021
H (26)	0.027	0.014
H (27)	0.040	0.023
H (28)	0.049	0.031
H (29)	0.041	0.023

Fukui Indices for Radical Attack (Fukui(0))

atom	Mulliken	Hirshfeld
C (1)	0.034	0.060
C (2)	0.016	0.035
C (3)	0.025	0.042
C (4)	0.018	0.038
C (5)	0.028	0.040
C (6)	0.018	0.034
C (7)	0.023	0.051
C (8)	0.042	0.058
C (9)	0.047	0.057
C (10)	0.016	0.034
C (11)	0.043	0.056
C (12)	0.021	0.043
O (13)	0.059	0.062
C (14)	-0.036	0.018
C (15)	-0.014	0.019
H (16)	0.055	0.029
H (17)	0.055	0.027
H (18)	0.046	0.024
H (19)	0.043	0.022
H (20)	0.056	0.031
H (21)	0.051	0.025
H (22)	0.063	0.034
H (23)	0.056	0.028
H (24)	0.036	0.020
H (25)	0.046	0.024
H (26)	0.036	0.020
H (27)	0.036	0.020
H (28)	0.043	0.027
H (29)	0.036	0.020

Conclusion

Quantum chemical parameters including the HOMO orbital energy (EHOMO) and the LUMO orbital energy (ELUMO), ionization potential (I), electron affinity (A), the absolute electronegativity (χ), hardness (η), softness (σ), the fraction of electron transferred (ΔN) have been studied. To the system under consideration, the calculation results indicated that the highest occupied molecular orbital EHOMO and the fraction of electron transferred (ΔN) have a good correlation with the corrosion inhibition efficiency (IE%). Electron donating substituents (NH_2, $-OCH_3$, -OH, $-CH_3$, $-CHCH_2$) increases the inhibition efficiency, in contrast, electron withdrawing substituent $-COOCH_3$, -COOH, -CHO, -F, $-NO_2$) have the opposite effect. The local reactivity from Fukui function confirmed that the pheny rings of crown ether have higher binding contribution to metal surfaces via delocalization of π-electron.

References

[1]. Uhlig, H. H.; Revie, R. W., Corrosion and Corrosion Control. 3rd edition. New York: John Wiley & Sons. 1985.

[2]. Qiang, Y.; Zhang, S.; Guo, L., Xu, S.; Feng, L.; Obot, I. B.; Chen, S. *J Clean Prod.* 2017, 152, 17-25.

[3]. Mobin, M.; Rizvi, M. *Carbohydr Polym*. 2017. 160, 172-183.

[4]. Douadi, T.; Hamani, H.; Daoud, D.; Al-Noaimi, M.; Chafaa, S. *J Taiwan InstChem E*ng. 2017. 71, 388-404.

[5]. Zarrouk, A.; Hammouti, B.; Lakhlifi, T.; Traisnel, M.; Vezin, H.; Bentiss, F. *Corros Sci*. 2015. 90, 572-584.

[6]. Yıldız, R.; Döner, A.; Doğan, T.; Dehri, İ. *Corros Sci.* 2014. 82, 125-132.

[7]. Mendonça, G. L.; Costa, S. N.; Freire, V. N.; Casciano, P. N.; Correia, A. N.; de Lima-Neto, P. *Corros Sci.* 2017. 115, 41-55.

[8]. Noor, E. A. *Corros Sci*. 2005. 47(1), 33-55.

[9]. Purwoko, A. A.; Hadisaputra, S. *Orient J Chem*. 2017. 33(2), 717-724.

[10]. Shetty, S. K.; Shetty, A. N. *J Mol Liq*. 2017. 225, 426-438.

[11]. Khaled, K.F. (2010). Studies of iron corrosion inhibition using chemical, electrochemical and computer simulation techniques. *Electrochimica Acta*, 55: 6523-6532

[12]. Oguzie, E.E., Ogukwe, C.E., Ogbulie, J.N., Nwanebu, F.C., Adindu, C.B., Udeze, I.O., Oguzie, K.L., and Eze, F.C. (2012c). Broad spectrum corrosion inhibition: corrosion and microbial (SBR) growth inhibiting effects of *piper guineense* extract. *Journal of material science*, 47: 3592-3601

[13]. Cardoso, S.P., Hollauer, E., Borges, L.E.P. and Gomes, J.A.C.P. (2006). QSPR prediction analysis of corrosion inhibitors in hydrochloric acid on 22%-Cr stainless steel. *Journal of Brazilian Chemical Society* 17: 1241-1249.

[14]. Pearson, R.G., (1988). Absolute electronegativity and hardness: application to inorganic chemistry, *Inorganic Chemistry*, 27: 734-740

[15]. Sastri, V.S. (1998). Corrosion inhibitors: principles and applications. New York: John Wiley & sons Ltd, West Sussex.

[16]. Parr, R.G., Szentpaly, L., Liu, S., (1999). Electrophilicity Index, *Journal of American Chemical Society*, 121: 1922-1924.

[17]. Obot, I.B., Obi-Egbedi, N.O. (2010). Theoretical study of benzimidazole and its derivatives and their potential activity as corrosion inhibitors. *Corrosion Science*, 52: 657-660.

[18]. Gomez, B., Likhanova, N.V., Dominguez-Aguilar, M.A., Vela, R. Martinez-Palou, A., Gasquez, J. (2006). Quantum Chemical Study of the Inhibitive Properties of 2-Pyridyl-Azoles, *The Journal of Physical Chemistry B*, 110: 8928-8934.

[19]. Delley, B. (1990). From molecules to solids with Dmol3 approach. *Journal of chemical physics*, 113: 7756-7764.

[20]. Gao, G. And Liang, C. (2007). Electrochemical and DFT studies of α-amino alcohols as corrosion inhibitors for brass. *Electrochimica Acta*, 52: 4554-4559

[21]. Xia, S., Qui, M., Yu, L., F. And Zhao, H. (2008). Molecular dynamics and density functional theory study of relationship between structure of imidazoline derivatives and inhibition performance. *Corrosion science*, 50: 2021-2029.

[22]. Gece, G., (2008). The use of quantum chemical methods in corrosion inhibitor studies, *Corrosion Science*, 50: 2981-2992.

[23]. Lukovits, I., Ka´lma´n, E., Zucchi, F. (2001). Corrosion inhibitors—correlation between electronic structure and efficiency, *Corrosion science,* 57: 3-9.

[24]. Musa, A.Y., Kadhum, A.H., Mohamad, A., Takriff, M.S. (2010). Experimental and theoretical study on the inhibition performance of triazole compounds for mild steel corrosion, *Corrosion Science*, 52: 3331-3340.