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Research Article

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Posted Date: May 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-502073/v1>

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Computational Exploration of Spectroscopic and hydrogen bonding analysis of Direct orange 26 Dye in combination with experimental and TD-DFT calculations.

By

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ABSTRACT:

The importance of this study stems from, it concentrates on new approach applying both practical and theoretical aspects to study structure of Direct orange dye 26 (DO-26) as an important dye widely used for dyeing of cotton or viscose for red orange direct printing. It also can be used for silk, wool, polyvinyl alcohol, polyamide fiber fabric and pulp dyeing. It proficiently compare practical with theoretical results of structural identification of the given important dye, via careful inspection of various phenomena detected in its two symmetrical arms around urea center. Direct orange dye 26 (DO-26) structure has been studied applying both practical spectroscopic and theoretical investigations. DFT-B3LYP/6-311++G(d,p) calculations are performed to investigate its structure, and the electronic vibrational properties. Correlation is found between experimental and calculated data. An intra-molecular hydrogen bonding interaction had been detected and characterized in dye skeleton using Atoms-in-molecule analysis employment. The hydrogen bonding present in the dye structure affecting its vibrational properties had been discussed. Natural population analysis like HOMO and LUMO and high quality molecular electrostatic potential plots along with various electronics had been presented at the same level of theory. Chemical reactivity descriptors from conceptual density functional theory point of view, structure activity relationship descriptor were obtained. The experimental UV/Visible and FT-IR spectral data of the dye DO-26 (**D1**) had been presented. These data had been supported by TD-DFT calculations to simulate the experimental spectra with computing the natural transition orbitals (NTO) and the orbital composition. The variation of charge transfer length (Δr) and variation in its dipole moment with respect to ground state ($\Delta\mu_{CT}$) had been computed in order to study the charge redistribution due to the excitations. Actually there is a problem that, degradation of this dye in wastewater by different techniques leads to various unknown fragments but on using theoretical possibilities it can be expected what happened in practical work.

Keywords: DFT-TD-DFT, DO-26 dye; Normal modes /FTIR, NTOs, Bader's atoms-in-molecule (AIM), transfer length (Δr)-ground state ($\Delta\mu_{CT}$).

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Highlights

- **This research deals with both practical and theoretical aspects to study structure of Direct orange dye 26 (DO-26).**
- **It is an important dye widely used for dyeing of cotton, silk, wool, polyamide fiber and pulp dyeing.**
- **The experimental UV/Visible and FT-IR spectral data of the dye DO-26 (D1) had been presented.**
- **This study involved careful inspection of various phenomena detected in its two symmetrical arms around urea center.**
- **DFT-B3LYP/6-311++G(d,p) calculations are performed to investigate its structure, and the electronic vibrational properties.**

1. Introduction

The relatively large direct dyes molecules are of great high affinity to cellulose fibers and mostly bind to them via Vander Waal forces. Direct dyes are those of more than one azo group, phthalocyanine, stilbene or oxazine containing compounds. In the color index, considered the direct dyes form the second largest dye class with respect to the amount of different dyes [1]. DO-26 is reddish orange to light yellowish red color textile dye. Therefore; DO-26 can be used for dyeing cotton or viscose for red orange direct printing. It also can be used for silk, wool, polyvinyl alcohol, polyamide fiber fabric and pulp dyeing [2–5]. The commercial dyestuff DO-26 has a general formula $C_{33}H_{22}N_6Na_2O_9S_2$ of M.Wt. = 756.67 g mol⁻¹ [6].

Pollution of water by dyes is a serious problem in developed countries. Approximately, 1–10% or more of dyes are discharged into waste streams without treatment by the textile industry worldwide. The effluents from the textile dyeing industry contain many organic pollutants and are a serious environmental hazard because of their lasting color, high chemical oxygen demand, and non-biodegradability [6]. Therefore, the understanding spectroscopic vibrational, electronic structural, tautomerism, electronic excitation, chemical reactivity and hydrogen bonding analysis of DO-26 to removal of dyes from waste water are a challenge for the affected industries.

DFT has been considered as an efficient tool for dyeing structural and vibrational properties of biomolecules [7, 8]. DFT when incorporated by proper functional exchange–correlation; it provides sufficient confidence about the results. For computational low cost B3LYP hybrid functions became popular because of its accuracy; it is combined with Becke three parameters exchanges and

with Lee, Yang and Parr's correlation. The B3LYP function combined with 6-311++G(d,p) basis set were used to calculate structure and vibrational properties of direct dye DO-26 molecule. On comparison of FTIR and UV-Visible spectra of DO-26 are shown good correlations between experimental and computational data. Most molecular calculated properties were electronic and thermodynamic. It also involved estimation of chemical reactivity and reaction paths. In DFT also Natural population analysis (NPA), HOMO, LUMO and molecular electrostatic potential (MESP) surfaces were calculated. They were used to discuss resulting intra-molecular charge transfers and electron density distribution.

Hydrogen bonding plays a pivotal role in determining the structures and properties of biomolecules [9]. The study of hydrogen bonding phenomena had been successfully studied applying Bader's atoms-in-molecule (AIM) theory [10]. The nature and strength of various types of hydrogen-bonded interactions had been efficiently described by the AIM theory. The AIM theory is able to describe the change in electron density distribution in a molecule as a result of either bond formation or complex formation. The reliability and stability in the values of AIM parameters have been studied and it was found that they are almost independent of basis set on the use of functional B3LYP in DFT [11]. However, it has been noticed that B3LYP function estimates weak intramolecular interactions as well as charge transfer effects [11–13].

2. Experimental

2.1. Chemicals and procedures

DO-26 was purchased from Anil Dyes and Chemicals Industries (India). A Perkin Elmer lambda 4B spectrophotometer had been used for measurements of the UV/Visible absorption spectra of the dye using 1.0 cm fused quartz cells at room temperature. A stock solution (400 mg/L) of Direct orange textile dye with the M.Wt. = 756.67 g mol⁻¹ was prepared by dissolving 200 mg in small amount of distilled water, then the solution was completed to 500 mL measuring flask. Dilute aqueous solutions of (1.057 x 10⁻³ M) DO-26 were used for most measurements in 10 mL measuring flask.

The FT-IR spectra of KBr discs containing D1 had been measured at wavenumber region 4000 – 400 cm⁻¹ using FTIR 4100, JASCO spectrophotometer.

2.2. Computational details

The Gaussian 09W software package [14] had been used for theoretical calculations. The molecular geometry for the studied compound had been fully optimized using density functional theory B3LYP method by using 6-311++G(d,p) basis set [15, 16]. Where (B3) [17–19] stands for Becke's three parameters combined with gradient-corrected functions of Lee, Yang and Parr (LYP) [20], During geometry optimization no symmetry constrains had been applied [21, 22]. The choice of

basis set 6-311++G(d, p) is mainly due to its flexibility, accuracy, consistent and better performance when using diffused Gaussian type triple- ζ potential [23, 24]. The vibrational frequencies have been determined and checked and proved that, all structures correspond to true minima of the potential energy surface at the same level of theory.

The Gaussian 09W software package has been used for NBO calculations using NBO 3.1 program implemented in the same program. The Gauss View version 5.0.9 [25] involving Chemcraft version 1.6 package [26] had been used throughout this work to optimize the structures of tested compounds. In addition, the Multiwfn v3.8 software program [27] has been used to compute quantum chemical descriptors from point of view of conceptual density functional theory (CDFT). The Multiwfn v3.8 software program [27] has been also used for Atom in molecule (AIM) analysis. The vertical linear-response TD-DFT approximation [28] has been also used for calculation of the first 80 low-lying excited states. The Polarizable Continuum Model (PCM) [29, 30] has been included in all steps of a modeling of bulk solvent effects.

Computing the natural transition orbitals (NTO) [31] have been used in analyzing the electronic properties of tested molecules excited states. The molecular fragments to occupy (occ.NTOs) and virtual natural transition orbitals (virt NTOs) had been performed by the orbital composition analysis taking into consideration the Hirshfeld percent contributions. The Multi wave function v3.8 software program [27] had been used to estimate the electronic transitions between the ground state (S_0) and the low-lying singlet excited states (S_n). In order to study the charge redistribution due to the excitations in tested molecules; the variation in dipole moment with respect to ground state ($\Delta\mu_{CT}$) [27] and the charge transfer length (Δr) [32][33] were computed.

The VMD 1.9 program [33] has been used for rendering the color mapped isosurface graphs of electrostatic potential (ESP) of the ground states of the studied dye; based on the data outputted by Multiwfn program. The VibAnalysis code [34, 35] with corresponding to VEDA program [36] has been used for calculation of the potential energy distribution (PED) for various vibrational normal modes of the studied DO-26 dye (**D1**).

3. Results and discussions

3.1. Density functional theory (DFT) studies

The molecular electrostatic potential maps, bond lengths, bond angles and dihedral angles as the optimized geometrical parameters were calculated. Also natural charges, natural population analysis, reactivity descriptors, and energetic were computed. All of these calculated parameters were analyzed for the studied dye D1 both in water and gas phases of the ground state and compared with the practical elemental analyses and spectroscopic data.

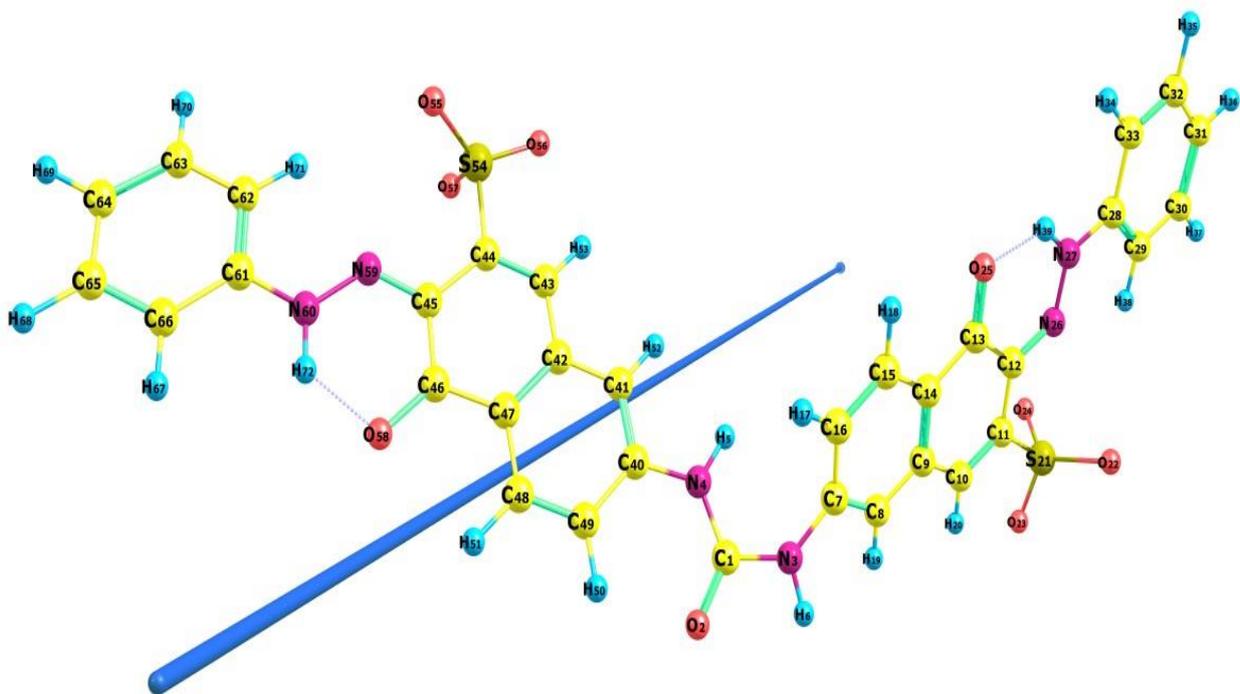
3.1.1. Optimized structure and hydrogen bonding of D1

Table (1) and Figure 1 present the computed parameters of D1 in this work; such as optimized geometry, numbering system, vector of the dipole moment, bond lengths, bond angles and dihedral angles.

Table 1. The values of computed parameters of DO-26 dye (D1) using B3lyp/6-311++G(d,p) (level of theory; selected bond lengths (A°), bond angles and dihedral angles).

Coordinate	Bond length (A°)	Coordinate	Bond Angles	Coordinate	Dihedral angles
R(C1,O2)	1.223	A(N3,C7,C8)	117.64	D(O2,C1,N4,C40)	5.74
R(C1,N3)	1.393	A(N3,C7,C16)	122.81	D(N3,C1,N4,C40)	-175.86
R(C1,N4)	1.377	A(C8,C7,C16)	119.44	D(C1,N3,C7,C8)	-151.94
R(N3,H6)	1.010	A(C7,C8,C9)	121.67	D(C1,N3,C7,C16)	31.98
R(N3,C7)	1.411	A(C12,C11,S21)	121.12	D(C1,N4,C40,C41)	-174.24
R(N4,H5)	1.010	A(C11,C12,C13)	120.19	D(C1,N4,C40,C49)	6.93
R(N4,C40)	1.411	A(C11,C12,N26)	116.82	D(N3,C7,C8,C9)	-175.75
R(C11,C12)	1.454	A(C13,C12,N26)	122.99	D(C8,C9,C10,C11)	-179.19
R(C11,S21)	1.851	A(C12,C13,C14)	117.12	D(C8,C9,C14,C13)	-179.99
R(C12,C13)	1.475	A(C12,C13,O25)	121.45	D(C9,C10,C11,S21)	178.10
R(C12,N26)	1.321	A(N26,N27,C28)	119.70	D(C11,C12,C13,O25)	179.93
R(C13,O25)	1.252	A(N26,N27,H39)	117.77	D(N26,C12,C13,C14)	-179.42
R(N26,N27)	1.303	A(C28,N27,H39)	122.53	D(N26,C12,C13,O25)	0.15
R(N27,C28)	1.401	A(N27,C28,C29)	121.09	D(C11,C12,N26,N27)	179.90
R(N27,H39)	1.030	A(N4,C40,C41)	117.23	D(C13,C12,N26,N27)	-0.32
R(C44,C45)	1.455	A(N4,C40,C49)	123.01	D(C12,N26,N27,C28)	179.75
R(C44,S54)	1.850	A(C41,C40,C49)	119.75	D(C12,N26,N27,H39)	-0.15
R(C45,C46)	1.476	A(C45,C44,S54)	120.81	D(N26,N27,C28,C29)	-0.30
R(C45,N59)	1.319	A(C44,C45,C46)	120.12	D(N26,N27,C28,C33)	179.76
R(C46,O58)	1.253	A(C44,C45,N59)	116.82	D(N4,C40,C41,C42)	-178.74
R(N59,N60)	1.306	A(C46,C45,N59)	123.06	D(C40,C41,C42,C43)	179.90
R(N60,C61)	1.400	A(C45,C46,C47)	117.16	D(C40,C41,C42,C47)	-0.06
R(N60,H72)	1.030	A(C45,C46,O58)	121.27	D(C41,C42,C47,C46)	-179.92
A(O2,C1,N3)	119.22	A(C47,C46,O58)	121.58	D(N59,C45,C46,O58)	-0.28
A(O2,C1,N4)	124.90	A(N59,N60,C61)	119.48	D(C44,C45,N59,N60)	179.90
A(N3,C1,N4)	115.86	A(N59,N60,H72)	117.72	D(C45,N59,N60,C61)	-179.67
A(C1,N3,H6)	110.27	A(C61,N60,H72)	122.80	D(C45,N59,N60,H72)	0.06
A(C1,N3,C7)	133.77	A(N60,C61,C62)	121.01	D(N59,N60,C61,C62)	0.18
A(H6,N3,C7)	115.93	D(O2,C1,N3,H6)	11.81	D(N60,C61,C62,C63)	179.97
A(C1,N4,H5)	116.56	D(O2,C1,N3,C7)	-170.64	D(C41,C42,C47,C48)	0.00
A(C1,N4,C40)	128.15	D(N4,C1,N3,H6)	-166.69	D(C44,C45,C46,O58)	179.89
A(H5,N4,C40)	115.18	D(N4,C1,N3,C7)	10.86	D(N59,C45,C46,C47)	179.67

Values are mean \pm SD triplicate assays.



DO-26 dye (D1)

Figure 1. The optimized geometry of DO-26 dye (D1) compounds using B3LYP/6-311++G(d,p) level of theory, the numbering system and vector of dipole moment.

The data in Table 1 refer to the maximum C–C bond length (among others) of 1.454 Å in naphthalene ring system that in good agreement with the reported value of 1.42 Å [37, 38]. The bond angle C37–C36–C27 calculated is found to be 119.75 Å; it shows excellent agreement with the reported value of 119.4 Å [37, 38]. The dye **D1** is considered urea derivative fragment in which the urea calculated bonds C1–O2, C1–N3 and C1–N4 give values of 1.223, 1.393 and 1.377 Å. The corresponding practical values of these bonds in **D1** are found to be 1.245, 1.345 and 1.329 Å. The selected angles in the tested dye O2C1N3 and N3C1N4 are found to be of the values 119.22° and 115.86°; while the respective angles in urea are found to be 120.34° and 118.29° [37, 38]. Thus, bonds are affected by the presence of two arms of **D1** (Figure 1) with sequence (right arm: C7 to H39) and (left arm: C40 to H58).

The computed values of dihedral angles around central urea derivatives are represented in Table 1. They show that, the angle N4C1N3C7 is of 10.9° degree right arm out of plane and the angle O2C1N4C40 is of 5.74° and degree left arm out of plane. This indicates that the carbon derivative is almost in the same molecular plane of urea. Also, atoms in angles C8C9C10C11, C11C12C13O25, C11C12N26N27, N26N27C28C29, N26N27C28C33 of the values 180, 180, 179.9, -0.3, 179.76 degree; refer to the planarity of

right arm component due to symmetry of the molecular structure. The left arm one is almost planar; which represented by angles N60C61C62C63, C41C42C47C48, C44C45C46O58 of values 180, 0.0 and 180.0 degrees respectively.

AIM theory calculations refer to the presence of hydrogen bonds in the skeleton of D1; that follows Koch and Popelier criterion [39]. The hydrogen bonding requires the existence of bond critical point (BCP) for the 'proton donor (H) and acceptor (A)' contact. Applying this theory to DO-26 it shows a lot of intra-molecular hydrogen bonding interaction O25-H39, O58-H72, O2-H50, O23H20, O74-H53 in diazo-carbonyl fragment in two arms. The application of this theory [39] actually required the value of electron density (ρ) in the range 0.002–0.040 a.u. and corresponding Laplacian ($\nabla^2\rho$) should be 0.024–0.139 a.u. These parameters have been calculated for the studied **D1** at BCP with sequence O25...H39, O58...H72, O2...H50, O23...H20, O74...H53 along with geometrical parameters of H-bonds and the data obtained are listed in Table 2.

Table 2. The calculated selected geometrical parameters (a.u) using B3lyp/6-311++G (d,p) level of theory, bond length (Å) and binding energy (kcal/mol) of DO-26 dye (D1).

There are three types of H-bonds have been detected in the basis of D1 topology [40] via calculated parameters. The characterization has been followed Rozas et al. [40] demands; at BCP in which; $\nabla^2\rho$ and $H < 0$ for strong H-bonding of covalent character. It also should be $\nabla^2\rho > 0$ And $H < 0$ for medium H-bond of partially covalent nature. Alternatively it should be $\nabla^2\rho > 0$ and $H > 0$ for weak H-bond. From the presented data in Table 2 it is clear that; Laplacian of charge density is positive for all BCP, $\nabla^2\rho = 0.15, 0.15, 0.066, 0.061, 0.062$ and 0.047 . Also the energy density $H < 0$ for the first two N27H39...O25 and N60H72...O58 and others is $H > 0$ suggesting the interaction to be medium H-bond of partially covalent nature in N27H39...O25 and N60H72...O58 and weak in nature for all other BCP. The value of $\nabla^2\rho$ is found to be negative and small in magnitude for strong covalent interactions, as in [Mn(III) porphyrin]Cl-trimethoprim complex ($\nabla^2\rho = -0.0786$ a.u.) [41]; and as in bis-dithiazolyl dimers [42]. By using $E_{\text{int}} = (V)$ at BCP as proposed by Espinosa et al [43]; the energy of interactions occur in tested dye has been theoretically calculated. The estimated interaction energy values of hydrogen bonding in the given dye for bonds O25...H39, O58...H72, O2...H50, O23...H20, O74...H53 are found to be -12.36, -12.41, -3.8, -3.53 and -3.57 kcal/mol, respectively. These data indicate the medium H-bond interactions for N27H39...O25 and N60H72...O58 bonds and other

bond are of week interaction [44]. The binding energy more accurate values have been obtained by applying another prediction equation [45] and the found values for bonds O25...H39, O58...H72, O2...H50, O23...H20, O74...H53 are found to be -8.78, -8.8, -3.26, -2.73 and -2.8 kcal /mol respectively.

4.1.2. The tautomeric relative stability of D1

From the above calculations and practical work data; the depicted three different tautomeric forms of the DO-26 (**D1**) dye are di-keto form (A, C₁₃=O₂₅, C₄₆=O₅₈), keto-enol forms (B and C) and di-enol forms (D and E) and corresponding four transition states (TS) (F-I) are suggested. The proposed relative potential energy surface diagram for different three tautomeric forms and TS of D1 (A–I), are represented in Figure 2.

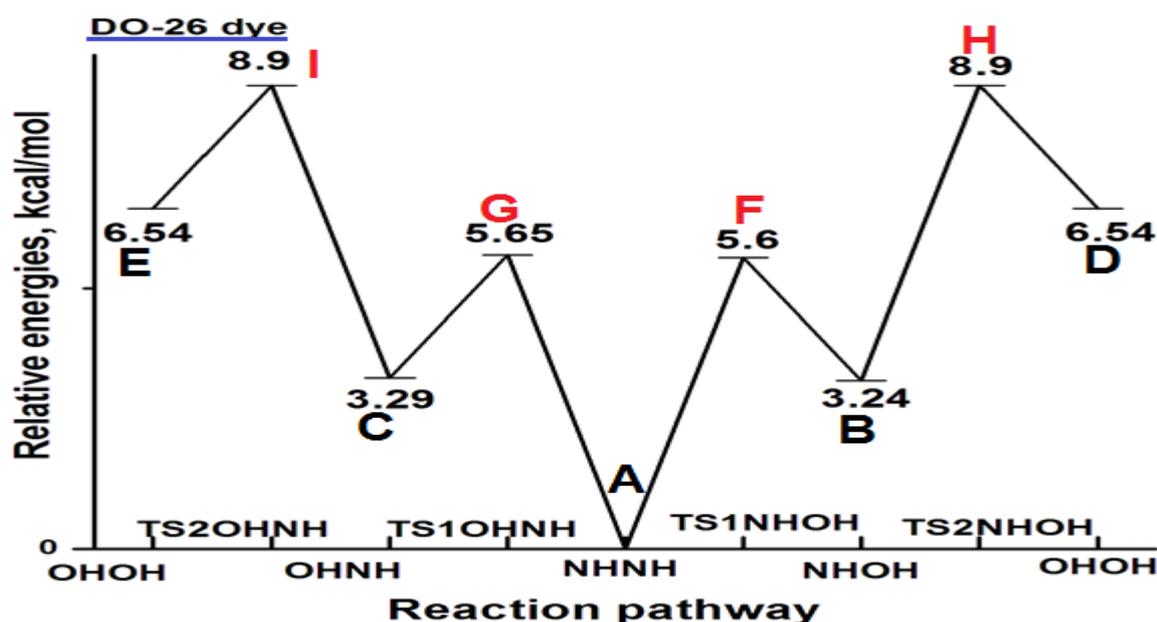


Fig. 2. Using the B3LYP/ 6-311++G(d,p) of the DFT theory; the calculated surface relative potential energy values are given for the different tautomeric forms transformations of DO-26 dye (D1).

Figure 2 represents data in this research; which give great benefit in explaining structural behavior of the studied dye and its stability. The DFT calculations reveal that the stability order of different forms (A-E) of the DO-26 dye is A > B > C > D= E as given by their calculated relative energy values of 0.0, 3.24, 3.29, 6.54 Kcal/mol respectively. These data refer to the di-keto form of D1 is the most stable tautomer in the gas phase. This conclusion is confirmed by the calculated energy values of corresponding four transition states (TS) (F-I) with respect to A with 5.6, 5.65, 8.9 Kcal/mol respectively; which have stability order of F<G<H=I (see Figure 2). The stability of the di-keto form (A) relative to the keto-enol (B), enol-keto (C) and the di-enol (D) forms may be attributed to the increasing in the strain effects within the moiety of these forms. On inspection of supplementary material (Figure S1), one can find transfer of the single proton between the oxygen

atoms (O25 or O58). On the other hand proton is moved in opposite directions relative to the nitrogen atoms (N27 or N60) (forms B and C). It is also noticed that; form C is less stable than form B; which may be attributed to the electrostatic attraction between the proton and the oxygen atom. The stability of **A** (the di-keto form) may be attributed to the planarity of right and left part arms for central carbonyl group C1=O2.

4.1.3. Normal mode analysis and FT-IR of D1

The vibrational normal mode analysis confirm that; the most of the calculated frequencies of the optimized geometry of D1 (**Figure 1**) are found to be real. Consequently; the D1 optimized geometry corresponds to a true minimum energy in the PES. The obtained frequency values applying the present theoretical model are scaled with a factor of 0.96 [46][46] to avoid errors due to neglect of inharmonic terms. All the vibrational modes are properly assigned applying the basis of PED. By using free VibAnalysis code [34, 35] with corresponding to VEDA program [36]; the various vibrational normal modes have been calculated. The calculated FTIR frequency intensities and assignments listed in Table 3; are selected in normal modes up to 400 cm^{-1} . All normal modes with all details up to 400 cm^{-1} are presented in Table S1 as supplementary information.

Table 3. Selected vibrational normal modes of analysis, including FT-IR values, for D1 obtained using B3LYP/6-311+G (d,p) level of theory

Figure (3a, b) presents simulated FT-IR spectra at 400 to 4000 cm^{-1} for DO-26 in comparison with experimental results. The DO-25 (**D1**) has two similar arms for the urea derivatives. Each arm is substituted naphthalene and benzene ring linked by diazonium fragment ($=\text{N}-\text{NH}-$). The N-H stretching frequencies of the rings are calculated and found to be in the range 3,473–3,133 cm^{-1} ; which is in good agreement with the found values in literature [47] of 3,200 and 3,500 cm^{-1} with strong or medium intensities.

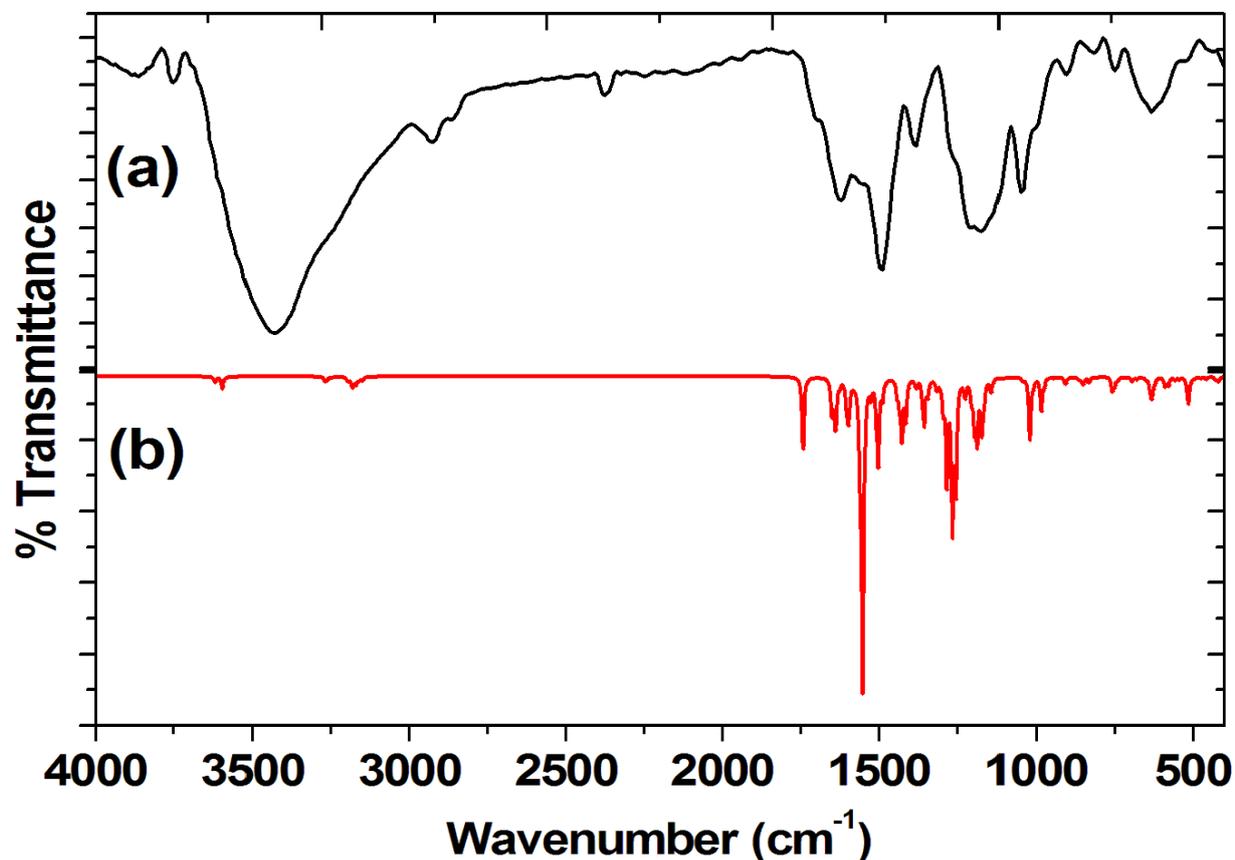


Figure 3. FT-IR spectra of the DO-26 dye (D1) in the region 400-4000 cm^{-1} : (a) Experimental spectra (b) simulated spectra.

N–H stretching vibration with a PED of almost 90-100 % is calculated at 3,473, 3,450, 3,138 cm^{-1} and presented in Table 3. The FT-IR practical value corresponding to this band is found to be 3,466 cm^{-1} . However, the NH group in acetyl-hydrazine molecule ($\text{CH}_3\text{-CO-NH-NH}_2$), is detected at 3,445 cm^{-1} and confirmed by the calculated one found at 3,640 cm^{-1} by DFT [48]. The N–H stretching band is apparently shifted due to hydrogen bonding with oxygen O25 or O58 attached to naphthalene ring. The inter-molecular hydrogen bonding in D1 is stronger than intra-molecular H-bonding as indicated by difference in calculated and experimental frequencies of the same dye indicates that.

The rings C–H stretching frequencies at the wavenumber range 3,117–3,024 cm^{-1} have been calculated. The C–H stretching of C49H50 group near to the C=O of central urea has been detected at 3,086 cm^{-1} ; which were found to be at 3,000 and 3,100 cm^{-1} with medium intensities in the published work [47]. The calculated C=C stretching vibrations and its mixing with other modes of naphthalene rings are found in lower region at frequency values of 1,574 and 1,559 cm^{-1} respectively. These theoretically calculated values are also correlated with that reported in literature [47] in which strong absorption band of naphthalene right arm has been detected at 1,571 cm^{-1} and falling range of 1,600–1,500 cm^{-1} .

The C–H bending of ring systems frequencies in plane and out of plane are calculated and found to be ascertained with C–C stretching region. The calculated C–H vibrational mode of strong intensity for naphthalene ring is found to be at $1,120\text{ cm}^{-1}$. The naphthalene ring torsion modes are always found in even lower frequency region [47].

The CH_2 stretching vibrations of weak intensities in the dye skeleton are detected at $2,954$ and $2,907\text{ cm}^{-1}$. The CH_2 bending vibration has been detected at $1,464\text{ cm}^{-1}$. The C–H lying between N14 and R3 stretching vibration has been practically detected as strong intensity band at $2,904\text{ cm}^{-1}$. The calculated C = O stretching band has been theoretically calculated at $1,625\text{ cm}^{-1}$; which actually fit the practically detected in FTIR value of D1 at $1,638\text{ cm}^{-1}$. These data are found to be in good correlation with the C = O stretching as a very strong band in the region $1,680\text{--}1,640\text{ cm}^{-1}$ previously reported elsewhere [47]. The C–N and C=N stretching vibrations coupled with N–H scissoring and CCN and HNN twisting vibrations respectively in acetyl-hydrazine molecule ($\text{CH}_3\text{--CO--NH--NH}_2$) are calculated and found to be $1,499$ and $1,428\text{ cm}^{-1}$. These theoretically calculated values are actually correlated with the practically detected values in the wavenumber range at $1,460\text{--}1,430\text{ cm}^{-1}$ in the FT-IR of tested dye. All of these bands of acetyl-hydrazine molecule ($\text{CH}_3\text{--CO--NH--NH}_2$) are found to be weak instead of intense band as previously reported [47]. The calculated frequencies belongs to N–N stretching has been practically detected at $1,300$ and $1,250\text{ cm}^{-1}$ respectively and bending vibrational deformation modes of the fragment of the same group has been practically detected at $1,352$ and 680 cm^{-1} . The theoretically calculated and experimental FT-IR frequencies of D1 at $400\text{--}4000\text{ cm}^{-1}$ are listed in Table 3 and graphically represented in Figure 4.

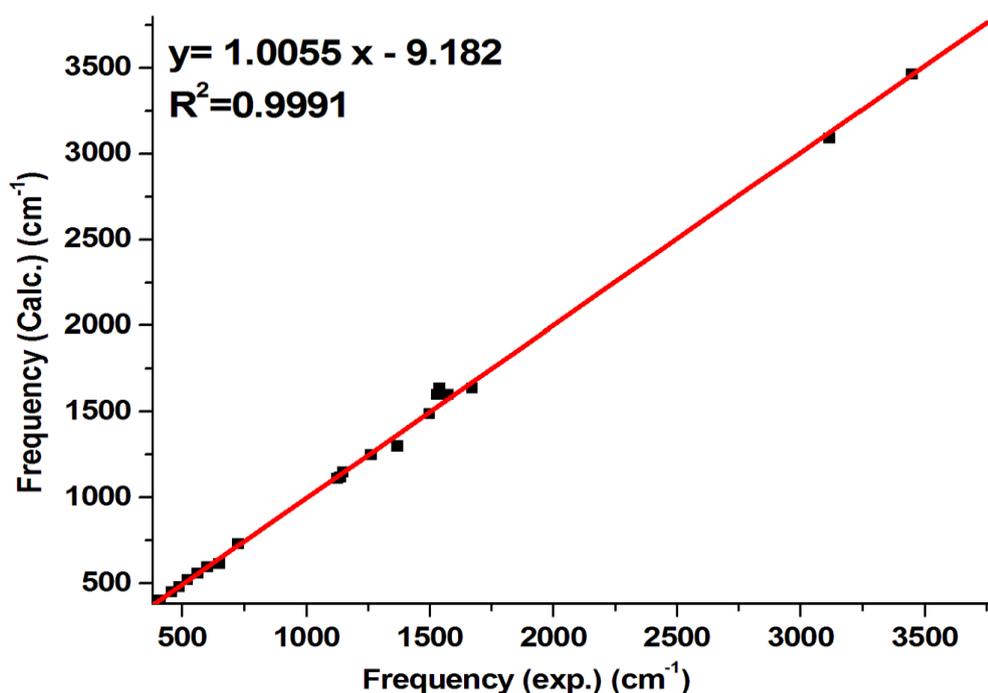


Figure 4. Correlation between experimental FT-IR and simulated IR spectra in the region $4000\text{--}400\text{ cm}^{-1}$ of the **DO-26 dye (D1)**.

Figure 4 shows a correlation between theoretically calculated and the practically detected frequencies in FT-IR of the dye DO-26. These data show good correlation exists with a coefficient of 0.9991. Such a correlation proved that the DFT/B3LYP scheme of theoretical calculation in the field of spectroscopy is efficiently reproduces the experimental results and can be used for vibrational analysis of biomolecules with a sufficient confidence.

3.1.4. Natural charges and natural population analysis (NPA) of D1

The NPA scheme at B3LYP/6-311++G(d, p) level had been used in theoretical calculation of atomic charges of the investigated molecule (**D1**) in gas. These charges are ranged from -1.001 to 2.299 e and the data obtained are depicted in Table 4. The obtained results proved that; this scheme is more reliable due to its low basis set dependency.

Table 4. Natural charge of selected atoms of DO-26 dye1 (D1) at B3lyp/6-311++G(d,p) level of theory.

Table 4 shows that; the carbon atoms in the skeleton of the dye DO-26 are either carrying positive or negative charges; it depends on its position. The negative charges are concentrated on O23, O24, O25, O55, O56 and O57 oxygen atoms of SO₃ groups. It also has been seen that the charge is around -1.0 e on each atom. The maximum positive charges on sulphur atoms (S21 and S54 atoms of SO₃ groups) have been detected. The nitrogen and oxygen atoms of urea and diazonium fragments are negatively charged and consequently they accept electrons. It is also noticed that; the increase of charge on N27 and N27 as compared to N26 and N59. The decrease in charge on O25 and O58 may be due to electron density transfer from proton donors N27H39 and N60H72 to proton acceptors O25 and O58 involved in hydrogen bonding. It is finally noticed that; charges on hydrogen atoms have positive values.

3.1.5. FMOs analysis

Table 5 represents Frontier molecular orbitals (FMOs) data. The represented calculated quantum chemical parameters values are E_{HOMO}, E_{LUMO}, energy gap (ΔE_{gap}), ionization energy (I), electron affinity (A) and Dipole moment [49–51].

Table 5. Energetic parameters and reactivity indices of synthesized DO-26 dye1 (D1) using B3lyp/6-311++G(d,p) level of theory.

Frontier molecular orbitals (FMOs)	ET,au	EHOMO,au	ELUMO,au	Eg,eV	I,eV	A,eV	μ , D
	-3073.35409	-0.06336	0.02557	2.42	1.72	-0.70	10.98
Global Reactivity Descriptor (GRD)	X,eV	η ,eV	S,eV	V,eV	ω , eV	N, eV	
	0.51	1.21	0.41	-0.51	0.11	2.49	

Values are mean \pm SD triplicate assays

The HOMO (ionization potential I= - E_{HOMO}) energy value usually determines the donating power of electrons of the tested group. Its high value indicates the ease of donating electron to the unoccupied orbital of the receptor molecule. The small value of E_{LUMO} (electron

affinities $A = -E_{\text{LUMO}}$), means more able to accept electron. The calculated E_{HOMO} of the tested dye is found to be -1.724 eV ; which is located on the SO_3 group system of right arm. On the other hand the E_{LUMO} , of DO-26 is found to be 0.696 eV ; which is mainly contributed by all left arm of the dye molecule. The energy (ΔE_{gap}) between HOMO and LUMO usually described the chemical reactivity of the molecule. In the present study, ΔE_{gap} is found to be 2.42 eV ; which indicates the high reactivity of the compound in oxidation reduction reaction. Hence the dye is highly reactive and recommends being use in dye sensitized solar cell (DSSC). The ionization potential I and electron affinity A are so important parameters. The determination of these two important parameters allows the calculation of the global reactivity descriptors. The A and I parameters depend mainly on the one-electron HOMO and LUMO orbital energy values. The molecule of less I value will be the better electron donor; while the molecule of high I value will be the better electron acceptor. From Table 5, it has 1.72 eV value of I and A is -0.7 eV and electronegativity is equal 0.51 eV . Figure 5 represents Frontier molecular orbitals of the studied DO-26 dye compounds (D1).

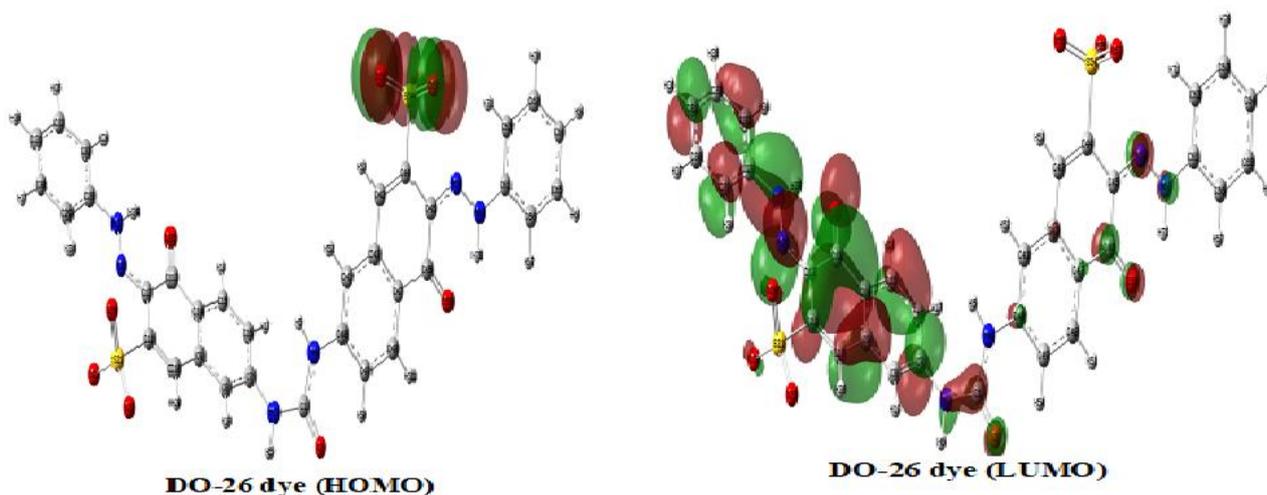


Figure 5. Frontier molecular orbitals of the studied DO-26 dye compounds (D1)

Figure 5, shows that the dispersion of charge densities of HOMOs and LUMOs indicates charge transfer to naphthalene with azo-phenyl ring (left arm of urea derivatives) from SO_3 group of right arm. The dipole moment vector is representing the direction of the electronic charge transfer motion and it equals 10.98 D .

3.1.6. Global reactivity descriptors of D1

The nature of chemical interactions and chemical reactivity of atoms, ions or molecules are considered important to explain the reactivity of the molecular dye DO-26 (D1). The CDFT, quantum chemical descriptors like chemical hardness (η), electronic chemical potential (μ), and electronegativity (χ) are related to the electron number (N) at constant external potential, $v(r)$, respectively [49–51] and expressed by the following equations (1 and 2).

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \quad (1)$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} \quad (2)$$

Also, Global electrophilicity index (ω), Global softness (S) and electronegativity (χ) are computed based on HOMO and LUMO energy values for **D1** using B3LYP/ 6-311++G(d,p) theory level of calculation [49, 50] as computed by application of equations (3-6):

$$\eta = (E_{HOMO} - E_{LUMO})/2 \quad (3)$$

$$\mu = -\frac{E_{HOMO} + E_{LUMO}}{2} = -\chi \quad (4)$$

$$\omega = \mu^2/2\eta \quad (5)$$

$$\chi = (E_{HOMO} + E_{LUMO})/2 \quad (6)$$

$$S = 1/2\eta \quad (7)$$

The computed **GRD** reactivity descriptors of the compound **D1** are represented in Table 5. These data have been considered very important to explain the reactivity and stability of studied **DO-26 (D1)**. **D1** has a value of $\eta = 1.21$ eV of chemical hardness and the softness value (0.41 eV); which indicates softness and chemical reactivity of studied. The results obtained are in good correlation with the found HOMO-LUMO band energy gaps of the synthesized dye. The calculated chemical potential (μ) value of the studied dye DO-26 (D1) presented in Table 5 means it has high chemical potential value (-0.5 eV); which refers to the high charge transfer occurs within tested dye.

The electrophilicity index (ω) is a thermodynamic parameter that measures energy changes in a chemical system saturated by adding electrons. It describes the chemical reactivity of a system. The calculated data presented in Table 5 proved that **D1** has Electrophilicity index value ($\omega = 0.11$ eV) and the Nucleophilicity index (N) is equal to +2.49 eV. These values indicate that the dye favors nucleophilic approximately 23 times more than electrophilic. Compound **D1** possesses electronegativity (X), value of 0.51 eV as a measure for tendency of molecule to attract electrons means it has high softness values (0.51 eV) and showed high reactivity,

3.1.7. Local reactivity descriptor of D1

To understand the chemical reactivity and site selectivity of theoretically tested compounds; it is very important to use the concepts of local and global reactivity descriptors [52, 53]. The Fukui function is the first derivative of the electronic density $\rho(r)$ of a system with respect to the number of electrons (N) at a fixed external potential $v(r)$ as defined by Yang and Mortier (1986) [54]. It has been used to analyze local molecular site selectivity of the molecules as given by Equation 8:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial v(r)} \right)_{v(r)} \quad (8)$$

The local descriptors such as electrophilic and nucleophilic Fukui functions had been more clarified by Parr and Yang [55, 56]. The calculation of Fukui functions is very important to determine the active sites of the **DO-26 dye** (D1). It mainly based calculation of the electronic density changes occurred during the molecule reactions. Usually Fukui functions $f^+(r)$, $f^-(r)$ and $f^0(r)$ are essentially calculated in three chemical situations such as electrophilic, nucleophilic and radical attacks using the following equations as [53, 56–58]:

$$f^-(r) = q_k(N) - q_k(N - 1) \approx \rho^{\text{HOMO}}(r) \quad \text{for electrophilic attack}$$

$$f^+(r) = q_k(N + 1) - q_k(N) \approx \rho^{\text{LUMO}}(r) \quad \text{for nucleophilic attack}$$

$$f^0(r) = \frac{1}{2}[q_k(N + 1) - q_k(N - 1)] \approx \frac{1}{2}[\rho^{\text{HOMO}}(r) + \rho^{\text{LUMO}}(r)] \quad \text{for Radical attack}$$

Where $q_k(N)$, $q_k(N + 1)$ and $q_k(N - 1)$ are the atomic population on the k th atom for the neutral molecule, its anionic and cationic species respectively. Chattaraj et al. [59] defined the local quantity called philicity ω_k^α associated with a site k in a molecule with the assistance of corresponding condensed-to-atom variants of Fukui function, f_k^α as in Equation (9).

$$\omega_k^\alpha = \omega f_k^\alpha \quad (9)$$

Where $\alpha = +, -$ and 0 correspond to local philic quantities describing nucleophilic, electrophilic and radical attacks, respectively. The highest ω_k^α corresponds to the most electrophilic site in a molecule. Softness s_k^α describe the reactivity of atoms in molecules had been proposed by Lee et al. [20, 59] and expressed by Equation (10).

$$s_k^\alpha = s f_k^\alpha \quad (10)$$

, Morell and Labbe et al [60] proposed another Dual descriptor ($\Delta f(r)$) concerning electrophilic and nucleophilic capacity of a given atomic site in the molecule which is given by:

$$\Delta f(r) = f^+(r) - f^-(r) \quad (11)$$

Where $\Delta f(r)$ is the difference between the nucleophilic and electrophilic Fukui function.

If $\Delta f(r) > 0$ refers to nucleophilic attack. If $\Delta f(r) < 0$ it may be favored for an electrophilic attack. The calculated data using the above equations at the level B3LYP/6-311++G (d,p) for Fukui functions indices, dual descriptor, condensed local softness, local and relative electrophilicity of DO-26 are given in Tables 6-7.

The values of Fukui functions $f^-(r)$ and $f^+(r)$ are presented in Table 6.

Table 6. Values of the Fukui functions and Dual descriptor of DO-26 dye (D1) using B3lyp/6-311++G(d,p).

From these data; it can be stated that the most electrophilic active sites in DO-26 molecule is located on O55, O56 and O57. Likewise, the active sites susceptible for nucleophilic attacks in the same dye are C7, C9, C10, C11, O25, N26, N27, N59 and N60. The same conclusion can be reached considering the Dual descriptor $\Delta f(r)$ regarding electrophilic and nucleophilic attack, also from the philicity indices Table (7).

Table 7. Values of the Condensed local Softnesses (Hartree*e), relative electrophilicity /nucleophilicity (dimensionless) and the Condensed local electrophilicity (ElectroP)/nucleophilicity (NucleoP) index (e*eV) of DO-26 dye (D1) using B3lyp/6-311++G(d,p).

The characteristic differences between the calculated values of parameters is mainly attributed the redistribution of electron density inside molecules due to high electronegativity of N and O atoms in skeleton, also the effect of $-C=O...HN$, $-SO_3^{-1}$ groups. The obtained results of the calculated functions are in good agreement with the last population analysis and computed HOMO and LUMO energies.

By using implemented code in Multi wave function v3.8 software program [37]; condensed local softness, local electrophilicity /Nucleophilicity index, and relative electrophilicity/Nucleophilicity have been also calculated for each atom in the studied molecule from CDFT point of view to complete the picture of the studied dye map. The careful inspection of these data revealed that; the dye molecule had the donation and the back-donation processes at their active center (O55, O56, O57, C7, C9, C10, C11, O25, N26, N27, N59 and N60); which is in good agreement with the Fukui functions data. It also agreed well with the obtained frontier orbital results represented in **Tables (6-7)**.

According to these results, one can conclude that the studied dye possess lot of active centers to interact with pocket protein surface, through donating electrons to orbitals and back donation process. The calculated local descriptors data revealed that the theoretical variation efficiencies of the investigative molecules agree well with the available experimental data in the same work.

3.1.8. Molecular electrostatic potential map (MEP)

Electrostatic potential (ESP) on molecular van der Waals surfaces have emerged as powerful tools in predicting, interpreting, and rationalizing trends in different areas of chemistry [61] as well as in drug design and molecular biology [62]. ESP-mapped surfaces are related to the electronic

density. Hence they are very useful descriptors for illustrating the charge distributions atoms of the molecules, visualizing variably charged regions on its surface. Therefore ESP determines most probable sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions in the molecule [62]. ESPs are usually used for studying and predicting intermolecular interaction [63]. The ESPs of studied compounds is very helpful in understanding their important interactions with biological receptors.

The negative ESPs values means attractive interaction of test charges; while positive ESPs values indicate repulsion. The electrostatic potential $V(r)$ (in a.u.) at a given point r (x,y,z) is defined in terms of the interaction energy between the electrical charges generated from electrons the molecule and nuclei positive proton located. The electrostatic potential $V(r)$ (in a.u.) is given by the equation (12)

$$V(r) = \sum_A^{nuclei} \frac{Z_A}{|R_A-r|} - \int \frac{\rho(r')}{|r-r'|} dr' \quad (12)$$

Z_A and R_A are the charge and position of nucleus A, and $\rho(r')$ is the electron density at position r' , all in atomic units. ESP-mapped surfaces of the studied compound, **D1** are shown in Figure 6.

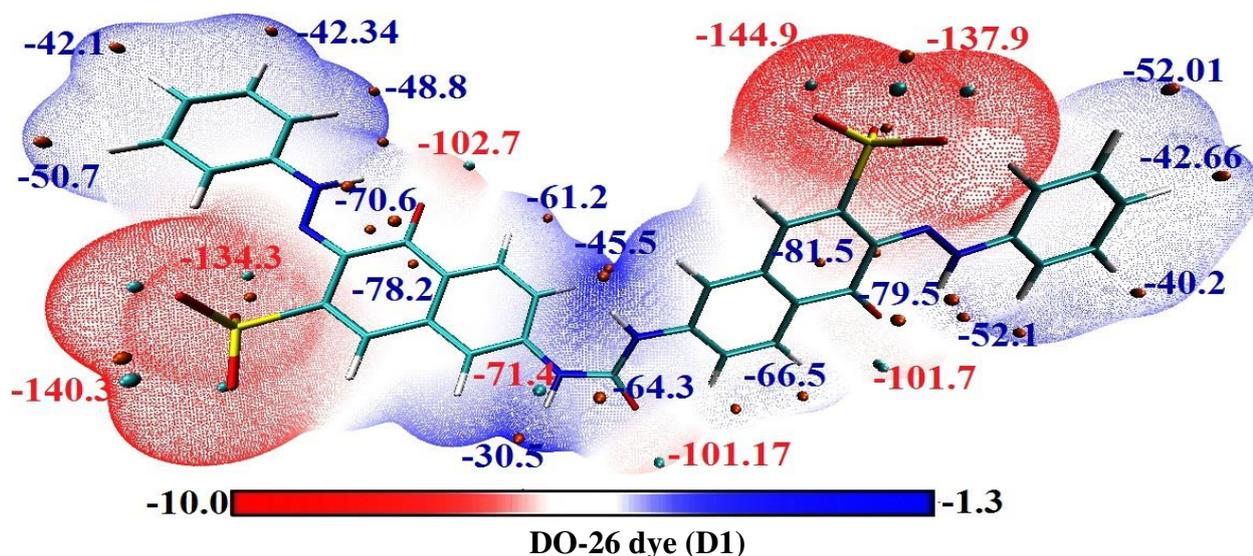


Fig. 6. ESP-mapped surfaces of the synthesized DO-26 dye compound (**D1**)

Module of Multi wave function program is used for the quantitative molecular surface analysis and it is capable of partitioning the whole van der Waals surface into multiple fragments. It also allows discussion of the characteristics of the ESP distribution of studied dye **D1**.

The surface of DO-26 (D1) exhibits large negative value of ESP around the $-\text{SO}_3^-$ groups (-144.9, -140.3 kcal/mol). $\text{C13}=\text{O25}\dots\text{H39N27}$ and $\text{C46}=\text{O58}\dots\text{H72N60}$ (-101.7 and 102.7 kcal/mol) with spreading the negative charge on different active sites.

As the electron redistribution ability of the different chelation **D1** the global minima of ESPs and the global maxima of ESPs on the surfaces of the studied compounds are localized. This means that the expected interactions of dye D1 with a target protein will be mostly polar (electrostatic or hydrogen bonding) via the most reactive centers. Careful inspection of these ESPs values confirms on the ability to induce intra-molecular charge transfer (ICT) and hydrogen bond interaction, hence can act as drug. It can be asserted on the basis of ESP-mapped, that an electrophile is attracted towards negative region of diazonium and urea center fragment with $-\text{SO}_3^-$ while a nucleophilic attack favors the electropositive region. These values indicate the same results from NPA and local reactivity descriptors analysis mentioned in above sections.

4.1.9. Electronic absorption spectra

Direct orange 26 dye (**D1**) has been synthesized and confirmed to possess antibacterial and application in printing and dyeing [64]. No correlation between experimental and calculated TDDFT UV/Vis spectra for DO-26 (D1) had been previously published elsewhere. To analyze how the UV-Visible spectrum of D1 is varied, the experimental absorption electronic spectra in water solvent and computed are depicted in Figure 7. The calculated absorption maximum wavelengths (λ_{max}), electronic excitation energies (ΔE), and oscillator strengths (f) of D1 in water are given in Table 8 together with the corresponding experimental values.

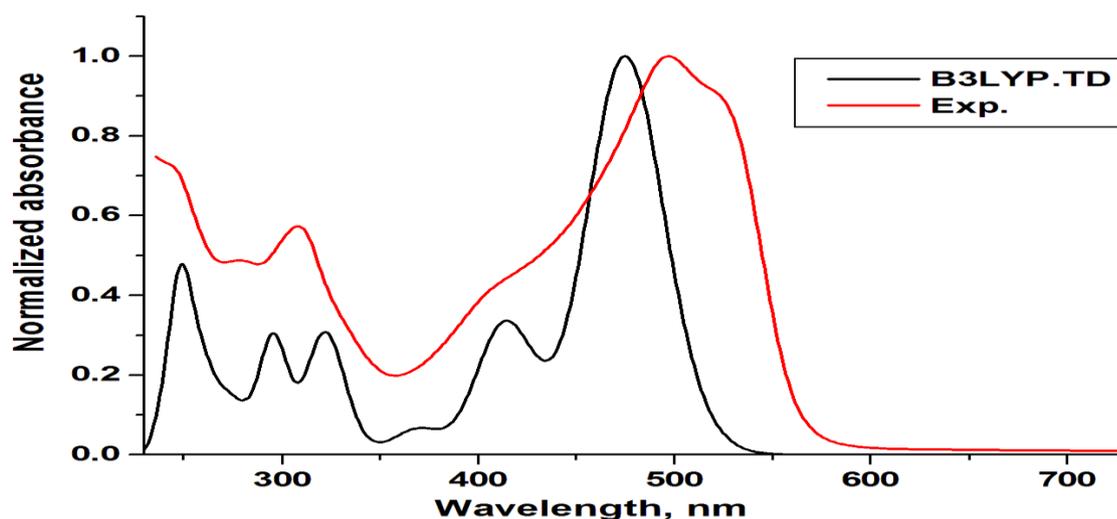


Figure 7: Experimental and theoretical UV/Visible spectra of dye (**D1**) obtained applying the TD-PCM-B3LYP (Water) /6-311++G(d,p) under level of approximation.

Table 8: UV spectra parameters that characterized dye D1 in water such as (λ_{\max}), electronic excitation energies (ΔE), and oscillator strengths (f); both theoretical and experimental data

	λ_{\max} (nm)		ϵ (mol ⁻¹ .cm ⁻¹ .L)	f	ΔE (eV)		Transition assignment
	Exp.	TD-DFT			Exp.	TD-DFT	
$S_0 \rightarrow S_1$	511	475 (H \rightarrow L(0.5403))	13,395	1.19	2.43	2.61	$\pi \rightarrow \pi^*$
$S_0 \rightarrow S_2$	491	466 (H-1 \rightarrow L(0.584))	14,514	0.25	2.53	2.66	$\pi \rightarrow \pi^*$
$S_0 \rightarrow S_3$	416	412 (H-2 \rightarrow L(0.629))	6,777	0.44	2.98	3.00	$\pi \rightarrow \pi^*$
$S_0 \rightarrow S_4$	321	319 (H-1 \rightarrow L+2(0.492))	5,440	0.21	3.86	3.88	$\pi \rightarrow \pi^*$
$S_0 \rightarrow S_5$	302	303 (H \rightarrow L+2(0.616))	8,313	0.03	4.11	4.1	$\pi \rightarrow \pi^*$
$S_0 \rightarrow S_6$	272	267 (H-12 \rightarrow L+1(0.239))	7,077	0.02	4.54	4.64	$\pi \rightarrow \pi^*$

These data show six absorption bands with maxima at 511 nm ($\epsilon = 13,395 \text{ M}^{-1}.\text{cm}^{-1}$), 491 nm ($\epsilon = 14514 \text{ M}^{-1}.\text{cm}^{-1}$), 416 nm ($\epsilon = 14514 \text{ M}^{-1}.\text{cm}^{-1}$), 321 nm ($\epsilon = 6777 \text{ M}^{-1}.\text{cm}^{-1}$), 302 nm ($\epsilon = 5440 \text{ M}^{-1}.\text{cm}^{-1}$), and 267 nm ($\epsilon = 7077 \text{ M}^{-1}.\text{cm}^{-1}$). Figure 8 Show natural transition orbitals (NTOs) occupied and unoccupied in the electronic transitions between the ground state (S_0) and six low-lying singlet excited states (S_n) of DO26 dye (D1).

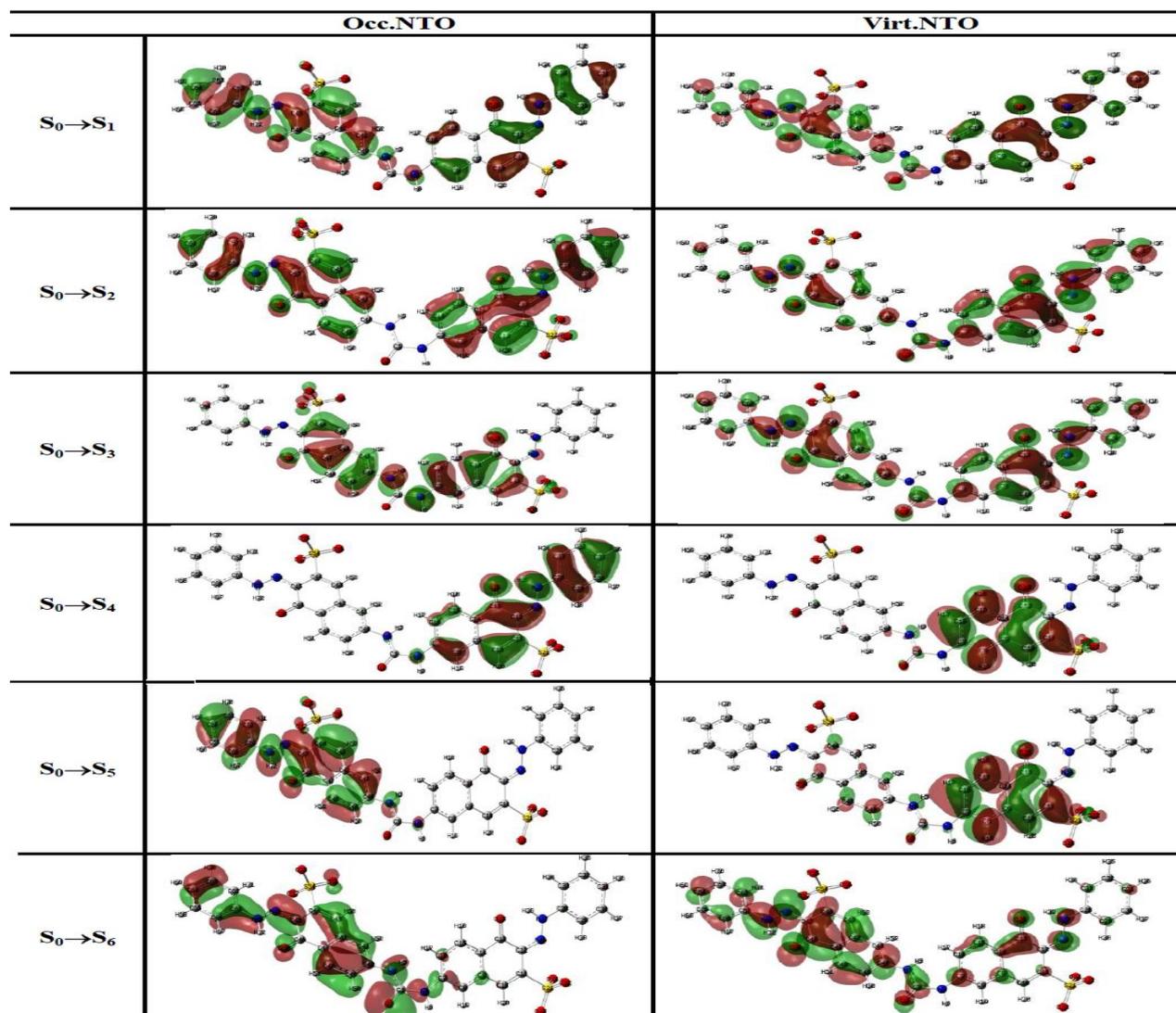


Figure 8: Natural transition orbitals (NTOs) occupied and non-occupied in the electronic transitions between the ground state (S0) and six low-lying singlet excited states (Sn) of DO-26 dye (D1) obtained at the PCM-B3LYP (Water) /6-311++G(d,p) level of approximation.

The data obtained in Figure 8 of the computed natural transition orbitals (NTOs) indicate that these electronic transitions can be assigned as π - π^* transitions.

The Hirshfeld population analysis is used to calculate percent contributions of molecular fragments to occupied and unoccupied natural transition orbitals in the electronic transitions between the ground state (S0) and six low-lying singlet excited states (Sn) of D1 obtained at the PCM-B3LYP (Water) /6-311++G(d,p) level of approximation and depicted in Table 9.

Table 9. The electronic transitions between the ground state (S0) and six low-lying singlet excited states (Sn) of D1 obtained at the PCM-B3LYP (Water) /6-311++G(d,p) level of approximation using *Hirshfeld* population analysis.

		Urea Center	Naph_R	AzoPh_R	Naph_L	AzoPh_L	Right-arm	Left-arm
S ₀ →S ₁	Occ.NTO	2.61	20.08	15.06	35.24	26.63	35.15	61.87
	Virt.NTO	3.68	29.90	21.66	25.52	18.82	51.56	44.33
S ₀ →S ₂	Occ.NTO	0.69	35.88	22.17	24.56	16.10	58.05	40.66
	Virt.NTO	3.33	42.47	31.90	12.58	9.10	74.37	21.68
S ₀ →S ₃	Occ.NTO	21.04	34.41	1.50	41.02	1.96	35.91	42.97
	Virt.NTO	3.69	29.82	22.12	24.88	19.04	51.95	43.92
S ₀ →S ₄	Occ.NTO	1.22	46.73	49.27	0.89	0.56	96.00	1.44
	Virt.NTO	3.38	93.73	0.94	1.60	0.25	94.66	1.85
S ₀ →S ₅	Occ.NTO	2.33	1.04	0.01	55.37	41.25	1.05	96.62
	Virt.NTO	3.53	89.14	0.96	6.17	0.10	90.09	6.27
S ₀ →S ₆	Occ.NTO	46.25	3.61	1.34	31.65	17.14	4.95	48.79
	Virt.NTO	5.27	12.39	7.42	44.02	30.75	19.81	74.77

These data of molecular orbital compositions are essentially based on the percent contributions of urea center, naphthalene right arm (Naph_R), naphthalene left arm (Naph_L), azo-phenyl right arm (Azoph_R) and azo-phenyl left arm (Azoph_L) molecular fragments to the occupied and virtual NTOs.

The first transition (S₀→S₁), is related to electrons occupied NTO of p_z and p_x orbitals that mainly localized on O55, O56 and O57 of the sulfonic group (S54-(O55, O56 and O57) with contributions of ~ 26%, 30% and 32%, respectively. From these data it is obvious that π -bonding interaction exists between the p_z orbitals of these atoms. The unoccupied NTO is composed of p_z orbitals mainly localized on C13, O25 and N26 of the active group in right naphthalene group with contributions of ~ 10%, 9.5% and 17%, respectively. From these data it is obvious that π^* -antibonding interaction exists between the p_z orbitals of these atoms. It is clear from data in Table

9, electron density $\pi \rightarrow \pi^*$ transition from left arm to right arm by around 17 % of electron localized over the entire molecule.

The second transition ($S_0 \rightarrow S_2$), is related to electrons occupied NTO of p_z , p_x and p_y orbitals mainly localized on O22, O23 and O24 of the sulphonic group (S21-(O22, O23 and O24) with contributions of ~ 31%, 25% and 33%, respectively as a result of π -bonding interaction exists between the p sub-orbitals of these atoms. The non-occupied NTO are composed of p_z orbitals that mainly localized on C13, O25 and N26 of the active group in right naphthalene group as $S_0 \rightarrow S_1$. A π^* -antibonding interaction exists between the p_z orbitals of these atoms is mainly related electron density $\pi \rightarrow \pi^*$ transition from left arm to right arm by around 20 % of electron localized over the entire molecule.

For the third transition ($S_0 \rightarrow S_3$), the occupied NTO the π -bonding interaction is concentrated between the p_z orbitals of urea center and left naphthalene arm with 22 and 41%, respectively. The un-occupied NTO is composed of p_z orbitals that mainly localized on the right naphthalene group and azo-phenyl with contributions of ~ 30% and 23%, respectively. A π^* -antibonding transition may be assigned as $\pi \rightarrow \pi^*$.interaction exists between the p_z orbitals of these atoms.

The fourth transition ($S_0 \rightarrow S_1$), as a result of electrons occupied NTO is mainly localized on right arm group (C7-H39) with contributions of naphthalene group ~ 47% and azo-phenyl 50%. The π -bonding interaction is due to $\pi \rightarrow \pi^*$ transition and exists between the p_z orbitals of these range atoms. The un-occupied NTO is found to be mainly localized right naphthalene group with contributions of ~ 94%. It is mainly occurred due to π^* -antibonding interaction exists between the p_z orbitals of these atoms.

The fifth transition ($S_0 \rightarrow S_5$), as a result of electrons occupied NTO is mainly localized on left arm of naphthalene and azo-phenyl with contributions of ~ 56% and 41%, respectively and attributed to π -bonding interaction exists between the p sub-orbitals of these atoms. The non-occupied NTO is composed of p_z orbitals and mainly localized on right naphthalene group with contribution ~ 90%. A π^* -antibonding transition may be assigned as $\pi \rightarrow \pi^*$ interaction exists between the p_z orbitals of these atoms.

For the 6th transition ($S_0 \rightarrow S_6$), is essentially related to the occupied NTO π -bonding electron interactions exist between the p_z orbitals of urea center and left naphthalene arm with 47 and 31%. Consequently, the non-occupied NTO is composed of p_z orbitals mainly localized left naphthalene group and azo-phenyl left part with contributions of ~ 45% and 31%, respectively; resulting in π^* -antibonding interaction leading to $\pi \rightarrow \pi^*$ transition exists between the p_z orbitals of these atoms.

These detailed discussions are confirmed by Figure 8; which illustrate Natural transition orbitals (NTOs) occupied and unoccupied due to transitions between the ground state (S_0) and six low-lying singlet excited states (S_n) of DO26 dye (D1) obtained at the PCM-B3LYP (Water) /6-311++G(d,p) level of approximation.. This details discussion clearly shows a π -bonding interaction

among the specific groups of atoms as mentioned above. The NTOs data clearly discussed π -antibonding interactions among all these contributing species. The nature of vertical electronic transitions in the studied compound (D1) is analyzed via determining the topology of the molecular orbitals involved in these transitions. The NTOs of the first electronic transition ($S_0 \rightarrow S_1$), associated with the ICT band, are given in Figure 8. It is noticed that both occupied and virtual NTOs demonstrate the typical π -type molecular orbital characteristic. They are clearly delocalized over the entire molecule including the two arms. The details of the active space of molecular orbital wave function representation and its surfaces (see the supporting information for details in supplementary Figure S2 and Table S2).

These six transitions and calculated parameters are given in Table 10.

Table 10. Charge transfer (CT) length (Δr) and variation in dipole moment ($\Delta\mu_{CT}$) indices of the six electronic excitations for the studied **D1** are obtained at the PCM-B3LYP(Water)/6-311++G(d,p) level of approximation.

	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_3$	$S_0 \rightarrow S_4$	$S_0 \rightarrow S_5$	$S_0 \rightarrow S_6$
Δr (Å)	7.61	5.36	4.06	3.75	9.22	4.70
$\Delta\mu_{CT}$ (a.u.)	3.34	2.12	2.94	7.10	7.10	2.17

The data in Tables 9-11 refer to the variation in the electron density distribution of the occupied NTOs as a symmetry reason to the electron-donating or accepted ability of two arms; which considered as a good evidence of the intramolecular charge transfer nature.

In order to study the extent of charge transfer (CT) or charge redistribution during the excitations, the Δr index and variation of dipole moment ($\Delta\mu_{CT}$) of excited state with respect to ground state are computed for the studied molecules using Multiwfn code [27]. The obtained data are depicted in in Table 10. The Δr index [33] can be considered as a measure of charge transfer (CT) length. It can be used to discriminate between local ($\Delta r \leq 1.5$ Å) and charge transfer ($\Delta r \geq 2.0$ Å) electronic excitations. According to Δr values, it can be seen that the charge transfer character in the six transitions, For D1, Δr has value for $S_0 \rightarrow S_1$ (7.61 Å), $S_0 \rightarrow S_2$ (5.36 Å), $S_0 \rightarrow S_3$ (4.06 Å), $S_0 \rightarrow S_4$ (3.75 Å), $S_0 \rightarrow S_5$ (9.22 Å) and $S_0 \rightarrow S_6$ (4.70 Å) transitions, respectively. We can conclude that all transitions may belong to charge transfer type. The dipole moment change upon excitations ($\Delta\mu_{CT}$) is another important factor to assess their CT behavior. For D1, $\Delta\mu_{CT}$ has value for $S_0 \rightarrow S_1$ (3.34 Debye), $S_0 \rightarrow S_2$ (2.12 Debye), $S_0 \rightarrow S_3$ (2.94 Debye), $S_0 \rightarrow S_4$ (7.10 Debye), $S_0 \rightarrow S_5$ (7.10 Debye) and $S_0 \rightarrow S_6$ (2.17 Debye) transitions, respectively. Therefore, it is obvious that the CT

lengths (Δr) and dipole moment change ($\Delta \mu_{CT}$) of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$, $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$ electronic excitations belong to charge transfer type.

4. Conclusions

DFT calculations have been carried out on DO-26 dye (D1) applying the B3LYP/6-311G method to study the structure characters and vibrational analysis of the tested dye. Highly interesting correlation had been found between experimental and calculated parameters such as bond lengths and vibrational frequencies. Complete assignment of FTIR spectra vibrational modes of DO-26 (D1) is successfully performed at wavenumber range 400 to 4000 cm^{-1} . The AIM analyses actually revealed the presence of intra-molecular hydrogen bonding within two arms of the dye molecule. The obtained data successfully characterized them as medium and weak interactions. The effect of hydrogen bonding on structure and vibrational properties of the tested dye had been professionally also discussed. NBO analysis, HOMO–LUMO and MESP plots had been used to explain chemical reactivity of DO-26 dye (D1) molecule. Various electronic transition parameters have been calculated which actually provide further description and threw more lights on the chemical reactivity and direction of chemical reactions detected in the behavior of DO-26.

Acknowledgement: Authors acknowledge the support of this research by instruments, chemicals and measurements, and programs of Theoretical Calculations given by the Chemistry, Mathematic Departments at Cairo University, and Egyptian Ministry of Health:

5. Authors Declarations

Funding: N/A

Conflict of Interest: The authors declare that they have no conflicts of interest.

Availability of data and material: It is available in transparent forms.

Code Availability: The Gaussian 09W software package has been used for NBO calculations using NBO 3.1 program implemented in the same program. The Gauss View version 5.0.9 [25] involving Chemcraft version 1.6 package

Authors Contributions:

Mohamed A. Zayed: Writing the manuscript and revision of all of its contents.

Mahmoud A. Noamaan: Made all theoretical calculations and share paper writing.

Zahraa A. M. Abo-Ayad: : Made all experimental work and share paper writing.

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Table 1. The selected bond length (Å), bond angles and dihedral angles, (degree) of DO-26 dye (D1) at B3lyp/6-311++G(d,p) level of theory.

Coordinate	Value	Coordinate	Value	Coordinate	Value
R(C1,O2)	1.223	A(N3,C7,C8)	117.64	D(O2,C1,N4,C40)	5.74
R(C1,N3)	1.393	A(N3,C7,C16)	122.81	D(N3,C1,N4,C40)	-175.86
R(C1,N4)	1.377	A(C8,C7,C16)	119.44	D(C1,N3,C7,C8)	-151.94
R(N3,H6)	1.010	A(C7,C8,C9)	121.67	D(C1,N3,C7,C16)	31.98
R(N3,C7)	1.411	A(C12,C11,S21)	121.12	D(C1,N4,C40,C41)	-174.24
R(N4,H5)	1.010	A(C11,C12,C13)	120.19	D(C1,N4,C40,C49)	6.93
R(N4,C40)	1.411	A(C11,C12,N26)	116.82	D(N3,C7,C8,C9)	-175.75
R(C11,C12)	1.454	A(C13,C12,N26)	122.99	D(C8,C9,C10,C11)	-179.19
R(C11,S21)	1.851	A(C12,C13,C14)	117.12	D(C8,C9,C14,C13)	-179.99
R(C12,C13)	1.475	A(C12,C13,O25)	121.45	D(C9,C10,C11,S21)	178.10
R(C12,N26)	1.321	A(N26,N27,C28)	119.70	D(C11,C12,C13,O25)	179.93
R(C13,O25)	1.252	A(N26,N27,H39)	117.77	D(N26,C12,C13,C14)	-179.42
R(N26,N27)	1.303	A(C28,N27,H39)	122.53	D(N26,C12,C13,O25)	0.15
R(N27,C28)	1.401	A(N27,C28,C29)	121.09	D(C11,C12,N26,N27)	179.90
R(N27,H39)	1.030	A(N4,C40,C41)	117.23	D(C13,C12,N26,N27)	-0.32
R(C44,C45)	1.455	A(N4,C40,C49)	123.01	D(C12,N26,N27,C28)	179.75
R(C44,S54)	1.850	A(C41,C40,C49)	119.75	D(C12,N26,N27,H39)	-0.15
R(C45,C46)	1.476	A(C45,C44,S54)	120.81	D(N26,N27,C28,C29)	-0.30
R(C45,N59)	1.319	A(C44,C45,C46)	120.12	D(N26,N27,C28,C33)	179.76
R(C46,O58)	1.253	A(C44,C45,N59)	116.82	D(N4,C40,C41,C42)	-178.74
R(N59,N60)	1.306	A(C46,C45,N59)	123.06	D(C40,C41,C42,C43)	179.90
R(N60,C61)	1.400	A(C45,C46,C47)	117.16	D(C40,C41,C42,C47)	-0.06
R(N60,H72)	1.030	A(C45,C46,O58)	121.27	D(C41,C42,C47,C46)	-179.92
A(O2,C1,N3)	119.22	A(C47,C46,O58)	121.58	D(N59,C45,C46,O58)	-0.28
A(O2,C1,N4)	124.90	A(N59,N60,C61)	119.48	D(C44,C45,N59,N60)	179.90
A(N3,C1,N4)	115.86	A(N59,N60,H72)	117.72	D(C45,N59,N60,C61)	-179.67
A(C1,N3,H6)	110.27	A(C61,N60,H72)	122.80	D(C45,N59,N60,H72)	0.06
A(C1,N3,C7)	133.77	A(N60,C61,C62)	121.01	D(N59,N60,C61,C62)	0.18
A(H6,N3,C7)	115.93	D(O2,C1,N3,H6)	11.81	D(N60,C61,C62,C63)	179.97
A(C1,N4,H5)	116.56	D(O2,C1,N3,C7)	-170.64	D(C41,C42,C47,C48)	0.00
A(C1,N4,C40)	128.15	D(N4,C1,N3,H6)	-166.69	D(C44,C45,C46,O58)	179.89
A(H5,N4,C40)	115.18	D(N4,C1,N3,C7)	10.86	D(N59,C45,C46,C47)	179.67

Values are mean \pm SD triplicate assays.

Table 2. The selected geometrical parameters (a.u), bond length (Å) and binding energy, (kcal/mol) of **D1** at B3lyp/6-311++G(d,p) level of theory.

	N27H39...O25	N60H72...O58	C1O2...H50C49	S21O23...H20C10	S54O56...H53C43	N4H5...H17C16
HB length (Å)	1.764	1.766	2.211	2.334	2.345	2.135
Density of all electrons	0.0427	0.0428	0.0180	0.0156	0.0159	0.0125
Lagrangian kinetic energy G(r)	0.0379	0.0380	0.0144	0.0133	0.0134	0.0097
Hamiltonian kinetic energy K(r)	0.0015	0.0015	-0.0023	-0.0020	-0.0020	-0.0021
Potential energy density V(r)	-0.0394	-0.0395	-0.0121	-0.0112	-0.0114	-0.0076
Energy density E(r) or H(r)	-0.0015	-0.0015	0.0023	0.0020	0.0020	0.0021
Laplacian of electron density	0.1455	0.1458	0.0665	0.0611	0.0618	0.0470
Binding energy of HB (BE=0.5V(r))[93]	-12.36	-12.41	-3.80	-3.53	-3.57	-2.37
Binding energy of HB based on electron density [95]	-8.78	-8.80	-3.26	-2.73	-2.80	-2.05

Table 3. Selected vibrational analysis at B3LYP/6-311+G(d,p) level of theory for **D1** (corresponding FTIR values are also included)

Freq.	Sc. Freq.	IR int.	FTIR	PED %^a with vibrational assignments^b (mode)
3617	3473	56.5	3466	(-93.2%) ν (N3H6)+(- 6.8%) τ (N3C7C16H17)
3594	3450	115.7		(+100.0%) ν (N4H5)
3269	3138	33.6		(+91.3%) ν (N60H72)+(+ 8.7%) τ (N59C45C46O58)
3263	3133	31.3		(+74.1%) ν (N27H39)+(+ 15.8%) τ (H39N27C28C33)+(- 10.2%) γ (N26N27C28H39)
3247	3117	7.8	3090	(-89.9%) ν (C49H50)+(-10.1%) ν (C48H51)
3150	3024	7.6		(+36.1%) ν (C65H68)+(-24.8%) ν (C64H69)+(-24.4%) ν (C66H67)+(+14.7%) ν (C63H70)
1742	1672	668.2	1638	(+72.3%) ν (C1O2)+(-10.6%) ν (C1N4)+(-8.6%) δ (C1N4H5)+(+8.5%) δ (C1N3H6)
1648	1582	230.8		(-100.0%) ν (C13O25)
1640	1574	83.4	1600	(-58.3%) ν (C43C44)+(-41.7%) ν (C48C49)
1638	1573	120		(+38.9%) ν (C65C66)+(+ 36.7%) ν (C62C63)+(+24.7%) ν (C43C44)
1637	1571	239.1		(+64.6%) ν (C10C11)+(+35.4%) ν (C15C16)
1624	1559	34.7		(-27.0%) ν (C61C62)+(- 26.6%) ν (C10C11)+(- 23.3%) ν C64C65+(+ 22.5%) ν C63C64
1603	1539	212	1638	(-47.2%) ν (C13O25)+(-28.6%) ν (C46O58)+(- 24.2%) ν (C10C11)
1597	1533	300.2		(-66.5%) ν (C46O58)+(+34.5%) ν (C13O25)
1593	1529	101.3	1600	(+66.5%) ν (C43C44)+(33.5%) ν (C40C49)
1580	1516	19.9		(+34.3%) ν (C7C16)+(+24.3%) ν (C10C11)+(-23.0%) ν (C14C15)+(+18.3%) ν (C9C14)
1561	1499	218.9	1490	(+ 100%) ν (C12N26)
1558	1496	526.6		(+33.2%) ν (C45N59)+(+22.5%) ν (C12N26)+(-22.5%) ν (N59N60)+(+21.8%) δ N59 (N60H72)
1525	1464	41.6		(-50.9%) δ (C62C63H70)+(-49.1%) ν (N60C61)
1441	1384	129.3	1300	(-38.6%) ν (C45N59)+(+33.0%) ν (C41C42)+(+ 29.0%) ν (C44C45)
1426	1369	526.1		(-100%) ν (C45N59)
1414	1357	365		(-100%) ν (C12N26)
1380	1325	61.4		(-100%) ν (C44C45)
1316	1263	56.9	1250	(+100%) ν (N26N27)
1294	1242	232.3		(+100.0%) ν (N4C40)

1265	1214	1336.6		(+56.7%) v (C1N3)+(-43.3%) v (C1N4)
1254	1203	804		(+100.0%) v (N59N60)
1196	1148	213.6	1150	(-100.0%) v (S54O56)
1193	1145	245		(+100.0%) v (S21O23)
1187	1140	80	1120	(+100.0%) δ (C65C66H67)
1186	1138	443.2		(+100.0%) v (C28C33)
1173	1126	289.4	1110	(-53.4%) v (S21O24)+(+64.6%) v (S21O22)
1163	1117	102.3		(+48.3%) v (S21O23) +(-32.1%) v (S21O22) +(-19.6%) v (S21O24)
757	727	59.2	730	(+23.3%) τ (C28C29C30C31)+(+20.6%) γ (N27C28C29C33)+(+18.4%) γ (C31C32C33H35)+(+14.6%) τ (C28C33)
757	727	62.2		(+30.0%) τ (C61C66C65C64)+(-15.9%) γ (N60C61C62C66)+(-13.4%) τ N59N60C61C66
679	652	23.6	615	(+100.0%) δ (C7C8C9)
648	623	22		(+100.0%) v (C29C30)
637	611	57.2		(+100.0%) v (C44C45)
632	607	82.8		(+100.0%) δ (C31C32C33)
628	603	35.5	597	(+100.0%) δ (C31C32C33)
623	598	21.9		(+100.0%) γ (N3C7C8C16)
622	597	19.2		(+40.2%) γ (N4C40C41C49)+(-29.9%) τ (C43C42C47C48)+(-29.9%) γ (C43C44C45S54)
592	568	20.4	560	(+100.0%) v (C46C47)
588	564	69.3		(-64.2%) δ (C8C9C14)+(+35.8%) δ (C13C14C15)
578	555	79.3		(+100.0%) δ (C40C41C42)
557	535	27.2	520	(+100.0%) v (N4C40)
545	523	21.8		(-100.0%) v (C13C14)
511	490	36.6	480	(-100.0%) δ (C45C46C47)
508	488	1.4		(-51.0%) δ (C29C28C33) +(-49.0%) v (C12C13)
477	458	4	450	(-41.2%) δ (C45C46O58)+(-29.9%) v (C45C46)+(-28.9%) δ (C46C45N59)
428	411	17.2	400	(+100.0%) δ (C13C14C15)
425	408	11.7		(-100.0%) τ (C43C42C47C48)
419	402	38		(+100.0%) δ (C13C14C15)

^a PED <10 % are not included in assignments.

^b Symbols: ν = Stretching, δ = Bending, τ and γ = torsional motions, + = out of phase, - = in phase

Expressions represent: (direction of phase, percentage contribution in normal mode%) vibrational normal mode (Atom composition mode motions)

Table 4. Natural charge of selected atoms of DO-26 dye1 (D1) at B3lyp/6-311++G(d,p) level of theory.

Atoms	Charge	Atoms	Charge	Atoms	Charge
C1	0.817	O25	-0.666	C49	-0.261
O2	-0.661	N26	-0.153	H50	0.241
N3	-0.63	N27	-0.272	H51	0.223
N4	-0.623	C28	0.135	H52	0.202
H5	0.403	C29	-0.209	H53	0.241
H6	0.401	C30	-0.189	S54	2.298
C7	0.161	C31	-0.234	O55	-0.984
C8	-0.24	C32	-0.204	O56	-0.999
C9	0.113	C33	-0.231	O57	-0.985
C10	-0.262	H34	0.205	O58	-0.671
C11	-0.207	H35	0.195	N59	-0.187
C12	0.03	H36	0.194	N60	-0.282
C13	0.484	H37	0.202	C61	0.137
C14	-0.197	H38	0.267	C62	-0.21
C15	-0.115	H39	0.417	C63	-0.189
C16	-0.287	C40	0.181	C64	-0.238
H17	0.213	C41	-0.214	C65	-0.206
H18	0.229	C42	-0.014	C66	-0.235
H19	0.201	C43	-0.222	H67	0.202
H20	0.24	C44	-0.256	H68	0.193
S21	2.299	C45	0.16	H69	0.193
O22	-0.983	C46	0.454	H70	0.201
O23	-1.001	C47	-0.166	H71	0.268
O24	-0.981	C48	-0.12	H72	0.415

Values are mean \pm SD triplicate assays.

Table 5. Energetic parameters and reactivity indices of synthesized DO-26 dye1 (D1) at B3lyp/6-311++G(d,p) level of theory.

Parameters	ET,au	EHOMO,au	ELUMO,au	Eg,eV	I,eV	A,eV	μ , D
D1	-3073.35409	-0.06336	0.02557	2.42	1.72	-0.70	10.98
Parameters	X,eV	η ,eV	S,eV	V,eV	ω , eV	N, eV	
D1	0.51	1.21	0.41	-0.51	0.11	2.49	

Values are mean \pm SD triplicate assays.

Table 6. Values of the Fukui functions and Dual descriptor of DO-26 dye (D1) at B3lyp/6-311++G(d,p) level of calculation.

Atom	f(-)	f(+)	Δf	Atom	f(-)	f(+)	Δf
C1	0.000	0.007	0.007	C28	0.000	0.015	0.015
O2	0.000	0.009	0.009	C29	0.000	0.034	0.034
N3	0.000	0.009	0.009	C30	0.000	0.003	0.003
N4	0.000	0.000	0.000	C31	0.000	0.040	0.040
C7	0.000	0.053	0.053	C32	0.000	0.007	0.007
C8	0.000	0.004	0.004	C33	0.000	0.023	0.023
C9	0.000	0.051	0.051	H39	0.000	0.001	0.001
C10	0.000	0.018	0.018	C40	0.000	0.008	0.007
C11	0.000	0.037	0.037	C41	0.000	0.000	0.000
C12	0.000	0.021	0.021	C47	0.000	0.004	0.004
C13	0.000	0.131	0.131	C48	0.000	0.003	0.003
C14	0.000	0.036	0.036	O55	0.333	0.000	-0.333
C15	0.000	0.044	0.044	O56	0.324	0.000	-0.324
C16	0.000	0.013	0.013	O57	0.334	0.000	-0.334
S21	0.000	0.000	0.000	O58	0.001	0.007	0.006
O22	0.000	0.002	0.002	N59	0.001	0.012	0.011
O23	0.000	0.000	0.000	N60	0.000	0.005	0.005
O24	0.000	0.002	0.002	C61	-0.001	0.001	0.002
O25	0.000	0.100	0.100	C62	0.003	0.002	-0.001
N26	0.000	0.200	0.200	C63	-0.001	0.000	0.001
N27	0.000	0.075	0.075				

Values are mean \pm SD triplicate assays

Table 7. Values of the Condensed local Softnesses (Hartree^{*e}), relative electrophilicity/nucleophilicity (dimensionless) and the Condensed local electrophilicity (ElectroP)/nucleophilicity (NucleoP) index (e^{*e}V) of DO-26 dye (D1) at B3lyp/6-311++G(d,p) level of calculation.

Atoms	s ⁻	s ⁺	Atoms	s ⁺ /s ⁻	s ⁻ /s ⁺	Atoms	ElectroP	NucleoP
C1	-0.076	-0.027	C1	0.36	2.78	C1	0.000	-0.094
O2	-0.144	-0.075	O2	0.52	1.92	O2	-0.001	-0.178
N3	-0.039	-0.026	N3	0.67	1.49	N3	0.000	-0.048
N4	-0.020	-0.015	N4	0.73	1.36	N4	0.000	-0.024
C7	-0.125	-0.032	C7	0.25	3.95	C7	0.000	-0.154
C8	-0.070	-0.059	C8	0.84	1.19	C8	0.000	-0.086
C9	-0.094	-0.010	C9	0.11	9.23	C9	0.000	-0.117
C10	-0.087	-0.114	C10	1.30	0.77	C10	-0.001	-0.108
C11	-0.053	-0.014	C11	0.27	3.73	C11	0.000	-0.066
C12	-0.071	-0.036	C12	0.51	1.97	C12	0.000	-0.088
C13	-0.203	-0.029	C13	0.14	6.94	C13	0.000	-0.250
C14	-0.062	-0.027	C14	0.43	2.34	C14	0.000	-0.077
C15	-0.091	-0.039	C15	0.42	2.36	C15	0.000	-0.113
C16	-0.076	-0.052	C16	0.68	1.46	C16	0.000	-0.094
S21	-0.046	-0.189	S21	4.08	0.25	S21	-0.001	-0.057
O22	-0.073	-0.418	O22	5.69	0.18	O22	-0.003	-0.091
O23	-0.099	-0.337	O23	3.40	0.29	O23	-0.002	-0.123
O24	-0.070	-0.411	O24	5.84	0.17	O24	-0.003	-0.087
O25	-0.252	-0.089	O25	0.35	2.83	O25	-0.001	-0.311
N26	-0.294	-0.002	N26	0.01	176.82	N26	0.000	-0.364
N27	-0.145	-0.090	N27	0.62	1.60	N27	-0.001	-0.179
C28	-0.021	0.000	C28	-0.01	-101.57	C28	0.000	-0.026
C29	-0.080	-0.018	C29	0.22	4.52	C29	0.000	-0.099
C30	-0.089	-0.046	C30	0.51	1.95	C30	0.000	-0.110
C31	-0.173	-0.103	C31	0.60	1.67	C31	-0.001	-0.214
C32	-0.097	-0.063	C32	0.65	1.55	C32	0.000	-0.119
C33	-0.078	-0.052	C33	0.66	1.52	C33	0.000	-0.097
C40	-0.083	-0.052	C40	0.62	1.61	C40	0.000	-0.103
C41	-0.040	-0.074	C41	1.85	0.54	C41	-0.001	-0.049
C42	-0.072	-0.007	C42	0.10	10.25	C42	0.000	-0.088
C47	-0.054	-0.034	C47	0.63	1.59	C47	0.000	-0.067
C48	-0.089	-0.074	C48	0.83	1.21	C48	-0.001	-0.110
C49	-0.071	-0.106	C49	1.50	0.67	C49	-0.001	-0.087
S54	-0.037	-0.195	S54	5.21	0.19	S54	-0.001	-0.046
O55	-0.062	-0.442	O55	7.09	0.14	O55	-0.003	-0.077
O56	-0.068	-0.324	O56	4.75	0.21	O56	-0.002	-0.084
O57	-0.065	-0.442	O57	6.76	0.15	O57	-0.003	-0.081
O58	-0.218	-0.138	O58	0.63	1.59	O58	-0.001	-0.270
N59	-0.243	-0.015	N59	0.06	15.82	N59	0.000	-0.300
N60	-0.118	-0.128	N60	1.08	0.92	N60	-0.001	-0.146
C61	-0.019	-0.006	C61	0.30	3.33	C61	0.000	-0.023
C62	-0.065	-0.030	C62	0.46	2.20	C62	0.000	-0.080
C63	-0.074	-0.056	C63	0.75	1.33	C63	0.000	-0.092

Table 8: Absorption maximum wavelengths (λ_{\max}), electronic excitation energies, and oscillator strengths of **D1** in water.

	λ_{\max} (nm)		ϵ (mol ⁻¹ .cm ⁻¹ .L)	f	ΔE (eV)		Transition assignment
	Exp.	TD-DFT			Exp.	TD-DFT	
S₀→S₁	511	475 (H→L(0.5403))	13,395	1.19	2.43	2.61	$\pi \rightarrow \pi^*$
S₀→S₂	491	466 (H-1→L(0.584))	14,514	0.25	2.53	2.66	$\pi \rightarrow \pi^*$
S₀→S₃	416	412 (H-2→L(0.629))	6,777	0.44	2.98	3.00	$\pi \rightarrow \pi^*$
S₀→S₄	321	319 (H-1→L+2(0.492))	5,440	0.21	3.86	3.88	$\pi \rightarrow \pi^*$
S₀→S₅	302	303 (H→L+2(0.616))	8,313	0.03	4.11	4.1	$\pi \rightarrow \pi^*$
S₀→S₆	272	267 (H-12→L+1(0.239))	7,077	0.02	4.54	4.64	$\pi \rightarrow \pi^*$

Table 9. Percent contributions of molecular fragments to occupied and unoccupied natural transition orbitals in the electronic transitions between the ground state (S_0) and six low-lying singlet excited states (S_n) of **D1** obtained at the PCM-B3LYP (Water) /6-311++G(d,p) level of approximation using *Hirshfeld* population analysis.

		Urea Center	Naphth_R	AzoPh_R	Naphth_L	AzoPh_L	Right-arm	Left-arm
S₀→S₁	Occ.NTO	2.61	20.08	15.06	35.24	26.63	35.15	61.87
	Virt.NTO	3.68	29.90	21.66	25.52	18.82	51.56	44.33
S₀→S₂	Occ.NTO	0.69	35.88	22.17	24.56	16.10	58.05	40.66
	Virt.NTO	3.33	42.47	31.90	12.58	9.10	74.37	21.68
S₀→S₃	Occ.NTO	21.04	34.41	1.50	41.02	1.96	35.91	42.97
	Virt.NTO	3.69	29.82	22.12	24.88	19.04	51.95	43.92
S₀→S₄	Occ.NTO	1.22	46.73	49.27	0.89	0.56	96.00	1.44
	Virt.NTO	3.38	93.73	0.94	1.60	0.25	94.66	1.85
S₀→S₅	Occ.NTO	2.33	1.04	0.01	55.37	41.25	1.05	96.62
	Virt.NTO	3.53	89.14	0.96	6.17	0.10	90.09	6.27
S₀→S₆	Occ.NTO	46.25	3.61	1.34	31.65	17.14	4.95	48.79
	Virt.NTO	5.27	12.39	7.42	44.02	30.75	19.81	74.77

Table 10. Charge transfer (CT) length (Δr) and variation in dipole moment ($\Delta\mu_{CT}$) indices of the six electronic excitations for the studied **D1** obtained at the PCM-B3LYP(Water)/6-311++G(d,p) level of approximation.

	S₀→S₁	S₀→S₂	S₀→S₃	S₀→S₄	S₀→S₅	S₀→S₆
Δr (Å)	7.61	5.36	4.06	3.75	9.22	4.70
$\Delta\mu_{CT}$ (a.u.)	3.34	2.12	2.94	7.10	7.10	2.17

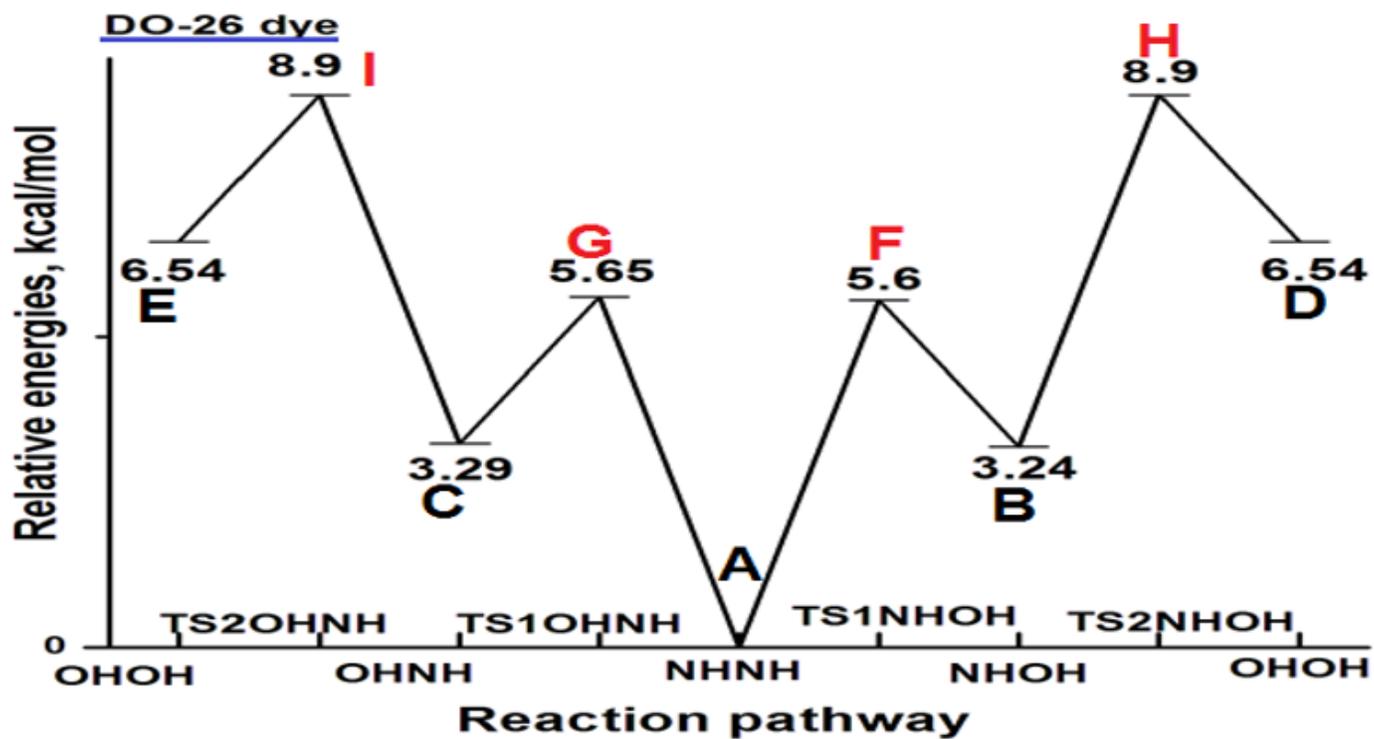


Figure 2

Using the B3LYP/ 6-311++G(d,p) of the DFT theory; the calculated surface relative potential energy values are given for the different tautomeric forms transformations of DO-26 dye (D1).

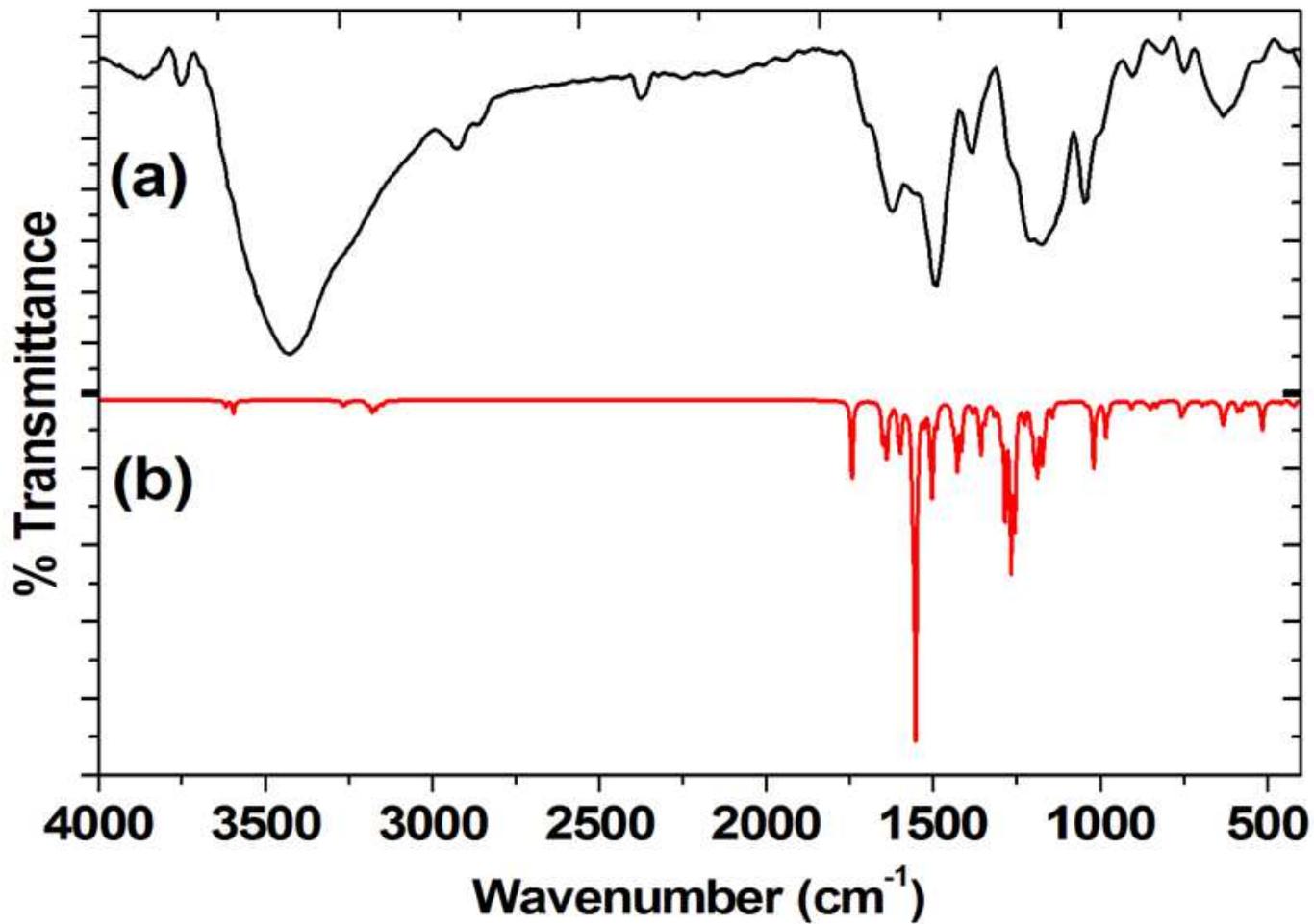


Figure 3

FT-IR spectra of the DO-26 dye (D1) in the region 400-4000 cm^{-1} : (a) Experimental spectra (b) simulated spectra.

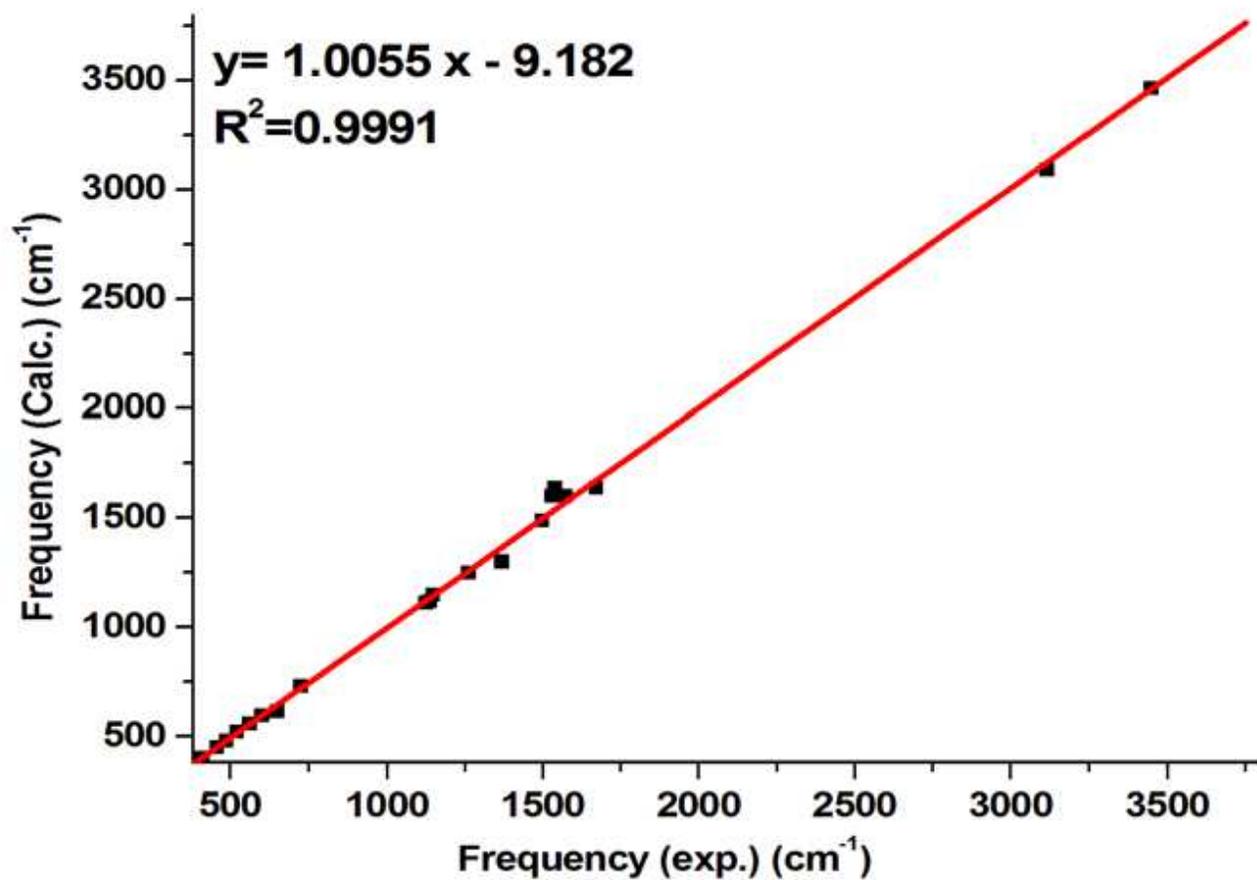


Figure 4

Correlation between experimental FT-IR and simulated IR spectra in the region 4000-400 cm⁻¹ of the DO-26 dye (D1).

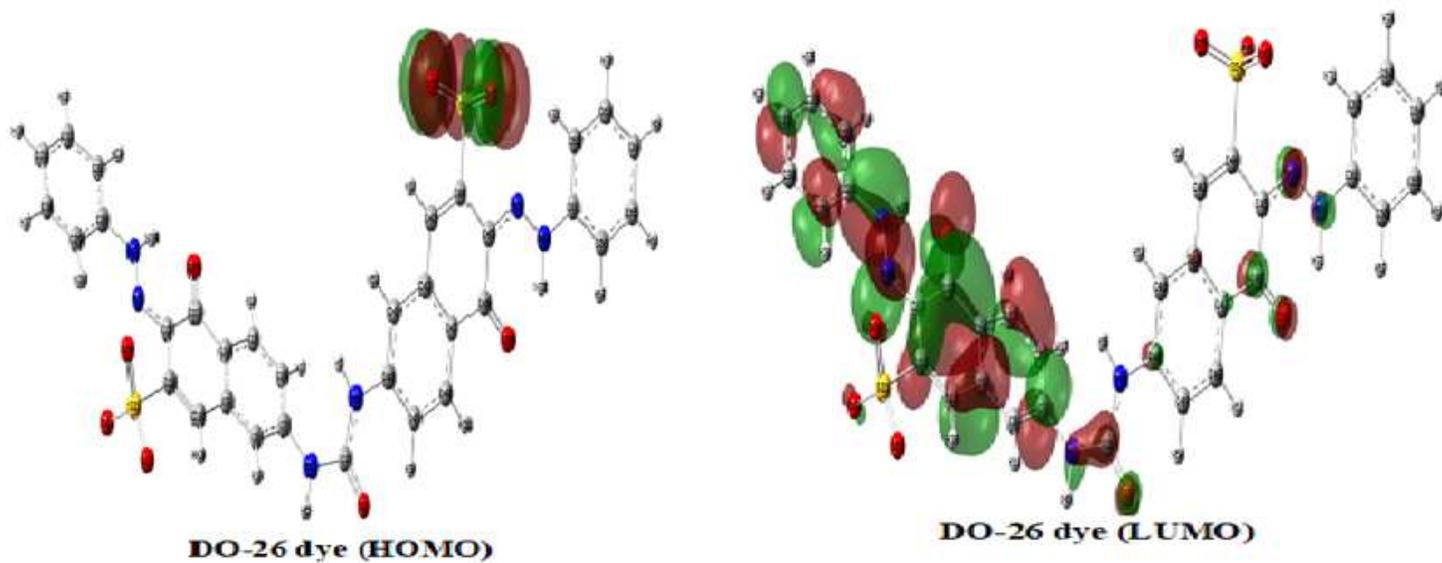


Figure 5

Frontier molecular orbitals of the studied DO-26 dye compounds (D1)

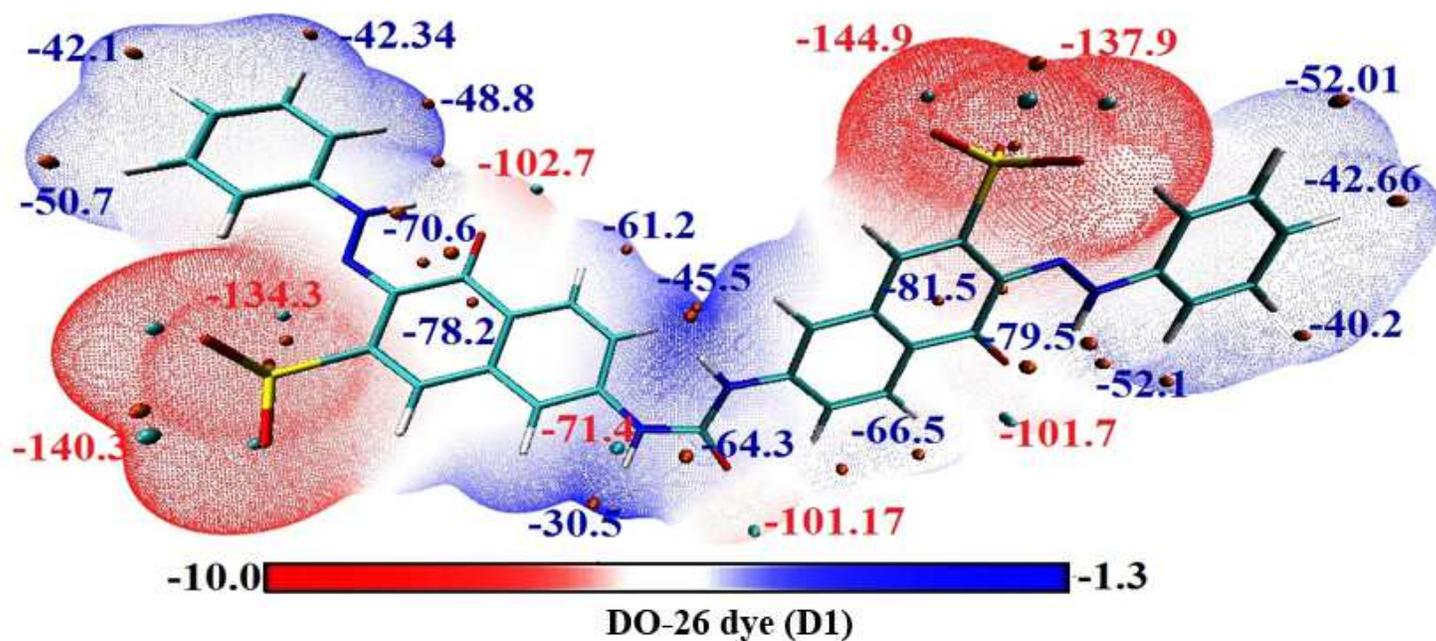


Figure 6

ESP-mapped surfaces of the synthesized DO-26 dye compound (D1)

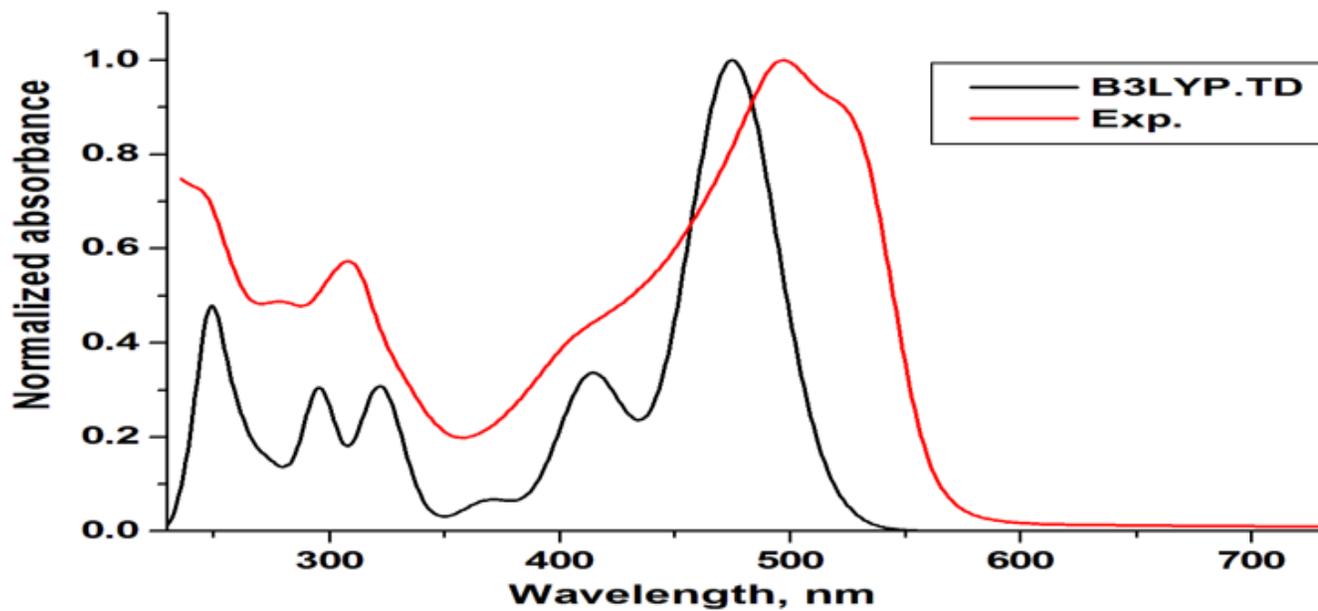


Figure 7

Experimental and theoretical UV/Visible spectra of dye (D1) obtained applying the TD-PCM-B3LYP (Water) /6-311++G(d,p) under level of approximation.

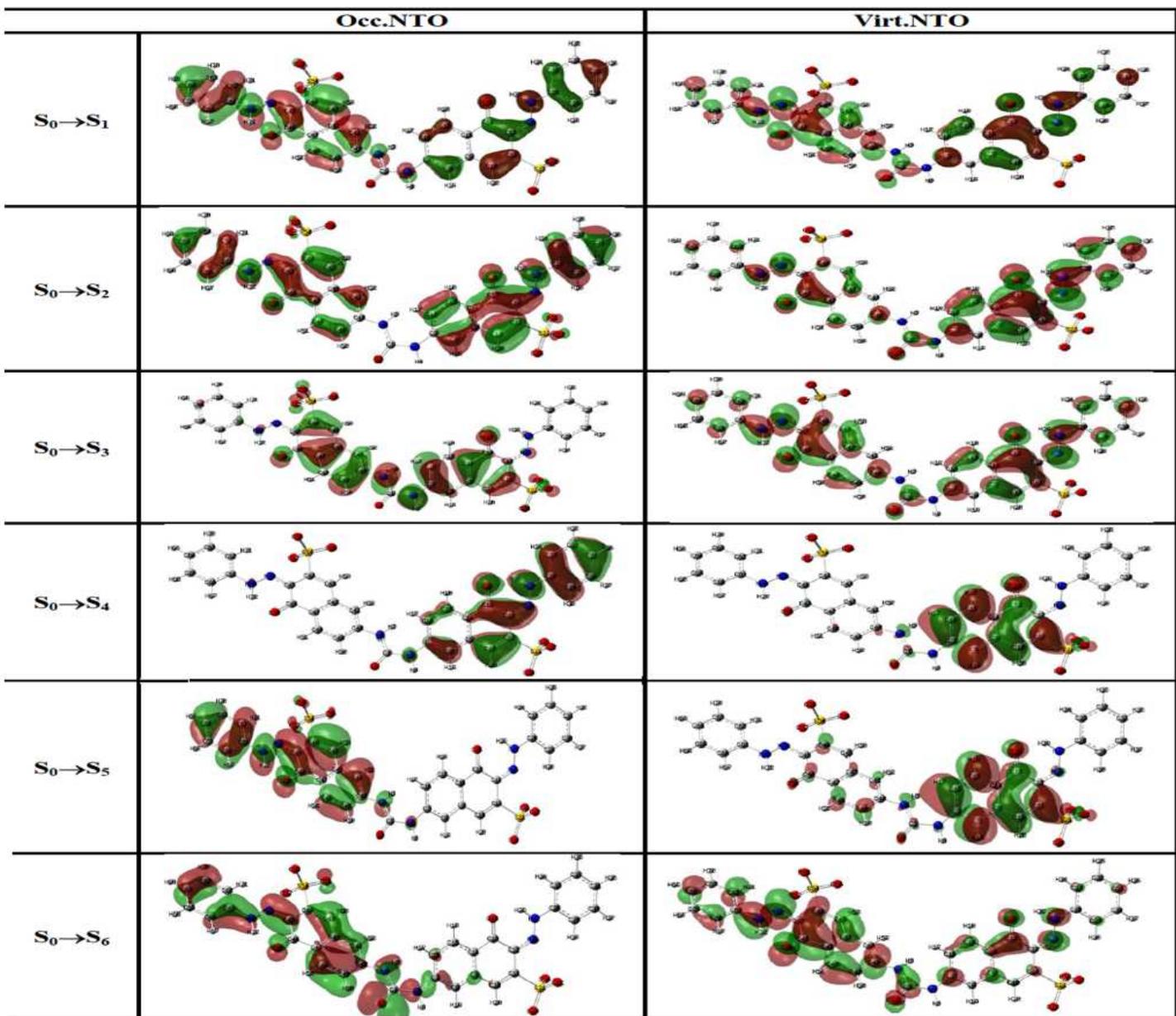


Figure 8

Natural transition orbitals (NTOs) occupied and non-occupied in the electronic transitions between the ground state (S_0) and six low-lying singlet excited states (S_n) of DO-26 dye (D1) obtained at the PCM-B3LYP (Water) /6-311++G(d,p) level of approximation.

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