International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 9 No. 3 Nov. 2014, pp. 1362-1367
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http://www.ijias.issr-journals.org/

# Density functional theory study of Reactive Violet 5R azo dye

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**ABSTRACT:** The destructive oxidation of dyes and textile effluents has recently received considerable attention since colored aromatic compounds have proven to be degraded effectively by a variety of AOPs. We calculated its electronic and optical properties by using DFT and TD-DFT methods at B3LYP/6-311+G(,p) level in solvent (IEF-PCM model) To determine the reactivity and the active sites of azo dye reactive violet5R (V5R). The results showed that V5R is polar and high soluble in water. A good correlation was obtained between the predicted and experimental absorption bands of V5R (R2=97%).

**KEYWORDS:** Reactive violet 5R, DFT, TD-DFT, UV/vis, PCM.

## 1 INTRODUCTION

Several industries, such as textile, ceramic, paper, printing and plastic use dyes in order to color their product. In the coloring process, these industries also consume substantial volumes of water, and as a result, large amount of colored wastewater are generated. The present of dyes in water is undesirable since even a very small amount of these coloring agents is highly visible and may be toxic to aquatic environment [1–5]. Azo dyes, characterized by nitrogen to nitrogen double bonds (–N=N–), account for up to 70% of all textile dyestuffs produced, and are the most common chromophore in reactive dyes [6].

Many physical and chemical methods including adsorption, coagulation, precipitation, filtration, and oxidation have been used for the treatment of azo dye-contaminated effluents [7]. Jain et *al.* studied the degradation of Violet 5R (V5R) in a mixture of bacterial strains and they proved the potency of bioremediation strategy in decolorizing and degrading VR5 [8]. Density functional theory (DFT) is a convenient method to determine the electronic properties and reactivity of azo dyes.

Time dependent density functional theory (TDDFT) appears the most reliable method to predict UV/vis spectra of azo dyes with an intermediate size[9-10]. Jacquemin et *al.*reported the methodology choice and reproduction of the UV/visible spectra of a large series of dyes by using PBE0 and B3LYP hybrid functionals in polarisable continuum model (PCM) [9, 11, 12,13].

In this paper, focus is on determining the electronic and optical properties of V5R azo dyes by using DFT and TDDFT methods.

## MATERIALS AND METHODS

### *Materials*

- Violet 5R azo dye was obtained from hight school of textiles, Casablanca, Morocco.

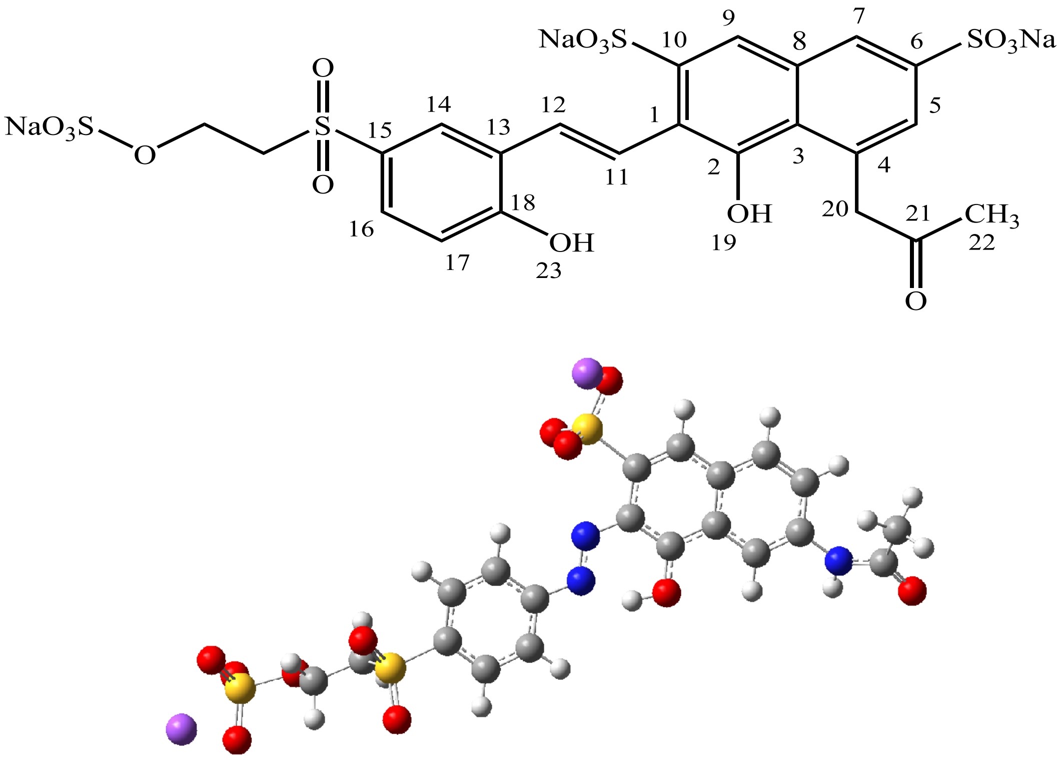


*Fig.1. Chemical and optimized structures of violet 5R obtained at B3LYP/6-31+G(d,p) level*

***Table.1 Violet 5R molecul***

| | | |
|---|---|---|
| **Name** | Reactive Violet 5R | |
| **Synonyms** | 2,7-naphthalenedisulfonic acid | |
| **Molecular Structure** | Molecular Formula: | C20H16N3Na3O15S4 |
| | Molecular Weight: | 735.58 |
| | CAS Registry Number: | **12226-38-9** |

- Experimental UV/visible spectra for reactive Violet 5R azo dye was recorded on a *spectrometer in our laboratory* in water solvent.

## THEORETICAL DETAILS

Geometry optimization and frequency calculations for colorant V5R have been carried out at B3LYP/6-31+G(d,p) level (DFT method) as implemented in Gaussian 09 [14]. To determine the reactivity of violet5R , the electronic properties were calculated at the same level of theory (B3LYP/6-31+G(d,p)).

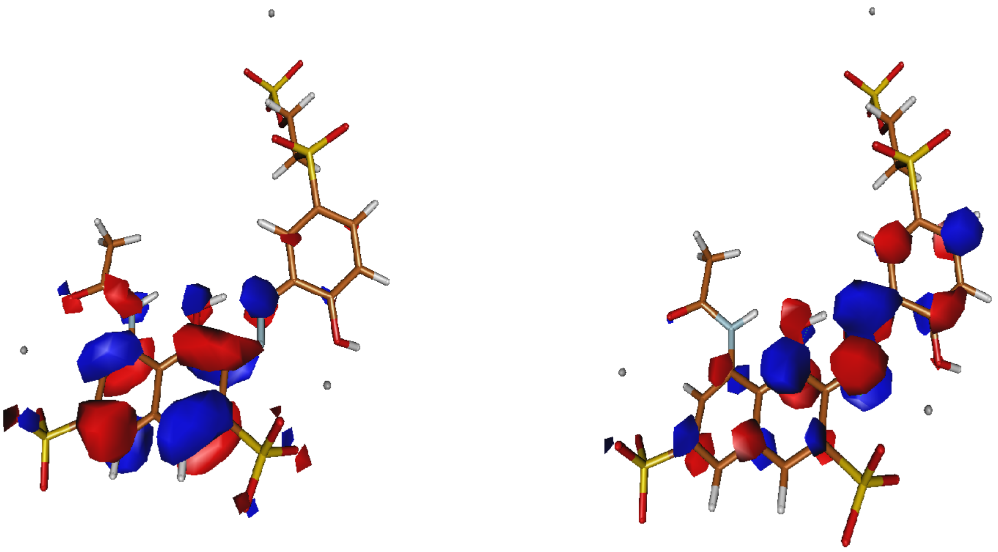
The condensed Fukui functions were computed using Mulliken population analysis method [15].

Excited singlet state (ES) energies were calculated from the optimized geometries at B3LYP/6-31+G(d,p)level (TDDFT method)[16]. In PCM model, the solute is embedded into a cavity surrounded by a dielectric continuum characterized by its dielectric constant ($\varepsilon_{CH3OH}$=32.613)[17]. The molecular orbitals and the optimized geometries were visualized by using Molden software (http://www.cmbi.ru.nl/molden/) and Gaussian View 5, respectively.

## RESULTS AND DISCUSSION

### ELECTRONIC PROPERTIES OF VIOLET 5R

The free solvation energie for V5R is -109 kcal/mol. It's highly soluble in water. its chemical structure containing hydrophobic (phenyl rings) and hydrophilic (hydroxyl groups) parts. The high polarity of V5R is corroborated by the high values of permanent dipole moments of V5R 34 Debye, it’s an important parameter to determine the reactivity in molecular systems it represents a measurement of charge distribution in a molecule (Fig.2).



***HOMO*** ***LUMO***

***Fig.2. HOMO and LUMO charge distribution of V5R obtained at B3LYP/6-31+G(d,p) level.***

Violet 5R has the capacity to polarize other systems because of the high polarisability values of this reactive dye: 665 Boh$^3$ . The low energy of the LUMO orbital indicates that this azo dye can behave as soft electrophiles. The ionization potential (IP) is the energy required to remove an electron from the outer shell of a molecule system. High IP values indicate that the molecular system does not lose its electrons with facility. While, adding an electron to a molecular system is defined as electronic affinity (EA). High E.A values indicate that molecular systems tend to take electrons easily.

Violet 5R, azo dye has small gap energie (2.94 eV), which indicates that the azo dye is less stable and more reactive systems. Table 2 reports the electronic properties associated with the chemical potential for V5R.

To determine the active sites through Fukui indices for V5R, two types of charge distribution are calculated (i) electrostatic potential(ESP) and (ii) natural population (NPA) charges. In accordance with Fukui indices showed in Table 2, nitrogen atom N11 of the double N11=N12 for V5R is suggested to be a site for nucleophilic attack. This result is confirmed by the charge distribution in the LUMO orbitals of V5R (Fig.2), in which a high electronic density in nitrogen atoms of the double N11=N12 is present. In a recent study, Tizaoui and Grima reported that the oxidation of azo dyes by ozone proceed through electrophilic attack, and the attack occurs on sites possessing high negative charge density including multiply bonded species such –C=C- or –N=N- double bonds [18].

***Table.2. Fukui indices of V5R calculated at IEF-PCM/B3LYP/6-31+G(d,p) level.***

| | Violet5R | | |
|---|---|---|---|
| | Nucleophilic Attack | Electrophilic Attack | Radical Attack |
| C1 | -0.045 | -0.166 | -0.106 |
| C2 | 0.003 | 0.005 | 0.004 |
| C3 | -0.076 | -0.035 | -0.056 |
| C4 | 0.044 | -0.007 | 0.019 |
| C5 | -0.069 | -0.151 | -0.110 |
| C6 | 0.000 | 0.061 | 0.030 |
| C7 | -0.041 | -0.187 | -0.114 |
| C8 | -0.008 | 0.097 | 0.045 |
| C9 | -0.061 | -0.179 | -0.120 |
| C10 | 0.031 | 0.043 | 0.037 |
| N11 | -0.122 | 0.051 | -0.036 |
| N12 | -0.182 | -0.065 | -0.123 |
| C13 | 0.061 | -0.031 | 0.015 |
| C14 | -0.073 | 0.001 | -0.036 |
| C15 | 0.012 | -0.018 | -0.003 |
| C16 | -0.102 | -0.042 | -0.072 |
| C17 | -0.002 | 0.001 | 0.000 |
| C18 | -0.053 | -0.017 | -0.035 |
| O19 | -0.092 | -0.055 | -0.074 |
| N20 | -0.041 | -0.065 | -0.053 |
| C21 | 0.014 | 0.034 | 0.024 |
| C22 | 0.007 | -0.013 | -0.003 |
| O23 | -0.002 | -0.008 | -0.005 |

Electrophilic attack can be in different sites e.g. C1, C5, C7 and C9 for V5R. The charges distribution in HOMO orbitals for V5R confirmed that the mentioned positions are sites of electrophilic attack (Fig.3). Hihara et *al,* showed that C1=C2, C4=C5, C6=C7, C13=C14, C13=C18 and N11=N12 are almost all possible double bonds that can react with the single oxygen ($^1O_2$)[19]. The C9 and N12 are the favoured sites for radical attack in V5R i.e RO16 [20]. The authors excluded the reactivity of C3=C4 and N11=N12 with the $^1O_2$ due to the low electron density, $d_{HOMO}$ of the HOMO orbitals (See Fig. 2). The electrophilic site obtained by using NPA or ESP are in good agreement with the results obtained by Hihara et al [19].

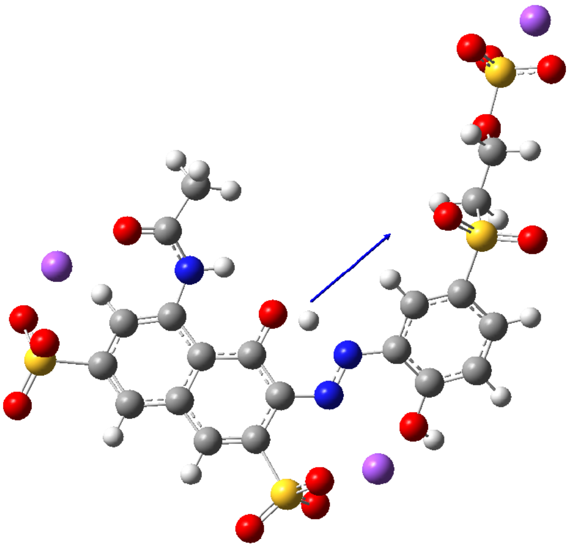


***Fig.3. Dipole moment orientations of V5R obtained at B3LYP/6-31+G(d,p) level.***

## UV/VIS SPECTRA OF V5R

The experimental UV/vis spectra of V5R were obtained in water solvent. The calculated electronic excited states are performed in gas and in PCM by using TD-DFT method at B3LYP/6-31+G(d,p) level (Table 3). The maximum absorption bands at 565 nm for V5R. The high absorption band obtained for V5R (565 nm) compared to RO16 (490 nm) [20] can be explained by increasing the conjugation in V5R with respect to RO16 (see HOMO orbitals of RO16 [20]). The maximum absorption band at 565 nm of V5R was obtained by using the equation of the linear correlation between gas and PCM values of V5R(Fig 4).

***Table.3. Electronic properties of V5R calculated at IEF-PCM/B3LYP/6-31+G(d,p) level.***

| | IA (eV) | EA (eV) | $\chi$ (eV) | $\eta$ (eV) | S (eV) | $\omega$ (eV) | $\alpha$ (Bohr$^3$) | $\mu'$ (Debye) |
|---|---|---|---|---|---|---|---|---|
| **Orbital consideration** | 6.20 | 3.25 | 4.72 | 2.94 | 0.17 | 3.79 | 665.27 | 34.19 |
| **Energy consideration** | 6.20 | 3.25 | 4.72 | 2.94 | 0.17 | 3.79 | 665.27 | 34.19 |

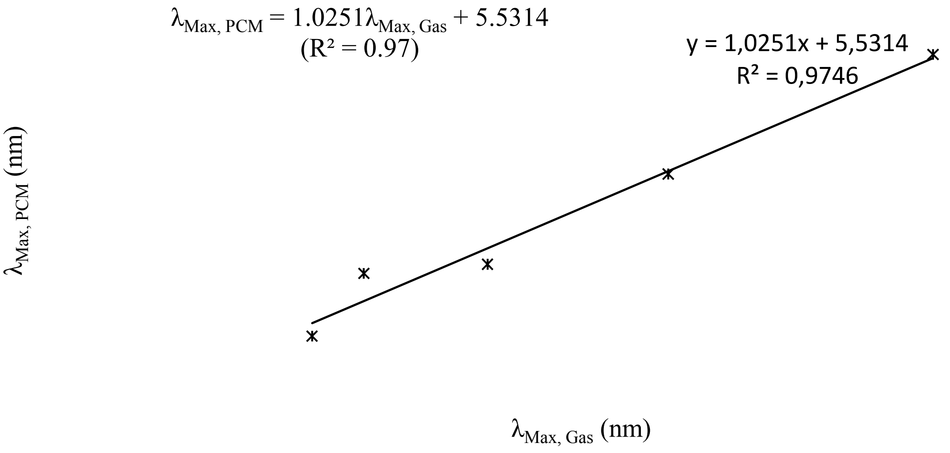


***Fig.4 . Linear correlation between calculated and experimental absorption bands for V5R obtained at B3LYP/6-31+G(d,p) level.***

The calculated absorption bands were underestimated in the gas phase. The PCM solvent induces a bathochromic shift of the absorption bands. A good correlation was obtained between the calculated and experimental absorption band values of V5R ($R^2$= 97 %).

## CONCLUSION

Using DFT method we showed that V5R is polar and high soluble azo dye in water, and N11 is the most active site involved in the degradation process . The UV/vis spectra of V5R is well reproduced using TDDFT method ($R^2$=97%) and the high maximum absorption band observed in V5R with respect to RO16 is mainly due to the extent of HOMO delocalization in V5R.

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