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Semi- empirical study of chemical reactivity of Basic red 18

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ABSTRACT

Structural properties of basic red 18 have been calculated using semi-empirical (implemented in Hyperchem package 8.0) at PM3 -method. According to the surface potential energy, atomic charge, bond length, electrostatic potential and molecular orbital have been studied to estimate the chemical reactivity of Basic red 18. Investigation refers that electrostatic potential has been despaired into two main regions the positive side of electronic density is focused on hydrogen atoms and Negative side of electronic density is focused into oxygen atoms. The atomic charge distribution of basic red 18 occurs on different atoms like, nitrogen atoms of Azo bridge (N10=N11) have negative charge equal to -0.015and -0.008 coulomb respectively and oxygen atoms of nitrite group(O8,O9) have negative charge equal to –O.588 and –O.584 respectively . Energies of HOMO is (-11.12582 ev) and LUMO is (-4.417902ev), since the energy gap equal to 6.742778 eV. The bond C3-N10 and C20-N21 are the most probable reactive site (weakest bonds) than other fifteen bonds in basic red 18 with highest probable to enter the first cleavage step of degradation reaction.

Keywords: Chemical reactivity, Quantum calculation methods, photodegradation, catalytic reactions, theoretical chemistry, Semi-empirical method.

INTRODUCTION

Basic red 18 as pigment has been used in textile factory of Hilla city in Iraq, since the waste water remove down into the river that a main source of drinking water of the people in the Hilla city. It is one of the synthetic dyes that's been used extensively by industries including dye houses, paper printer and textile dyers. A significant proportion of synthetic organic dye stuffs are lost annually to waste streams in textile processing, which eventually enter the environment [1].Color is usually the first contaminant to be considered in wastewater. Its presence in watercourses is unacceptable. A very small amount of dye in water is (10–50 mg. l^{-1}) highly visible, affects water transparency and gas solubility of water bodies [2]. Moreover, it may also affect photosynthetic activity in aquatic systems by reducing light penetration [3, 4]. Several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms [5]. The removal of textile dyes from wastewater is one of the most important environmental issues to be solved today. Many dyes used in textile industry are particularly difficult to remove by conventional waste treatment methods since they are designed to be resistant to degradation or fading by oxidizing agents and light. They must also be resilient to both high temperatures and enzyme degradation

resulting from detergent washing. For these reasons, biodegradation of these dyes is typically a slow process and complete mineralization of most dyes is rather difficult. Degradation products are toxic and carcinogenic amines to aquatic organisms [6–7]. Their presence in wastewater is unwanted and the removal of such compounds are difficult while many physical and chemical methods including adsorption, coagulation, precipitation, filtration, ozonisation and oxidation have been used for the treatment of dye-containing effluent[8]. Activated carbon is the most widely used adsorbent for the removal of color and treatment textile effluents. However, due to its high price, it is not used on a great scale [9]. This had led many workers to search for the use of cheap and efficient alternative materials such as biogases pith, carbonized bark, peat, soil, tree and Eucalyptus bark, chitin, rice husk wood and fly ash [10]. The chemical name of Basic red 18 pigment is: [2-[[4-[(2-chloro-4 nitrophenyl) azo]phenyl] ethyl amino] ethyl]trimethylammonium and the IUPAC name is: 2-[4-(2-chloro-4-nitrophenyl)diazenyl -N-ethylanilino]ethyl-trimethylazanium . The chemical structure consisted from two phenyl ring connected by azo bridge with different poison functional groups.

MATERIALS AND METHODS

Theoretical calculations were performed using computational implemented in the Hyperchem package 8.0.9 (2011) [11]. Optimized geometries of basic red18 been done with PM3-CI(4x4) [12,13]. The estimation of reactivity of basic red 18 toward the photodegradation reaction has been done by the calculation of Electrostatic potential , atomic charge, bond lengths ,the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are performed [14, 15].

RESULTS AND DISCUSSION

Energetic properties of basic red 18 were calculated using geometry optimization, semi-empirical method (PM3) as shown in figure1.

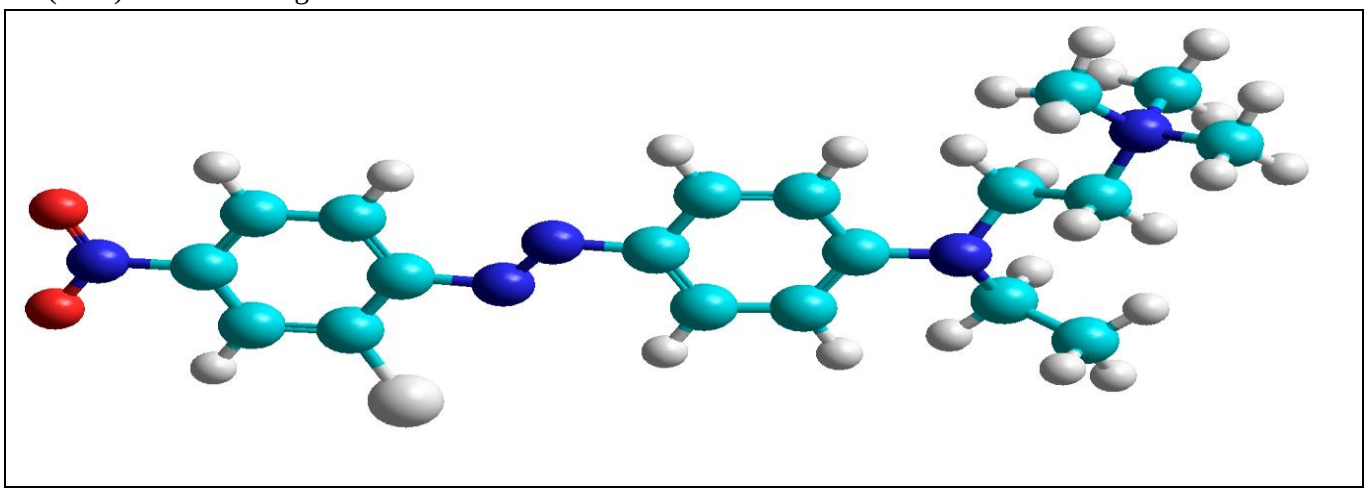
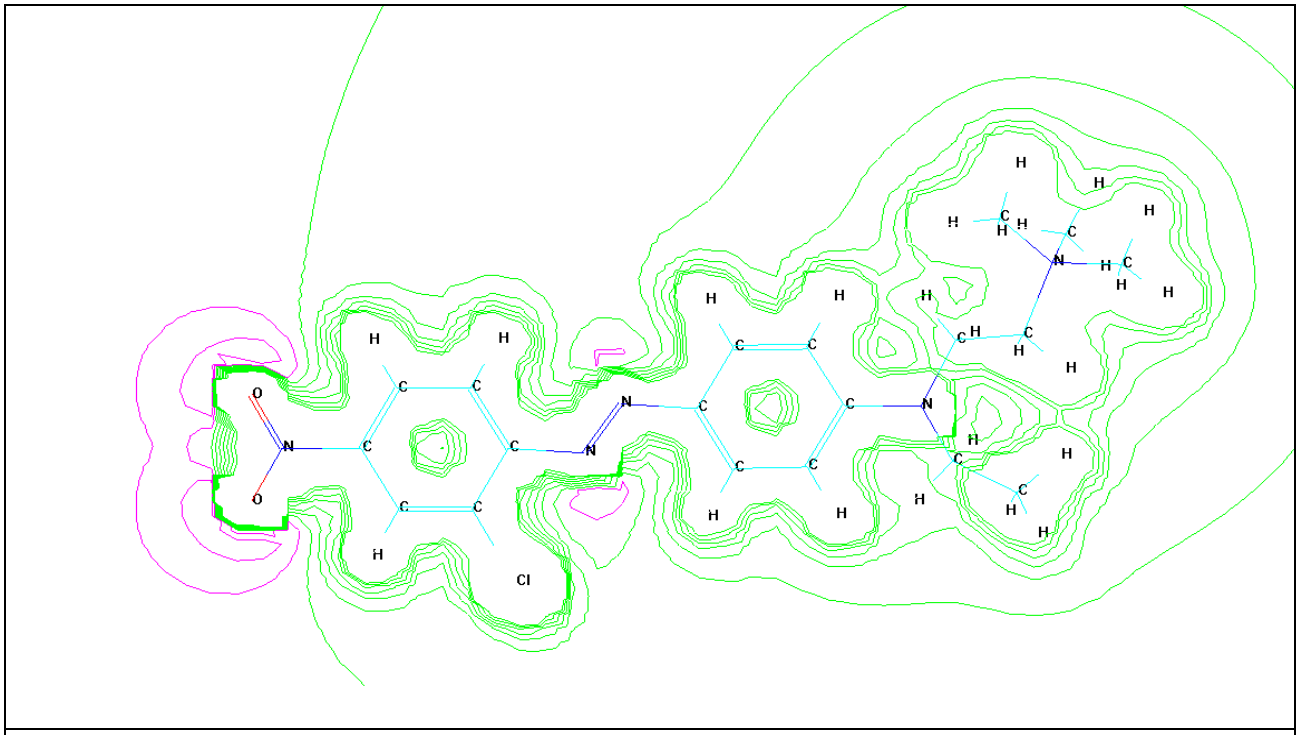
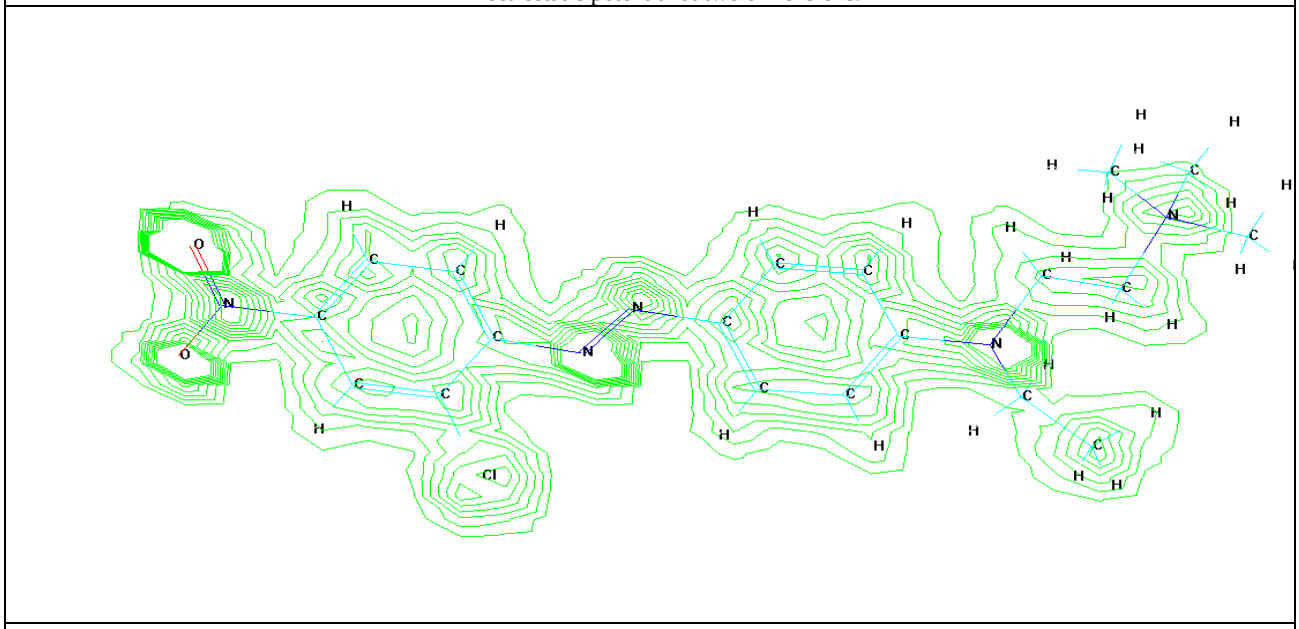


Figure.1 Geometry optimization of Basic Red 18 Balls and cylindrical view.

Geometry Optimized : The calculated electrostatic potential illustrated the active site of basic red 18 molecule .The positive side of electronic density is focused into hydrogen atoms provided with green color and negative side of electronic density is focused into oxygen atoms provided with red color .The atomic charge of basic red 18 that all the carbon atoms of phenyl ring have negative charge ,in another view the nitrogen atoms of azo bridge (N10=N11) have negative charge equal to -0.015 and -0.008 coulomb respectively and oxygen atoms of nitrite group (O8,O9) have negative charge equal to –0.588 and -0.584 for respectively. Figure 2 shows the electrostatic view.



A-Electrostatic potential at two dimensions.



B-Total charge density at two dimensions.

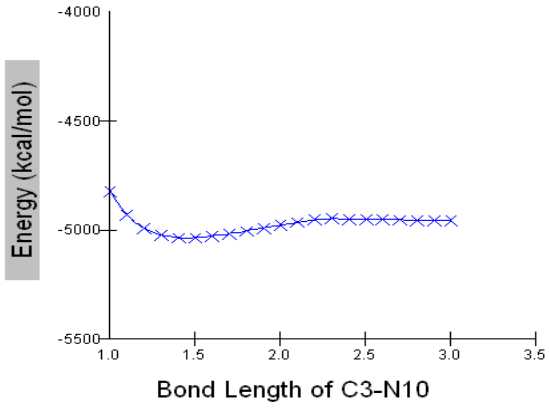
Figure 2. electrostatic view of basic red 18.

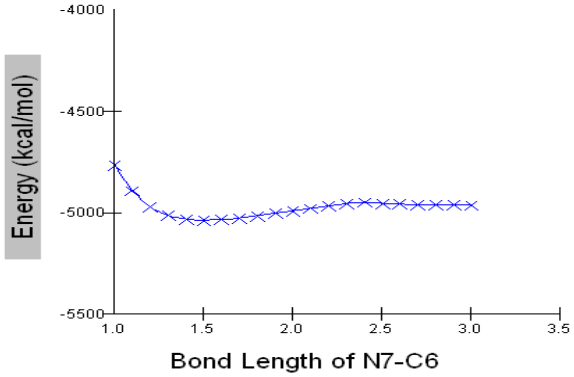
Bond strength has been measured for the main important bonds table 1.illustrates the stability of bond calculated by PM3 method. By comparing these bonds, they found the C3-N10 and C20-N21 as highest stable rather than other bonds is due to the break down at 1.43978Åwith 62.4873 kcal mol^{-1} and

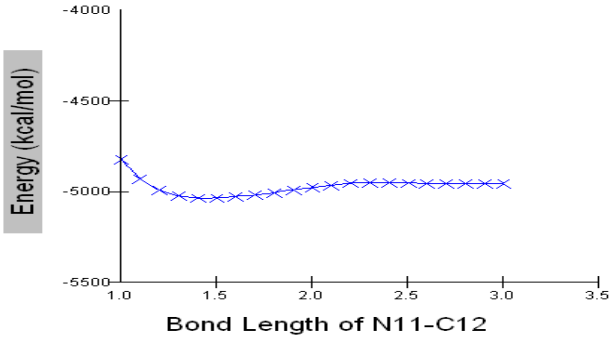
1.53272Åwith 64.9556 kCal mol^{-1} of bond dissociation energy have highest probability to enter the first cleavage step of basic red 18.figure 3 shows the potential energy stability of bonds length [16].

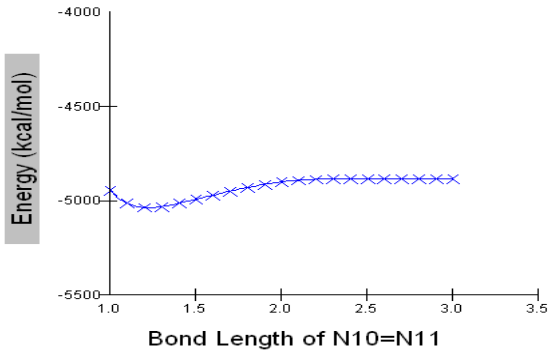
Table 1. Potential energy of stability and dissociation of Basic Red18 bonds calculated by kCal mol^{-1}

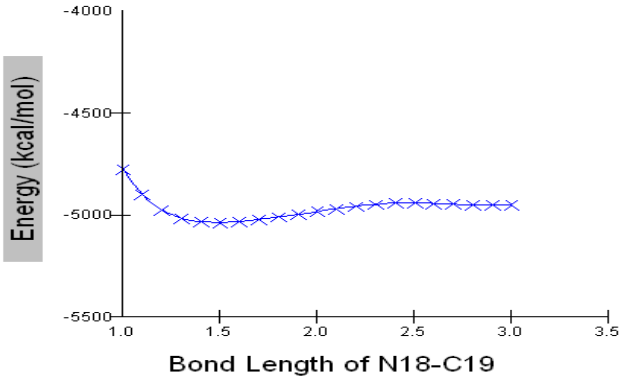
Bonds	Bond length Å	Energy of stability	Energy of dissociation	dissociation energy of Bond (ΔE)
N7-C6	1.50614	-5031.944	-4958.1254	73.8194
C3-N10	1.43978	-5033.4833	-4970.996	62.4873
N10=N11	1.23555	-5030.216-	-4886.2597	143.9566
N11-C12	1.44082	-5033.5068	-4956.9956	76..5108
C15-N18	1.45715	-5034.0039	-4929.5527	104.4512
N18-C19	1.48985	-5035.0097	-4949.9501	85.0596
C19-C20	1.53741	-5033.6201	-4950.5224	83.0977
C20-N21	1.53272	-5033.4438	-4968.4882	64.9556
N21-C24	1.51762	-5032.7065	-4940.1914	92.5151
N18-C22	1.50211	-5031.4721	-4942.2954	89.1767
C22-C23	1.51731	-5033.0722	-4932.2768	102.7954
N21-C25	1.51643	-5035.6621	-4960.4663	75.1958
N21-C26	1.5168	-5032.6474	-4968.488-	80.1372

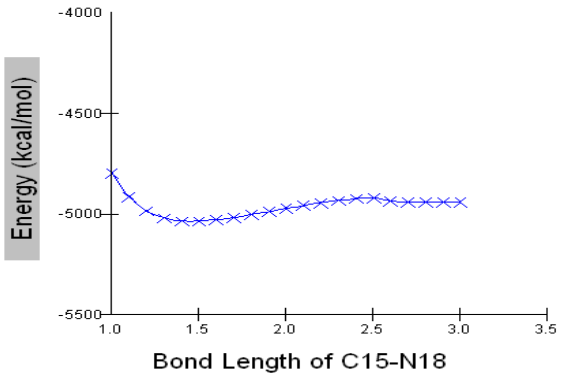









Energy (kcal/mol)
-4000
-4500
-5000
-5500
1.0
1.5
2.0
2.5
3.0
3.5
Bond Length of N18-C19


Energy (kcal/mol)
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-5500
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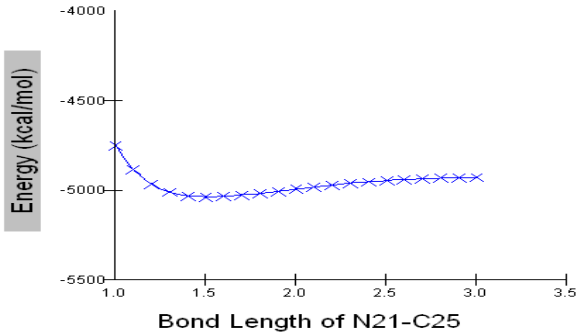
1.5
2.0
2.5
3.0
3.5
Bond Length of C15-N18


Energy (kcal/mol)
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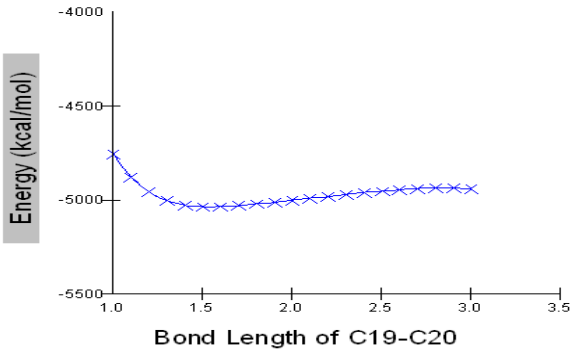
2.0
2.5
3.0
3.5
Bond Length of N21-C25


Energy (kcal/mol)
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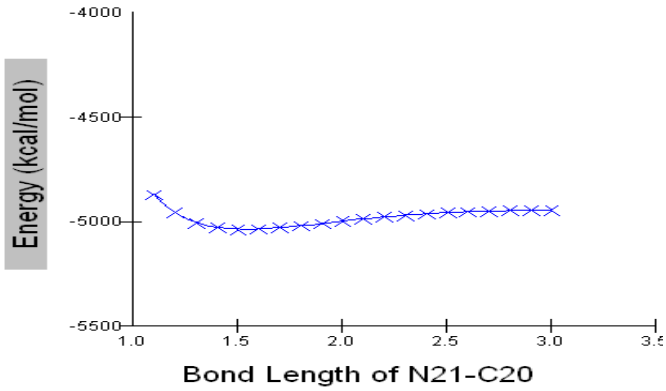
1.5
2.0
2.5
3.0
3.5
Bond Length of C19-C20


Energy (kcal/mol)
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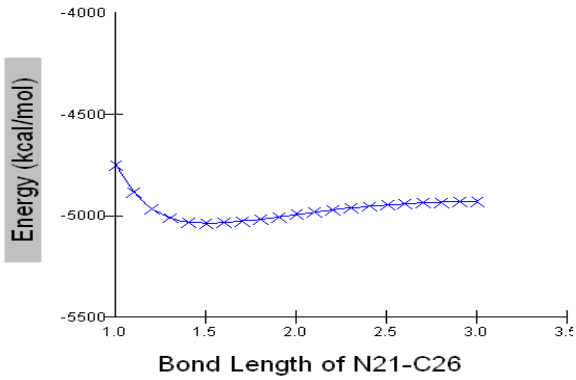
1.5
2.0
2.5
3.0
Bond Length of N21-C20


Energy (kcal/mol)
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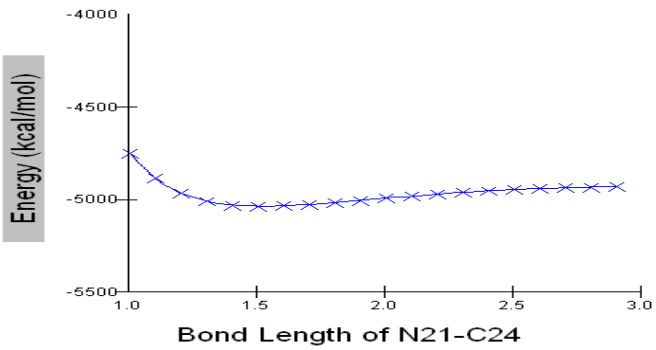
-5000
-5500
1.0
1.5
2.0
2.5
3.0
Bond Length of N21-C26


Energy (kcal/mol)
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-5500
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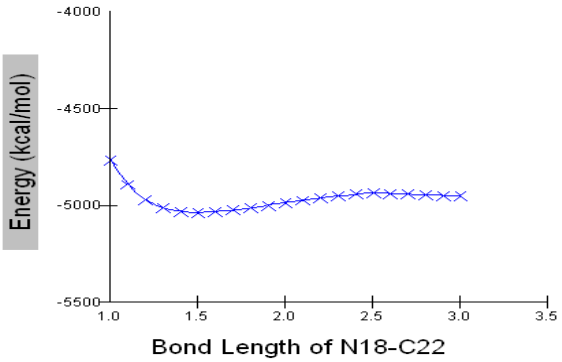
1.5
2.0
2.5
3.0
Bond Length of N21-C24


Energy (kcal/mol)
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-5000
-5500
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1.5
2.0
2.5
3.0
3.5
Bond Length of N18-C22

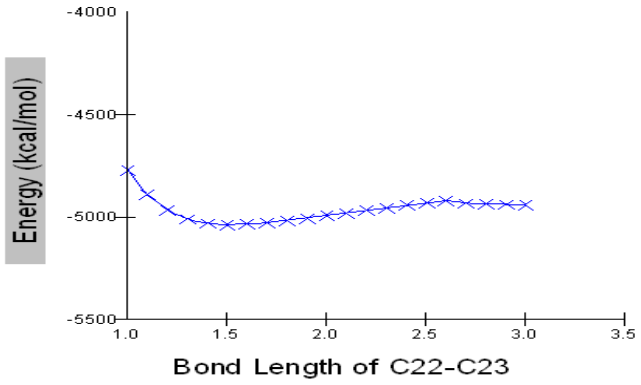


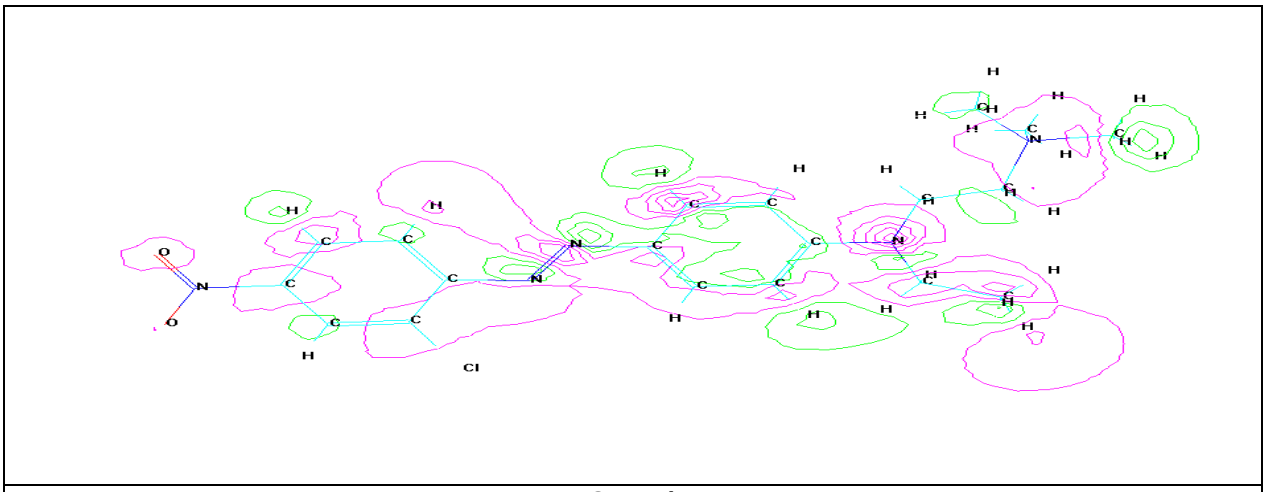
Figure 3. Potential energy stability of bond length of Basic red 18.

Potential energy stability of bond angles: Potential energy stability of main bond angle in Basic Red 18 molecule represents in Table2.The C25-N21-C24 has lowest angle value (108.747 degree) compare with other angles, so this angle is lowest stability (more active) than other angles.

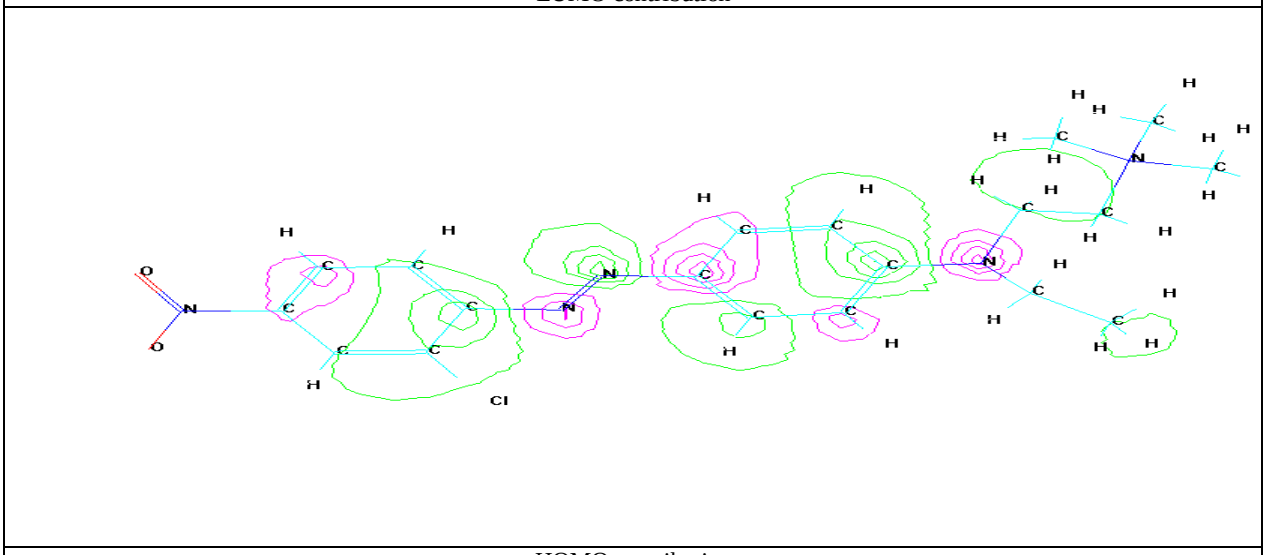
Table2. Potential energy stability of Basic Red18 angles calculated by degree units.

Bond angle	Bond angle stability
C6-N7-O9	119.103
C6-N7=O9	118.993
O8=N7-O9	121.903
C3-N10=N11	120.027
N10=N11-C12	119.754
C15-N18-C19	115.921
C15-N18-C22	116.036
C19-N18-C22	111.655
C19-C20-N21	113.099
C26-N21-C24	109.556
C26-N21-C25	109.493
C25-N21-C24	108.747
N18-C22-C23	111.685

The calculation of the molecular orbital (HOMO,LUMO) equal to -11.16068ev , -4.417902 eV since the energy gap equal to 6.742778eV as shown in Figure 4.This figure shows the nitrogen atoms is electrophilic attack due to the highest electronic density of HOMO orbital nitrogen atom show maximum net atomic charges and electron densities, that's focused on the part of this molecule, while the hydrogen atoms is nucleophilic attack because the highest density of LUMO orbital act accepted electron is focused on the this part [17].



LUMO contribution



HOMO contribution

Figure 4. Molecular orbital estimation in two dimensions view.

CONCLUSIONS

The bonds C3-N10 and C21-N18 are lowest stable bonds than other bonds in the basic red18, that's have heights probability to encourage the first cleavage step. The dye molecule has two different side of reactivity towards the reactions, one of them is electrophilic in nitrogenic atoms site and the other sites are nucleophilic sites.

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