

Original Research Article

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

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 ($E_{\text{LUMO}} - E_{\text{HOMO}}$), 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 (1-(2-nitrophenyl)-2,2,2-trifluoroethylamine) (molecule 6) showed the greatest Inhibition Efficiency (IE) of the Nitro benzenamine derivatives.

Keywords: A. Mild Steel; A. Acid solution; B. Modelling Studies; C. Acid inhibition

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 [7,8,9,10,11,12,13]. 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.

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 guarantees 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 Figures 1 and 2 respectively.

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-nitrobenzenamine, 3-nitrobenzenamine and 4-nitrobenzenamine on the corrosion of metal surface have being measured experimentally [16,17], however that of 2-nitro-5-*tert*-butylbenzenamine, 5-(buta-1,3-dienyl)-2-nitrobenzenamine and 5-(hepta-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].

83 The binding ability of the inhibitor to the metal surface increases with increasing the energy
84 of HOMO, decreasing energy of LUMO and low separating energy values.

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

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

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

98 Molecular volume and weight are quantum parameters that determine molecular size and
99 effective surface coverage. These invariably determine how effective a molecule can be
100 adsorbed on and cover metal surface, thereby isolating it from the corroding environment. As
101 the value of these parameters increase, so also the likely corrosion inhibition potentials of the
102 molecules increase [21].

103 The calculated quantum chemical parameters show that 2 nitro benzenamine with HOMO
104 and the LUMO orbital energies at -6.06eV and -2.17eV, respectively and separation energy
105 of 3.89eV this clearly marks 2 nitro benzenamine a corrosion inhibitor with higher reactivity
106 toward the metal surface as compared to 3 nitro benzenamine and 4 nitro benzenamine.
107 calculations reveal that its values for dipole moment, log p, polarizability, molecular weight
108 and molecular volume are 4.74debye, -4.35, 51.02, 138.126amu and 130.30Å³ respectively.

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

113 The effect of alkenyl substituent group in conjugation to the aromatic ring in the case of
114 inhibitors 4, 5 and 6 will further decrease the energy of the HOMO orbital, increase the
115 energy of the LUMO orbital and decrease the separation energy. With inhibitor 6 having the
116 lowest separation energy of 2.70eV, highest HOMO energy of -5.29eV and lowest LUMO
117 energy of -2.59eV. This clearly shows inhibitor 6 as the most reactive molecule with the
118 greatest binding ability to the surface of the metal. This great inhibiting potential could also
119 be attributed to the conjugated double bonds having sufficient π electrons thereby reducing
120 the energy gap between the HOMO and LUMO orbitals. The calculated dipole moment, log p
121 and polarizability show a gradual increase with the highest values being that of inhibitor 6,
122 Table 1. Inhibitor 6 has the highest molecular volume, 293.04Å³ and molecular weight,
123 268.316amu due to the attachment of deca-1,3,5,7,9-pentyl group to the aromatic ring, which
124 probably makes a better surface coverage of the metal surface which explains the highest
125 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 figure 3

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 figure 4. 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, 4 and 6 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 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 figure 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.

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-(4-allyl-1,3,5,7,9-pentyl)-2-nitrobenzenamine(inhibitor 6).

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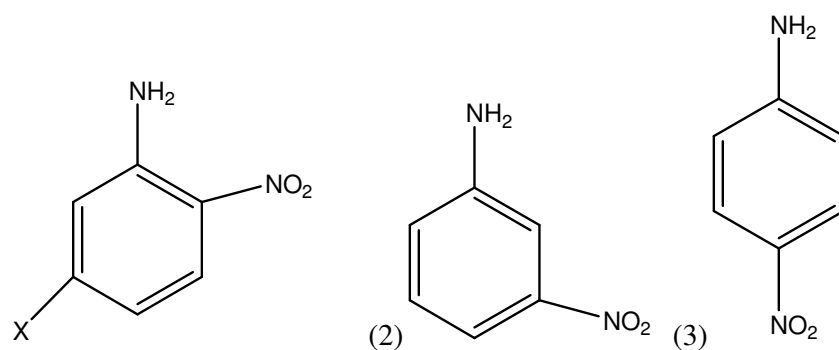
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Table 1: Quantum chemical parameters of Nitro aniline derivatives using DFT method

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



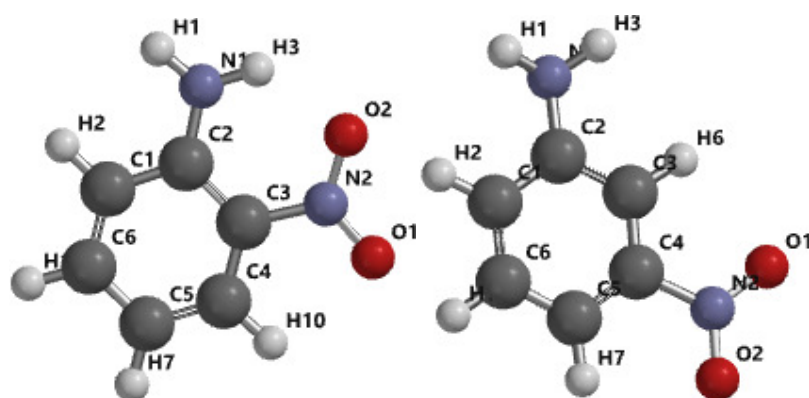
(1) X = H

(4) X = C₂H₃

(5) X = C₄H₅

(6) X = C₁₀H₁₁

Figure 1.Chemical structure of Inhibitors.



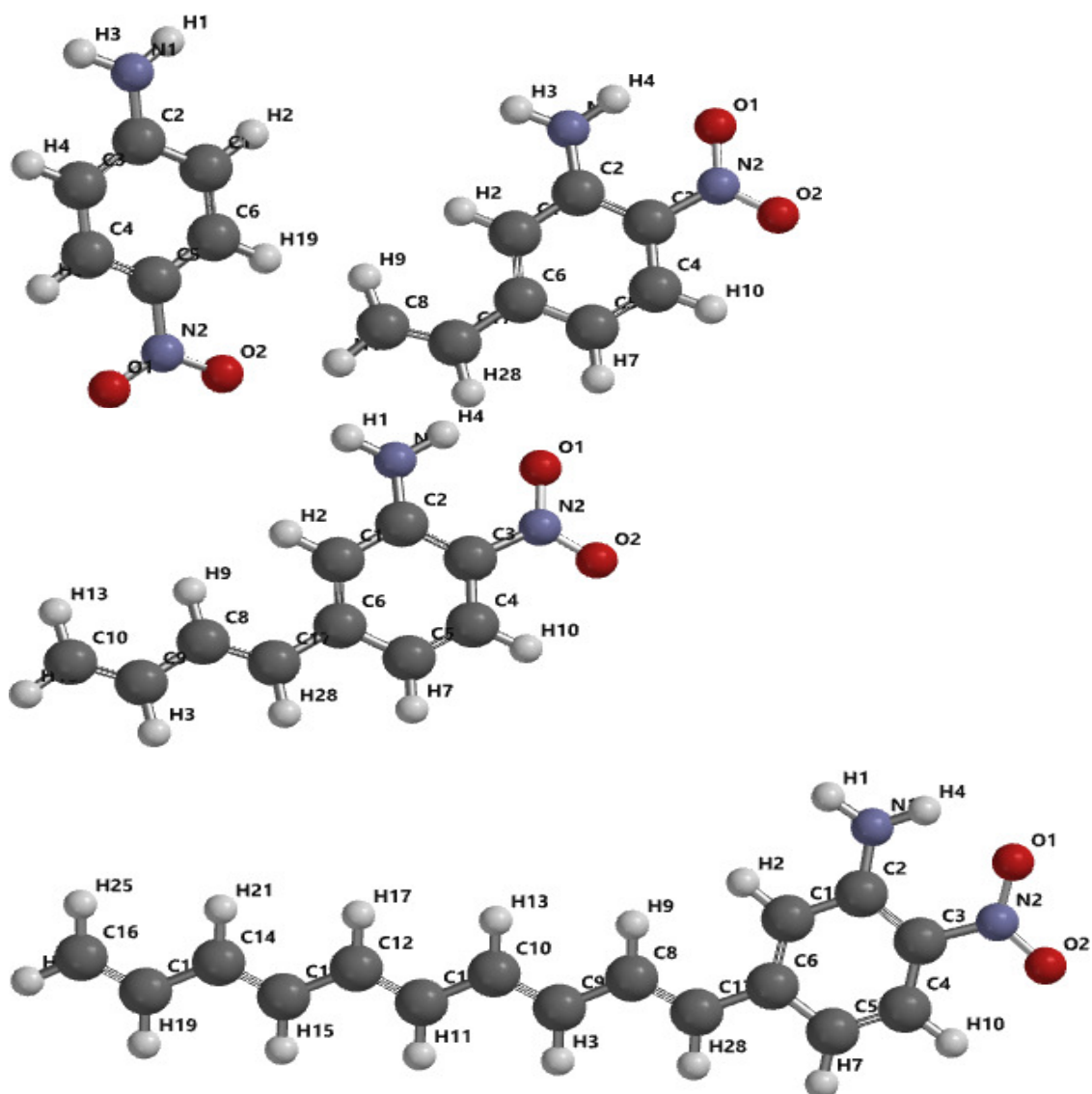


Figure 2: Labelled optimised structures

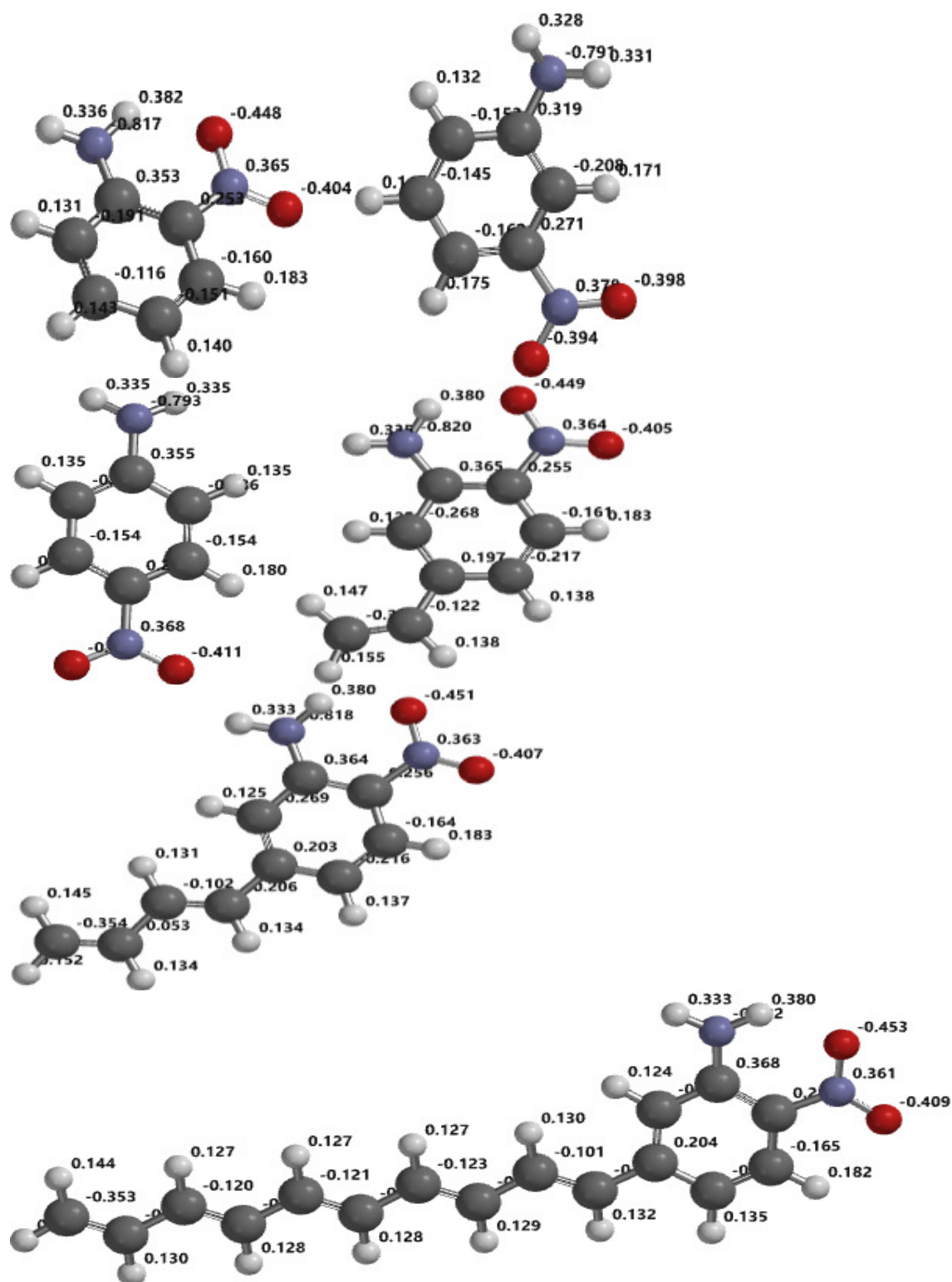
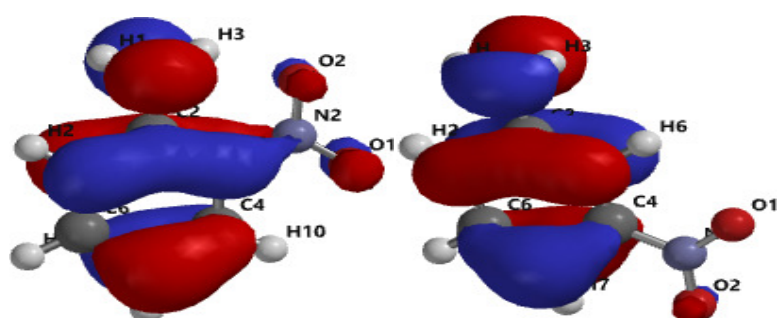
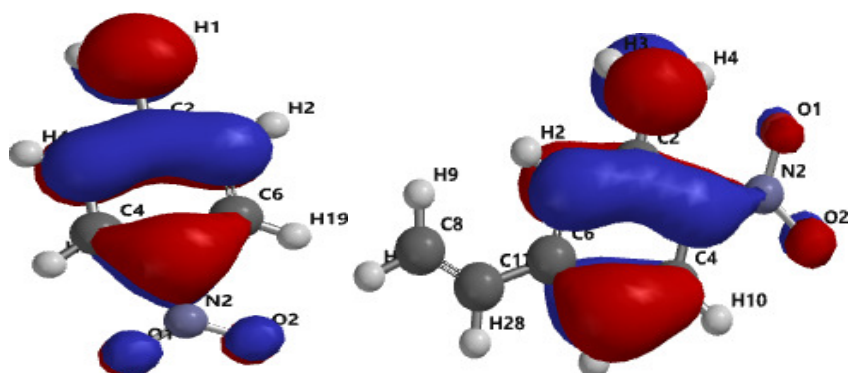


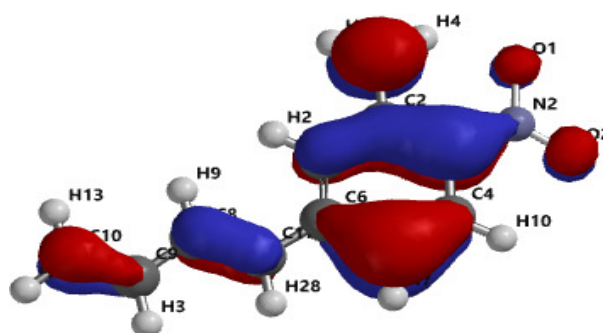
Figure 3: Optimised molecular structures of nitro benzenamine showing mulliken charges



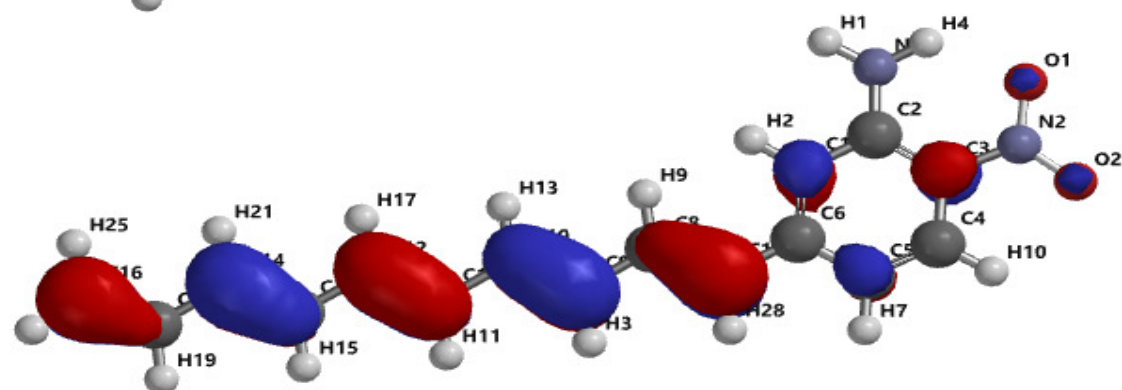
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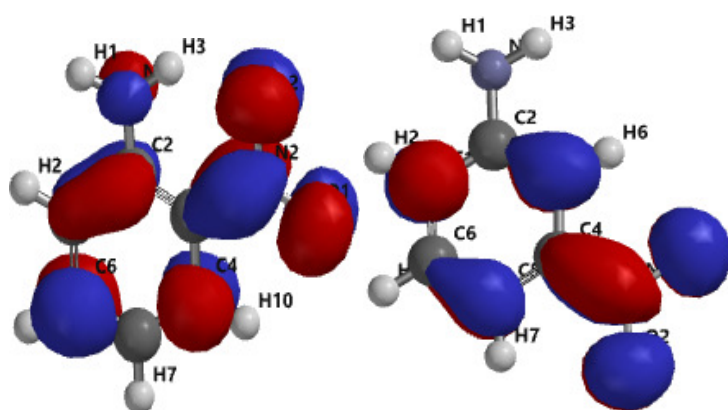
326 Figure 4: HOMO plot of optimised molecules

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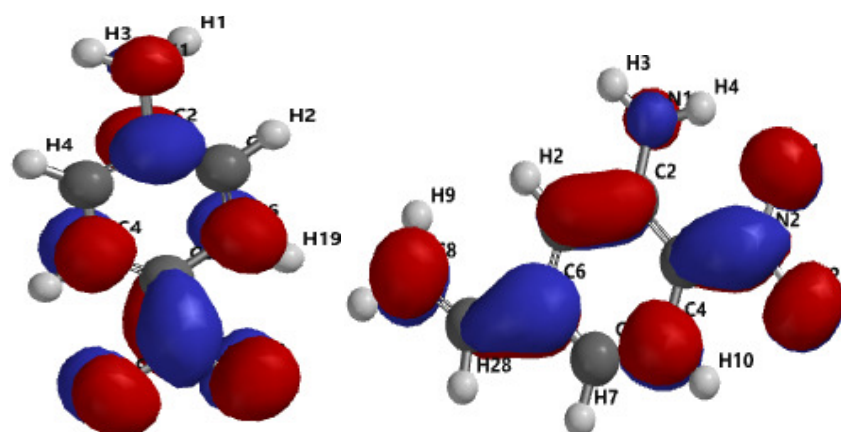
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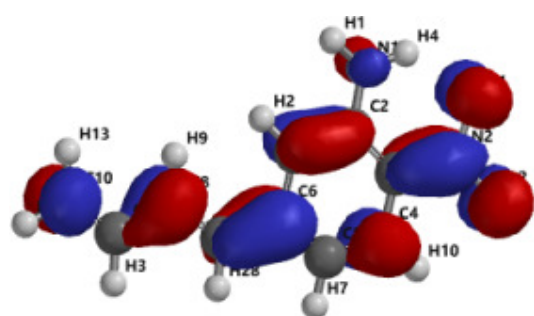
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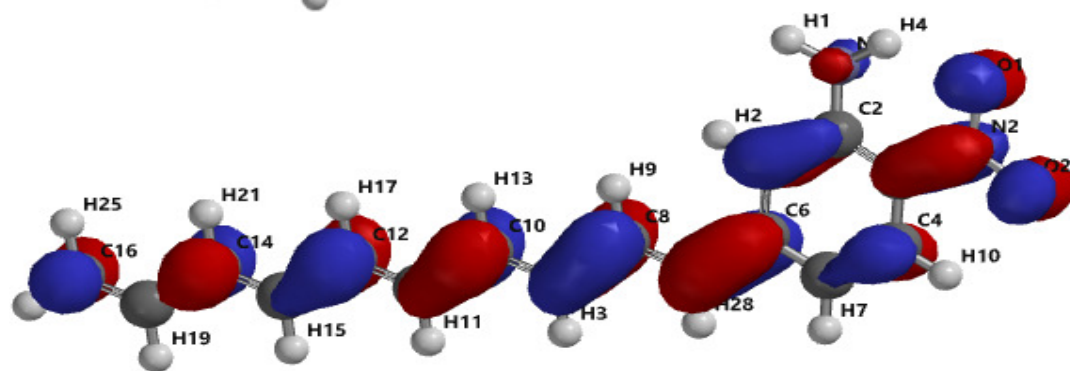
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335 Figure 5: LUMO plot of optimised molecules

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