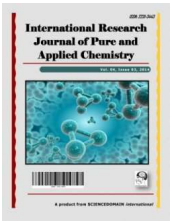

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Theoretical Study of the Efficiency of Some Nitro Benzenamine Derivatives in Acidic Medium to Serve as Excellent Organic Corrosion Inhibitors of Mild Steel

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Authors' contributions

This work was carried out in collaboration between all three authors. Author IAA designed the study and wrote the protocol. Author FKO preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance from author JAL. All three authors read and approved the final manuscript.

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ABSTRACT

A quantum chemical study of the efficiency of some nitro benzenamine derivatives as corrosion inhibitors of mild steel in acidic medium was investigated. Density Functional Theory (DFT) at the B3LYP/6-31G* level was used for the calculation. The calculated quantum chemical parameters related to the inhibition efficiencies are the orbital energies (E_{HOMO} and E_{LUMO}), Separation Energy (E_{LUMO}-E_{HOMO}), Dipole moment (μ), Substituent constant (Log P), Polarizability, molecular volume, molecular weight and mulliken charge of atom. The results showed that the Inhibition Efficiency was closely related to these quantum chemical parameters. Results revealed that 5-(deca-1,3,5,7,9-pentyl)-2-nitrobenzenamine (molecule 6) showed the greatest Inhibition Efficiency (IE) of the Nitro benzenamine derivatives.

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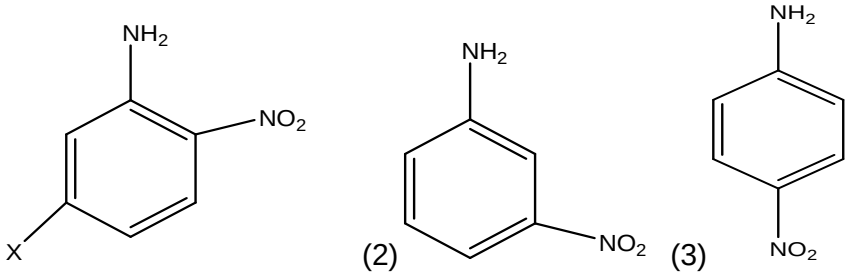
Keywords: Mild steel; acid solution; modelling studies; acid inhibition.

1. INTRODUCTION

One effective way of protecting metals against corrosion particularly in acid environment is by the use of organic inhibitors [1,2,3]. Organic inhibitors are effective corrosion inhibitors and they are not toxic to the environment [4,5,6]. High performing acid inhibitors are organic compounds containing hetero atoms such as N, S, O. The presence of aromatic ring, conjugated double bonds and substituent group such as NH_2, NO_2 could further enhanced the effectiveness of these organic inhibitors as excellent corrosion inhibitors [7-13]. The inhibiting action of these organic compounds is most often attributed to their adsorptive interactions with the metal surface. The use of quantum chemical parameters presents three main advantages: Firstly, the compounds with respect to the parent compound, various fragments and substituents can be directly characterized on the basis of their molecular structure only. Secondly, the proposed mechanism of action can be directly accounted for in terms of chemical reactivity of the compounds under study [1,7], and thirdly novel organic inhibitors could be simulated [8]. The theoretical prediction of the efficiency of corrosion inhibitors in selecting excellent corrosion inhibitors have continuously gained popularity especially with the significant progress in the building of sophisticated software packages which has being employed in quantum mechanical calculations [14-15]. The use of some organo nitro compounds such as nitro aniline and its derivatives as effective organic inhibitors is interesting and can offer a great deal of solution to the unending corrosion challenge [16-21]. However, it has not being extensively reported as such few reports exist in literature to date. Thus the aim of this study is to theoretically investigate the efficiency of some Nitro aniline derivatives with the view of simulating a nitro aniline compound to serve as an excellent organic corrosion inhibitor.

2. THEORETICAL METHOD

All the quantum chemical calculations were performed with SPARTAN'14. The full optimization was initially achieved by using molecular mechanics force fields (MMFF). The results from MMFF were further selected as input and re-optimized using Semi empirical AM1. The Semi empirical AM1 structures were selected as input and were re-optimized using Density Functional Theory (DFT) at the level of B3LYP methods which uses the exchange functional proposal by Becke [22] and all the correlations functional given by Lee, Yang and Parr [23]. The 6-31G* basis set has been used in conjunction with DFT method because it has the advantage of being flexible enough to guarantee reliable theoretical results and being small enough for rapid calculations. It represents an excellent compromise between completeness and economy. The molecular geometry was fully optimized without any constraint using analytical gradient procedure implemented within the program package [14,18,19,20,21]. The following quantum chemical indices were considered: The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), separation energy ($E_{LUMO} - E_{HOMO}$), dipole moment (μ), Log P, and Polarizability of the various nitro aniline derivatives. The chemical structures and optimized geometry of nitro benzenamine derivatives are shown in Figs. 1 and 2 respectively.



(1) X = H
(4) X = C_2H_3
(5) X = C_4H_5
(6) X = $C_{10}H_{11}$

Fig. 1. Chemical structure of inhibitors

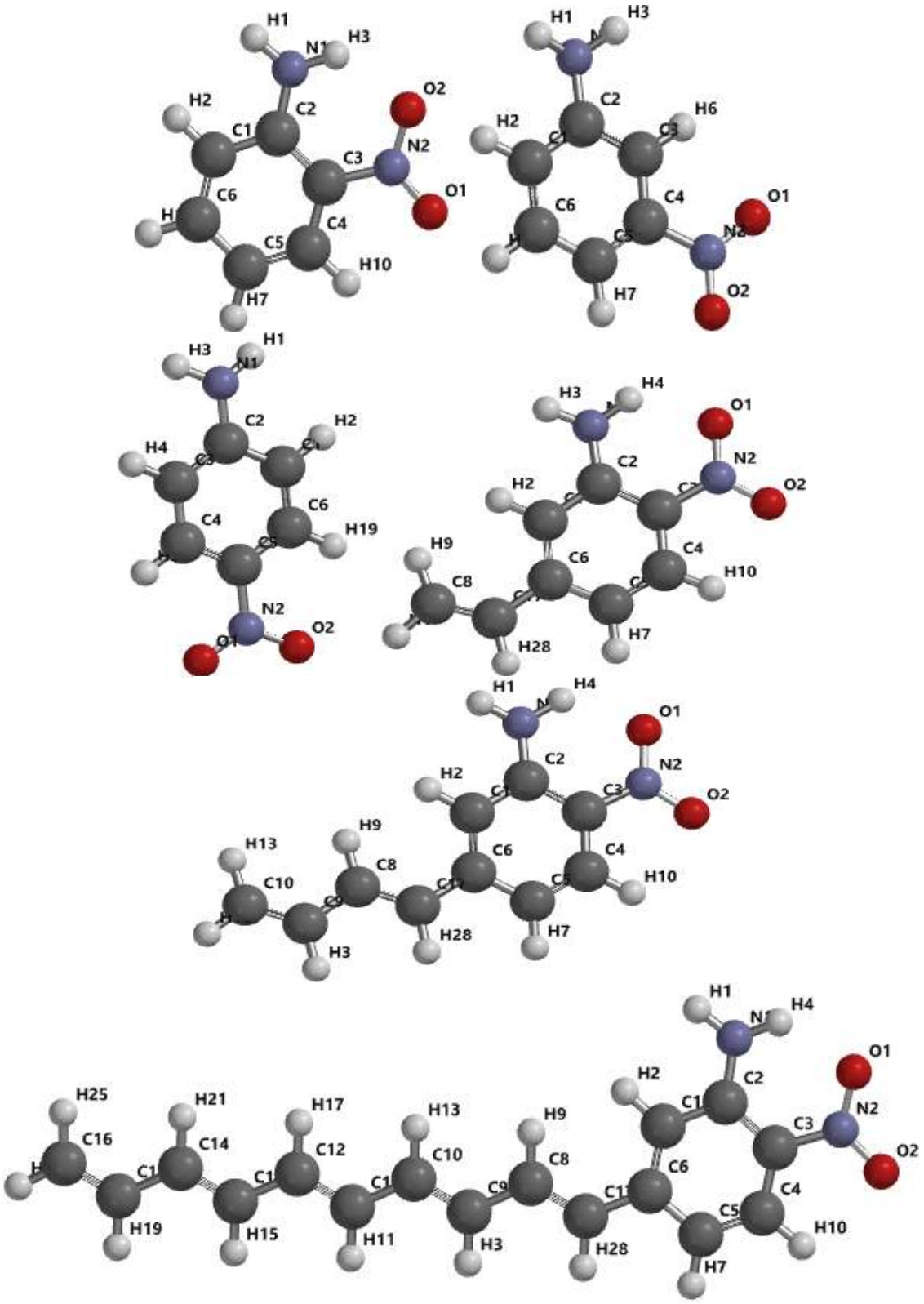


Fig. 2. Labelled optimised structures

3. RESULTS AND DISCUSSION

It is obvious from the molecular structure that the investigated nitro aniline compounds contain the amino group which has basic properties due to the presence of lone pair of electrons of the nitrogen atom. The importance of the basic properties of NH_2 group is the formation of complexes of amine with metal ions. The inhibition efficiency of some nitro aniline derivatives such as 2-nitro benzenamine, 3-nitro benzenamine and 4-nitro benzenamine on the corrosion of metal surface have being measured experimentally [16,17], however that of 2-nitro-5-vinyl benzenamine, 5-(buta-1,3-dienyl)-2-nitrobenzenamine and 5-(deca-1,3,5,7,9-pentyl)-2-nitrobenzenamine are yet to be experimentally explored. Quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}), separation energy ($E_{LUMO} - E_{HOMO}$), the net charge on the amino group, dipole moment, substituent constant (log p), polarizability, molecular volumes and molecular weights are tabulated in Table 1.

The E_{HOMO} is often associated with the electron donating ability of molecule [24,25,26]. Therefore, increasing values of E_{HOMO} indicates higher tendency for donation of electrons to the appropriate acceptor molecule with low energy and empty molecular orbital, thus increasing values of E_{HOMO} facilitate the adsorption of the inhibitor [25]. The E_{LUMO} indicates the ability of the molecule to accept electrons. Hence, the lower the value of E_{LUMO} the more apparent for the molecule to accept electrons [27]. The separation energy which indicates reactivity is the energy difference between the HOMO and the LUMO. The energy gap also relates to how soft or hard a molecule is. A larger energy gap indicates low reactivity to chemical specie, thus a soft molecule is more reactive than a hard molecule [25,26,27,28]. The binding ability of the inhibitor to the metal surface increases with increasing the energy of HOMO, decreasing energy of LUMO and low separating energy values.

Dipole moment (μ) is another useful quantum index for the prediction of the direction of a corrosion inhibition process. It is a measure of polarity in a bond and is related to the distribution of electrons in a molecule. Although literature is inconsistent on the use of dipole moment as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing high dipole moments on the metal surface should lead to better inhibition efficiency [29,30].

Polarizability is the ratio of induced dipole moment to the intensity of the electric field. The induced dipole moment is proportional to polarizability [31].

The values of log p (substituent constant) were also found to have a good relationship with the corrosion inhibition efficiencies of the studied inhibitors. Substituent constants are empirical quantities which account for the variation of the structure and do not depend on the parent structure but vary with the substituent. Hence increasing the value of Log P increases the inhibition efficiencies of organic inhibitors [32].

Molecular volume and weight are quantum parameters that determine molecular size and effective surface coverage. These invariably

Table 1. Quantum chemical parameters of nitro aniline derivatives using DFT method

Quantum chemical parameters	Molecule 1	Molecule 2	Molecule 3	Molecule 4	Molecule 5	Molecule 6
E_{Homo} (eV)	-6.06	-6.14	-6.25	-6.07	-6.02	-5.29
E_{Lumo} (eV)	-2.17	-2.24	-1.96	-2.34	-2.42	-2.59
$E_{Lumo} - E_{Homo}$ (eV)	3.89	3.90	4.29	3.73	3.60	2.7
Dipole moment (μ)	4.74	5.65	7.12	5.04	5.48	6.79
Log P	-4.35	-4.35	-4.35	-4.03	-3.51	-1.97
Polarizability	51.02	51.10	50.99	53.70	56.37	64.51
Volume ($Å^3$)	130.30	131.19	131.12	162.77	195.34	293.04
Weight (amu)	138.126	138.126	138.126	164.164	190.202	268.316

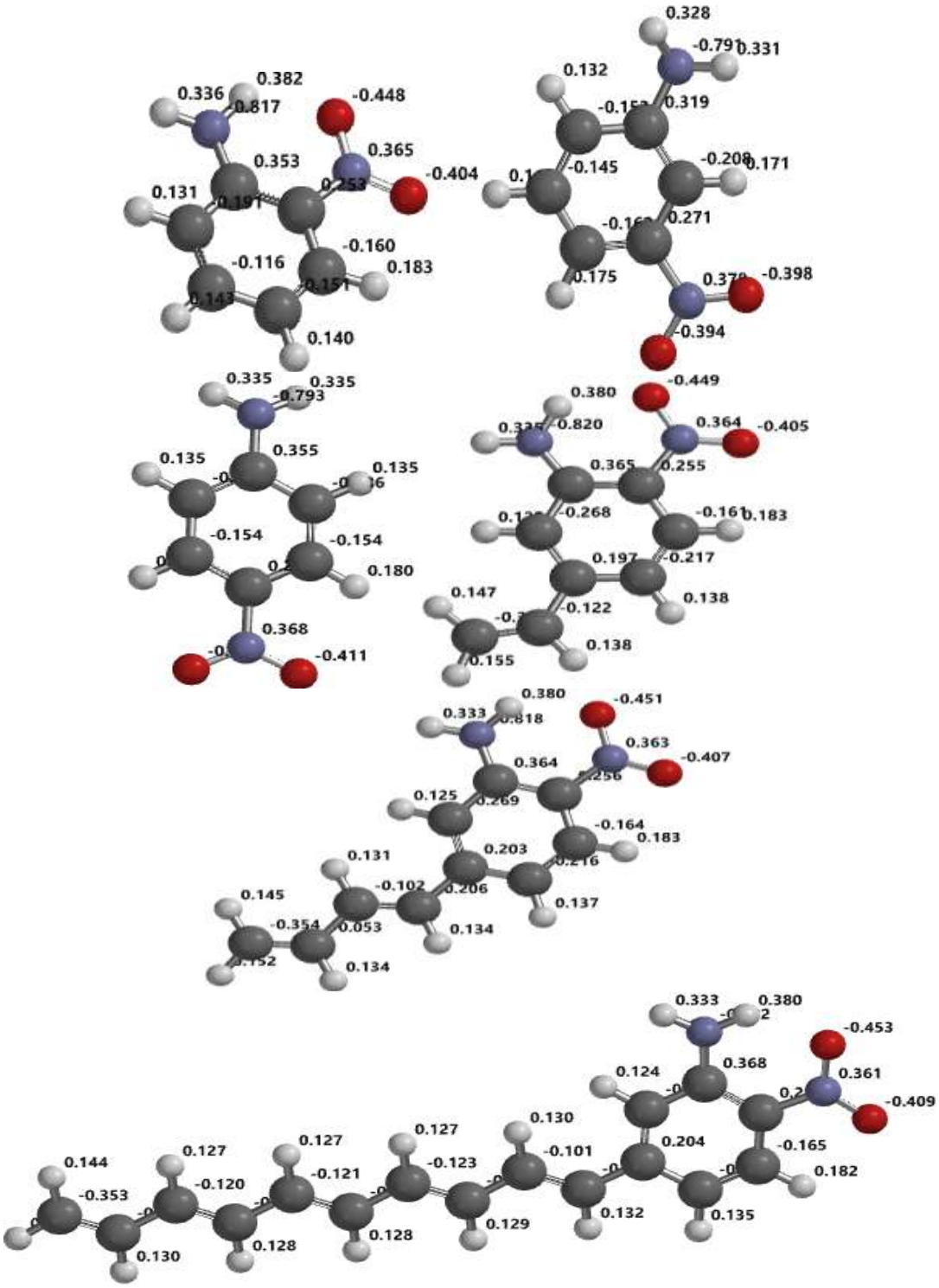


Fig. 3. Optimised molecular structures of nitro benzenamine showing mulliken charges

determine how effective a molecule can be adsorbed on and cover metal surface, thereby isolating it from the corroding environment. As the value of these parameters increase, so also the likely corrosion inhibition potentials of the molecules increase [21].

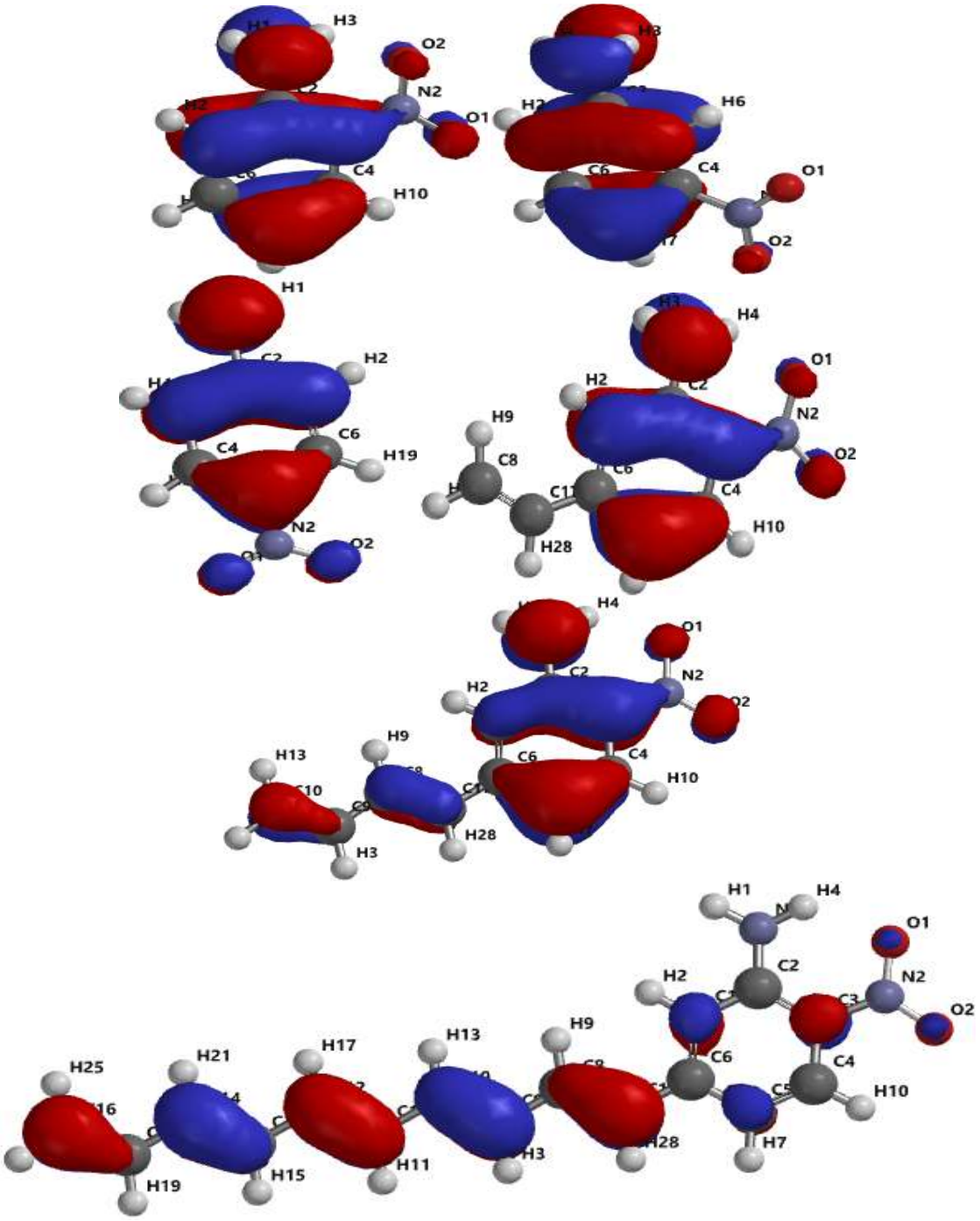


Fig. 4. HOMO plot of optimised molecules

The calculated quantum chemical parameters show that 2 nitro benzenamine with HOMO and the LUMO orbital energies at -6.06eV and -2.17eV, respectively and separation energy of 3.89eV this clearly marks 2-nitro benzenamine a corrosion inhibitor with higher reactivity toward the metal surface as compared to 3-nitro benzenamine and 4-nitro benzenamine. calculations reveal that its values for dipole moment, log p, polarizability, molecular weight and molecular volume are 4.74debye, -4.35, 51.02, 138.126 amu and 130.30Å^3 respectively.

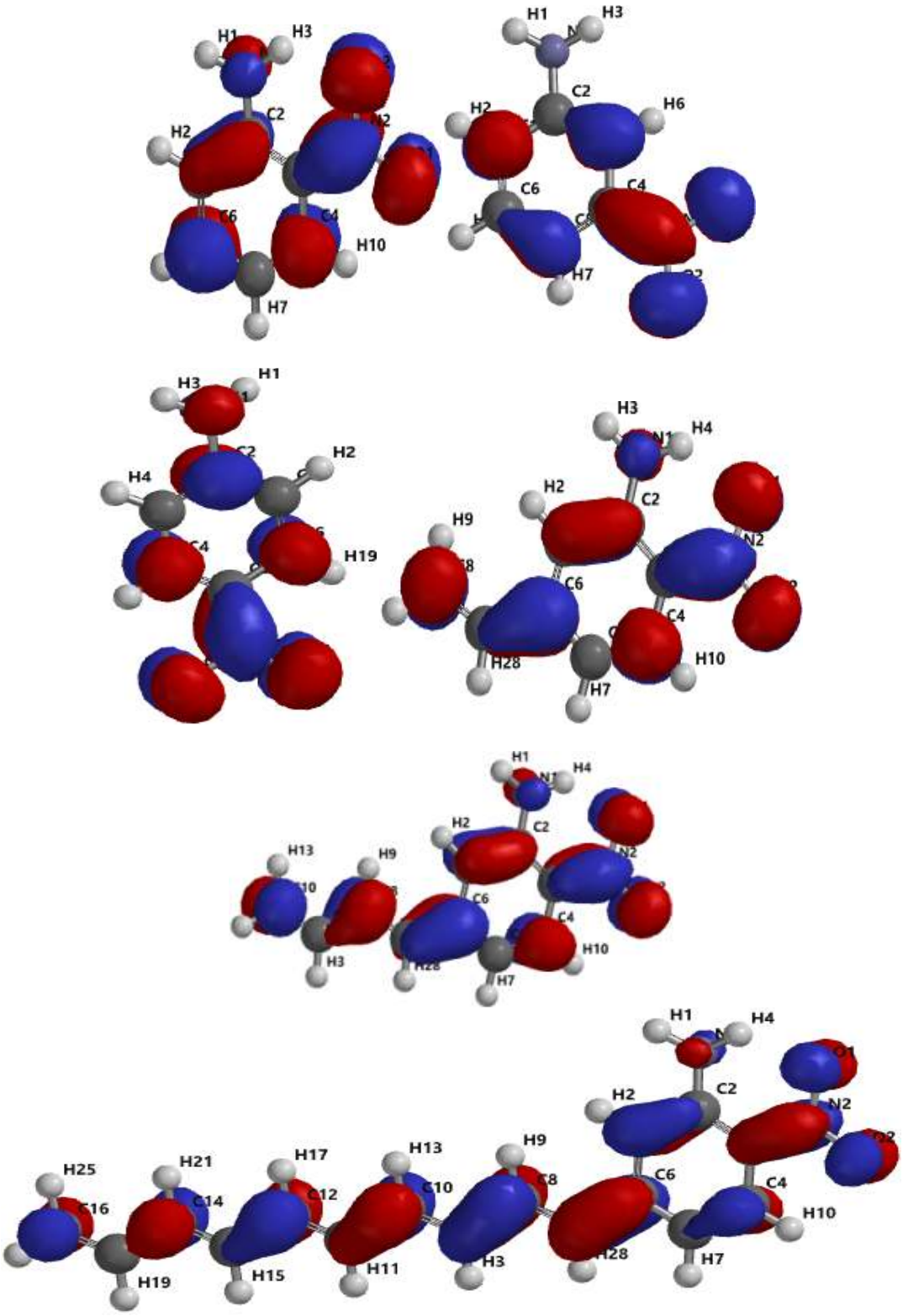


Fig. 5. LUMO plot of optimised molecules

The effect of nitro substituent on the meta and para position in the nitro benzenamine shows that the separation energy increases to 3.90 eV for 3-nitro benzenamine and 4.29 eV for 4-nitro benzenamine. Similar quantum chemical values were calculated for log p, polarizability, molecular weight and molecular volume except for dipole moment.

The effect of alkenyl substituent group in conjugation to the aromatic ring in the case of inhibitors 4, 5 and 6 will further decrease the energy of the HOMO orbital, increase the energy of the LUMO orbital and decrease the separation energy. With inhibitor 6 having the lowest separation energy of 2.70 eV, highest HOMO energy of -5.29 eV and lowest LUMO energy of -2.59 eV. This clearly shows inhibitor 6 as the most reactive molecule with the greatest binding ability to the surface of the metal. This great inhibiting potential could also be attributed to the conjugated double bonds having sufficient π electrons thereby reducing the energy gap between the HOMO and LUMO orbitals. The calculated dipole moment, log p and polarizability show a gradual increase with the highest values being that of inhibitor 6, Table 1. Inhibitor 6 has the highest molecular volume, 293.04Å^3 and molecular weight, 268.316 amu due to the attachment of deca-1,3,5,7,9-pentyl group to the aromatic ring, which probably makes a better surface coverage of the metal surface which explains the highest inhibition efficiency for the inhibitor 6.

The calculated Mulliken charge shows that the nitrogen atom of the amine group and the oxygen atoms could act as active centres for the adsorption of the nitro benzenamine molecule on the metal surface. The charge distribution over the whole molecule is shown in Fig. 3 above.

Molecular orbital calculations are performed to determine the molecular orbital coefficients of the HOMO and LUMO levels for the studied nitro benzenamine derivatives as corrosion inhibitors to explain the mechanism of their adsorptions on the metal surface. The HOMO electronic density distribution for the nitro benzenamine derivatives are shown in Fig. 4 above. It is evident from the calculations that the highest coefficients are found on the nitrogen atom of the amino group and the phenyl moiety which can be represented as active adsorption centres of the inhibitors. The adsorption of inhibitors 1, 2, 3 occurs through the lone pairs of electrons of the nitrogen (N_1) atom, oxygen atoms and π charges of the phenyl moiety and in the case of inhibitors 4, 5 and 6, adsorption occurs through the lone pairs of electrons of the nitrogen (N_1) atom, oxygen atoms, π charges of the phenyl and alkenyl moieties.

The LUMO plot is shown in Fig. 5. The highest coefficient is localised on the nitrogen atom which can facilitate the back donation from the metal surface to the amino group of the inhibitor. This will increase its adsorption on the metal surface and accordingly increases its inhibition efficiency. The adsorption mechanism of the nitro benzenamine inhibitors on the metal surface can be explained as electron donation from the inhibitor molecule to the metal surface and back donation from the d-orbital of the metal surface to the π anti-bonding counterpart of the inhibitor. In summary the above results indicate that the nitro benzenamine derivatives inhibitors are adsorbed on the metal surface through the nitro group, amine group and the highly electronegative nitrogen atom, the oxygen atoms and the π charge of the phenyl and alkenyl moieties.

4. CONCLUSION

Quantum chemical calculations based on DFT/B3LYP level were performed to find the relation between the molecular structure of the inhibitor and the inhibition efficiency. The calculated quantum chemical indices confirm that the bonding of an alkenyl group in conjugation to the aromatic ring increases the inhibition efficiency of the inhibitor toward the metal surface with the highest potential inhibition efficiency obtained for 5-(deca-1,3,5,7,9-pentyl)-2-nitrobenzenamine(inhibitor 6).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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