

Density Functional Theory (DFT) Study of a new 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one Dye for Its Use as Sensitizer in Molecular Photovoltaics

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Abstract: In this study, the geometries, electronic structure and the ground state properties of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one dye have been carried out using Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT). The excitation energies, absorption properties such as maximum wavelength and oscillator strength have been determined. The spectra in the range 200-700nm were found to originate from transitions. We have also investigated HOMO and LUMO levels in gas phase and solvent phases for this dye. Solvent effects have also been studied to describe changes in the energies and UV absorption and that accompanied change in the polarity of the dye. A large red shift of the absorption maximum in the polar solvent suggests an intra-molecular charge transfer character of the excited state. DFT calculation reveals that the small band gap of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one makes it a potential in photovoltaic applications and is also efficient as Dye Sensitized Solar Cells (DSSC).

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Keywords: HOMO, LUMO, Azo dye, Time dependent density theory (TD-DFT).

1.0 Introduction

Azo dyes are a versatile class of coloured organic dyes and receive a large amount of attention in the literature, as a consequence of their exciting biological properties and their applications in various fields, such as textiles, papers, leathers, additives, cosmetics and organic synthesis [1–3]. These form the largest class accounting for more than half the total of disperse dyes. They now cover virtually the whole of the spectrum from greenish yellow, orange, brown, red, bright pink, violet, blue, navy blue, green to black. They contain an enormous variety of structural types [4]. Interest in the design of azo dyes containing heterocyclic moieties stems from their high degree of brightness shade compared to analogous dyes derived from carbocyclic aromatic systems [5-7]. Azo dyes are of particular interest because they can be readily prepared with a wide range of donor and acceptor groups and also because the planarity of the azo bridge versus the non-planarity of other systems should contribute to larger π electron transmission effects and lead to higher optical activity [8-11].

Computational chemistry is, in its broadest sense, the application of computers to understand, interpret and predict chemical phenomena, i.e. the behaviour and properties of atoms, molecules and solids. Due to ongoing advances in computer hardware and software, computational chemistry has developed into an indispensable tool for, and a major branch of, modern chemistry. Computational chemistry methods range from those based on rigorous quantum chemistry (*ab*

initio methods) to semi-empirical methods that use empirical (experimental) data as input, to molecular mechanics methods that apply classical physics, and even to black-box methods (QSPR) that rely on statistical correlations without detailed physical models [12].

Developing molecular modelization approaches allowing an accurate prediction of the colour of dyes is still a major challenge, [13] because, on the one hand, the average human eye is able to tell apart shades differing by 1 nm only, and, on the other hand, actual stains are medium-sized molecules, possess a dozen π electrons, and are very sensitive to the environments. Currently, the most widely applied *ab initio* tool for modeling electronic spectra of structures is the time-dependent density functional theory (TD-DFT) [14]. TD-DFT calculations can incorporate environmental effects [15] and quickly give UV/Vis spectra for most organic [16-19] and inorganic [20-21] dyes.

Theoretical methods are a powerful tool for molecular design, and conclusions drawn from calculations are valuable guidelines for synthesis of new efficient dyes. In recent years, coumarin based dyes have been extensively studied from experimental and theoretical methods [22-27]. Time-Dependent Density Functional Theory (TDDFT/B3LYP) has been used to simulate the electronic absorption spectra of free coumarin dyes [28-32].

TDDFT calculations have been used to establish a relationship between the electronic structure of free

coumarin dyes and their efficiency as DSSC sensitizers [33]. Thus, the location of the first absorption band and the energy of the HOMO orbital were used as parameters to evaluate the electrochemical efficiency of coumarin dyes [34].

Despite these theoretical studies in the evaluation and prediction of azo dyes as DSSC sensitizers, scanty report exist on the properties of dyes that make them suitable as DSSC sensitizers. In this work, we try to study the ground-state properties of new 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one azo dye both in gas phase and in solvents using the density functional theory (DFT) method, with a view to understanding and predicting their efficiency as DSSC sensitizers.

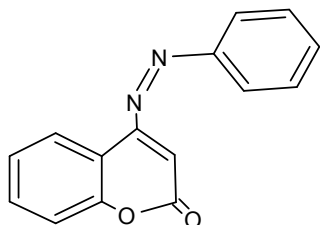


Fig. 1. Structure of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one

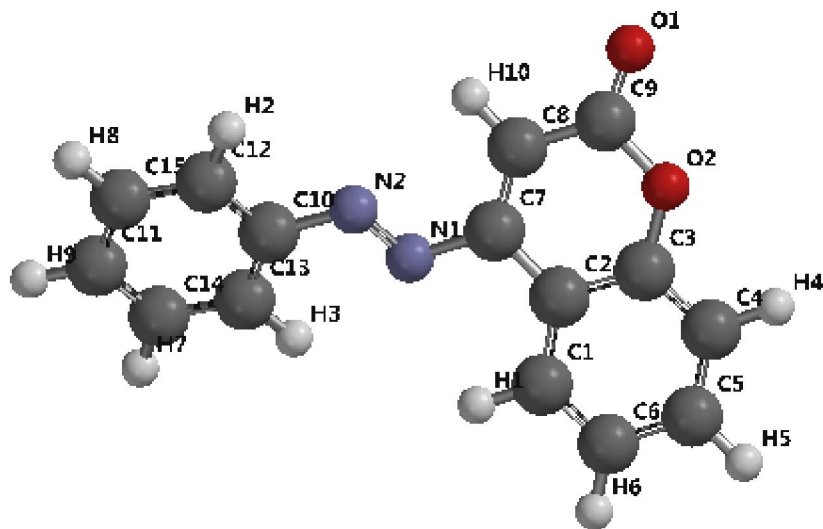


Fig. 2. Ground state optimized Structure of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one (at DFT Level B3LYP Functional and 6-31G* Basis Set).

3.1 Geometries of Optimized Structure

The optimized structure of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one at ground state has a symmetry of C_1 . The selected bond length N_2-C_{10} , N_2-C_7 , N_2-N_1 , C_9-O_1 , C_9-O_2 calculated by B3LYP/6-31G* are 1.415Å, 1.418Å, 1.260Å, 1.209Å, 1.396Å respectively. The selected bond angle $C_{10}-N_2-N_1$, $N_2-N_1-C_7$, $C_8-C_9-O_1$, $C_9-O_2-C_3$, $O_1-C_9-O_2$ are 115.19°, 114.22°, 125.96°, 122.62°, 117.88° respectively and the selected dihedral angle $C_{10}-N_2-N_1-C_7$, $H_{10}-C_8-C_9-O_1$, $O_1-C_9-O_2-C_3$ are 176.21°, 1.42°, 179.09° respectively.

2.0 Computational Method

The minimum ground state structure 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one was obtained by optimizing the ground state geometry at DFT level with B3LYP functional and 6-31G* basis set using SPARTAN 14 package. The geometry properties such as bond length, angle and dihedral were calculated using DFT/B3LYP/6-31G*. The energy gap, polarizability and dipole moment have been performed using DFT/B3LYP/6-311+G* and the spectroscopic properties such as IR and UV/Vis has been performed using 6-311+G** in gas phase. This study was also done in solvent phase on polar solvent (Ethanol) and non-polar solvent (Diethyl ether).

3.0 Results And Discussion

The ground state structure of new 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one has been optimized by using Spartan 14 package at DFT/B3LYP level at 6-31G* basis set. The ground state dipole moment (μ_e) is found to be 6.13 D.

Thus the calculated values agree similarly with the experimental values.

3.2 Electronic properties

The term band gap refers to the energy difference between the top of the valence band to the bottom of the conduction band; electrons are able to move from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy (Table 1) [35-36].

Table 1: Optimized geometry of calculated 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one

Bonds (Å), bond angles and dihedral angles (deg.)	Calculated	Expt.
N2-C10	1.415	1.355
N1-C7	1.418	1.372
N2-N1	1.26	1.281
C9-O1	1.209	
C9-O2	1.396	
C10-N2-N1	115.19	115.34
N2-N1-C7	114.22	110.78
C8-C9-O1	125.96	
C9-O2-C3	122.62	
O1-C9-O2	117.88	
C10-N2-N1-C7	176.21	
H10-C8-C9-O1	1.42	
O1-C9-O2-C3	179.09	

Expt. Value [41]

The measurement of the band gap of materials is important in the semiconductor, nonmaterial, solar industries, and also as a DSSC sensitizer. This demonstrates how the band gap of a material can be determined from its UV absorption spectrum. The band gap energy of insulators is large (> 4eV), but lower for

Table 2: Values of HOMO, LUMO, IP, EA, μ , η , S, ω and band gap for 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one at the B3LYP/6-31+G* level

	HOMO	LUMO	Band gap	EA	M	η	S	Ω	IP
Gas phase	-6.71	-3.26	3.45	3.26	-4.985	1.725	0.5797	7.203	-6.71
Ethanol	-9.06	-0.26	8.80	0.26	-4.66	4.40	0.2272	2.468	9.06
Diethyl ether	-9.05	-0.22	8.83	0.22	-4.635	4.415	0.2265	2.433	9.05

Global hardness and global softness are the basic chemical concepts, called global reactivity descriptors which have been theoretically justified within the framework of DFT. A hard molecule is characterized by a large energy gap and a soft molecule with a small energy gap [42]. Soft molecules are more reactive than the hard molecules because they could easily offer electrons to an acceptor. It indicates that 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one dye is a soft molecule, having a small value of chemical hardness, high value of electrophilicity index which corroborated with its small energy gap.

3.3 Absorption energies

If the absorption of a new material matches with the solar spectrum, is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. On the basis of the optimized ground state structure, we present in Table 5 the vertical energies (eV), molecular orbital (MO) contribution and oscillator strengths along with main excitation configuration of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one in gas, ethanol and diethyl ether

semiconductors (< 3eV) [35-36]. In this work, we have used DFT/BLYP/6-31+G* to estimate the band gap of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one to be 3.45eV (see table 2) in gas phase, which is a value suitable for its consideration as a potential DSSC sensitizers and in solar application. The energy gap was checked for the effect of solvents and we found that the band gap increases to 8.8eV and 8.83eV in ethanol and diethyl ether respectively. The calculated chemical hardness, electronic chemical potential, softness, electrophilic index, ionization energy and the electron affinity values of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one dye are summarized in Table 2.

Global local reactivity descriptors

$$\text{Chemical hardness, } \eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2}$$

$$\text{Softness, } S = \frac{1}{\eta}$$

$$\text{Ionization potential, IP} = -E_{\text{HOMO}}$$

$$\text{Electron affinity of the system, EA} = -E_{\text{LUMO}}$$

$$\text{Electronic chemical potential, } \mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}$$

$$\text{Electrophilic index, } \omega = \frac{\mu^2}{\eta}$$

phases. These values are calculated by TD-DFT method starting with optimized geometry obtained by B3LYP/6-311+G(d) level. The calculated wavelength λ_{abs} of the studied compound are 315.39, 329.99 and 315.91 in gas, ethanol and diethyl ether respectively. The maximum wavelength are found in the ultra-violet (UV) region but there is a large red shift of the absorption maximum in the polar solvent which suggests an intra-molecular charge transfer character of the excited state.

3.3.1 Light Harvesting Efficiency (LHE) and Oscillator Strength (f): Light harvesting efficiency (LHE) and Oscillator strength are important factors to compute the excitation energy transitions from spectral analysis. H.S. Nalwa [37] determined the efficiency of dye to response to the light by the expression in equation 1. The result from our study also agrees similarly with the earlier studied by Nadeem, 2014 [38]

$$\text{LHE} = 1 - 10^{-f} \dots \dots \dots 1$$

The light harvesting efficiency (LHE) of the dye should be as high as feasible to maximize the photo-current response. The oscillator strength is directly

obtained from TDDFT calculations. The high oscillator strength of 4-[(Z)-phenyldiazenyl]-2H-

Chromen-2-one dye may be due to better pi-conjugation.

Dye	ΔE	λ_{\max} (nm)	Oscillator strength, f	Dipole moment, D	LHE
Gas phase	3.45	315.39	0.46931	6.62	0.6606
Ethanol	8.8	329.99	0.80279	7.84	0.8425
Diethyl ether	8.83	315.91	0.4062	7.41	0.6075

3.4 The solvent effect on the absorption spectra

The strong solvatochromic behavior can be observed for dye molecules with large dipole moment changes during transitions between two electronic states. The solvatochromic behavior of a dye is the shift of absorption wavelength due to the presence of solvent with different polarity, which is due to the interaction between the solute and solvent molecules. Polar solvents such as water, alcohols and others may stabilize or destabilize the molecular orbitals of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

(i) $\pi \rightarrow \pi^*$ Transitions

In case of $\pi \rightarrow \pi^*$ transitions, the excited states are more polar than the ground state and the dipole-dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of $\pi \rightarrow \pi^*$ transition and absorption maximum appears ~10-20 nm red shifted in going from diethyl ether to ethanol solvent.

(ii) $n \rightarrow \pi^*$ Transitions

In case of $n \rightarrow \pi^*$ transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Therefore, in polar solvents the energies of electronic transitions are increased [39].

Table 4: Shows the Dielectric Constants (D) and Refractive Index (N) of selected solvents

Solvents	D	N	λ_{\max}
Ethanol	24.85	1.361	329.99
Diethyl ether	4.24	1.353	315.91

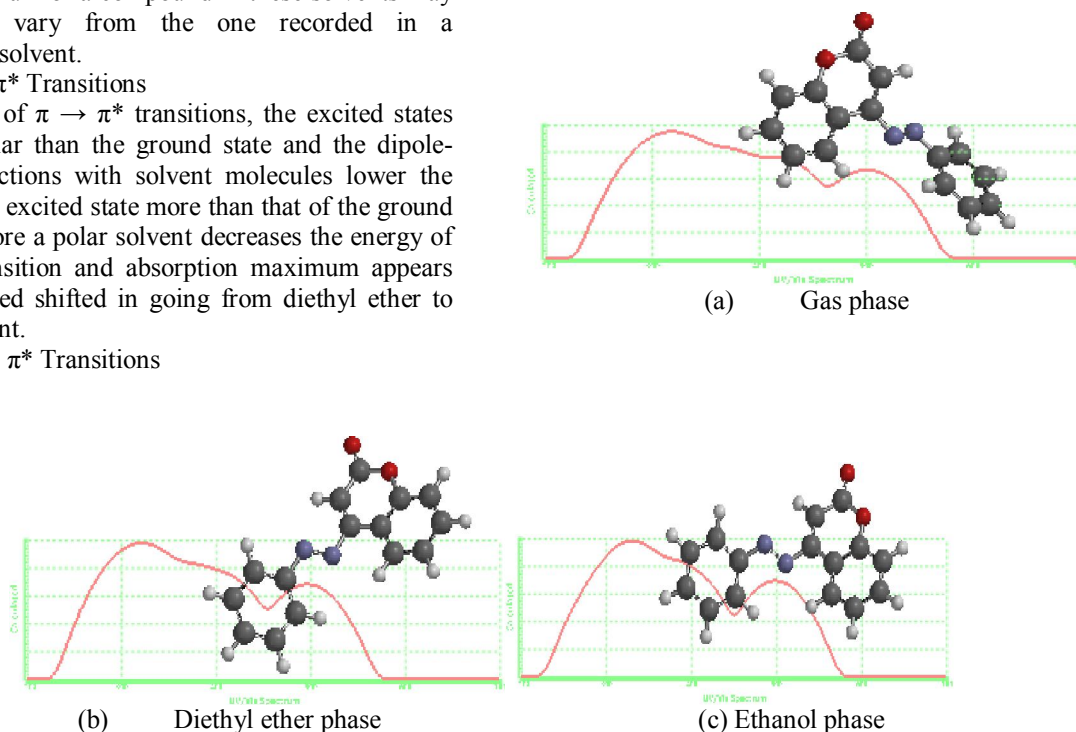


Fig. 3. Absorption spectra of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one in (a) Gas phase (b) Diethyl ether (c) Ethanol using DFT/B3LYP/6-311+G**

3.5 Infrared Spectroscopy: Characteristics infrared (IR) absorption bands such as $C=O_{\text{str}}$, $N=N_{\text{str}}$, $C-H_{\text{str}}$, $C-O_{\text{str}}$, $C=C_{\text{str}}$ among others have been observed for the azo dye. These give evidence on whether or not the dye contains some functional groups. Data and band assignments of the investigated azo dye are shown in Table 6. The IR spectra and the bands frequencies data

shows the presence of a band at 1796 cm^{-1} which corresponds to the $C=O$ stretching vibration of the lactone group. The IR spectra of the studied dye show the $-C=C-$ bands at $1659-1601 \text{ cm}^{-1}$. The bands in the $3230-3188 \text{ cm}^{-1}$ region are due to Ar-H stretching vibration while those appeared in the 3251 cm^{-1} region is due to lactone C-H stretching vibration. The C-H

deformation of the aromatic rings is observed at 779-874 cm^{-1} . The number and shape of these bands depends on the position and the type of substituent present. The bands appearing in the IR spectra of the dye at 1078 cm^{-1} is assigned to the stretching vibration

of C-N and that at 1554 cm^{-1} is assigned to the stretching vibration of N=N. The band appearing at 1279 cm^{-1} is assigned to the stretching vibration of C-O group of lactone presence in the coumarin substituent.

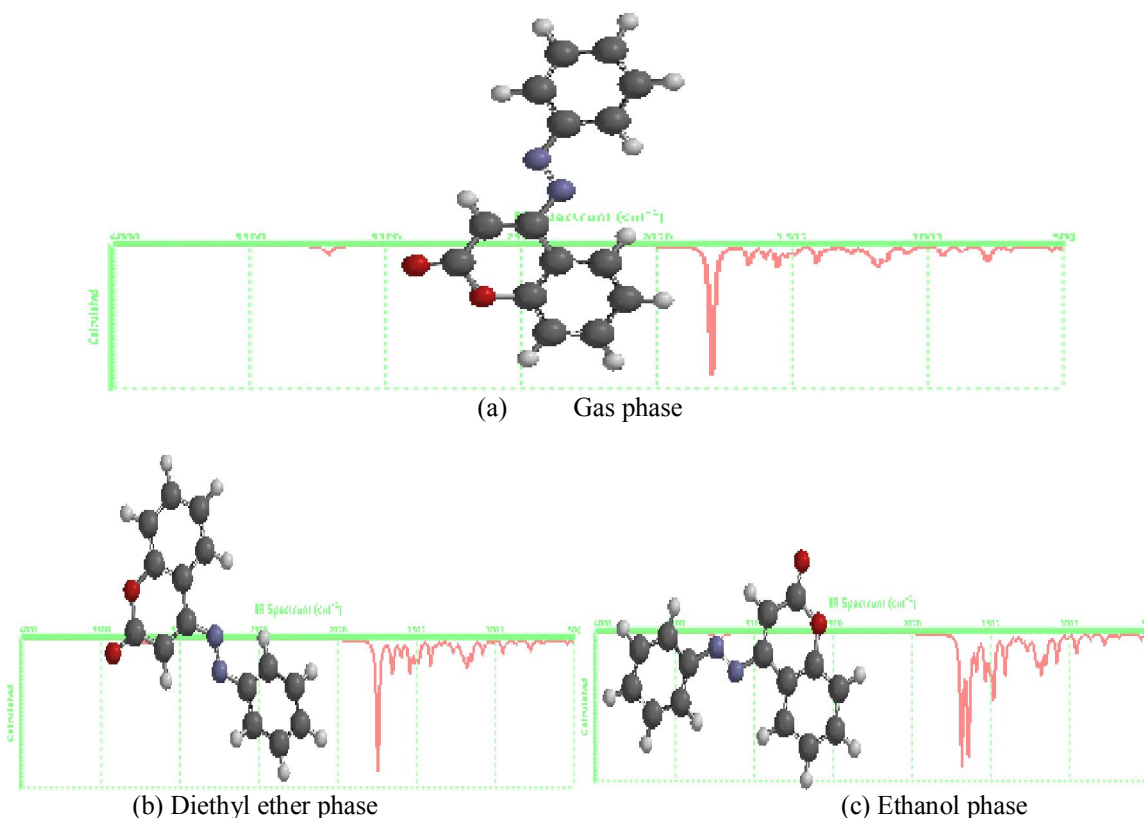


Fig. 4. Shows the infrared absorption spectra of 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one dye in (a) Gas phase (b) Diethyl ether phase (c) Ethanol phase using DFT/B3LYP/6-311+G*

Table 5: Computed TDDFT main vertical excitation energies (nm), oscillator strengths, and MO contribution (%) of 4-[(Z) - phenyldiazenyl]-2H-Chromen-2-one in Gas, Ethanol and Diethyl ether phases.

Gas phase		Ethanol		Diethyl ether	
Vertical energies (Oscillator strengths)	MO Contribution	Vertical energies (Oscillator strengths)	MO Contribution	Vertical energies (Oscillator strengths)	MO Contribution
500.16(0.0101)	H-1→L(84%)	498.48(0.0150)	H→L(71.54%)	495.77(0.0128)	H→L(77.41%)
416.54(0.0385)	H→L(94%)	397.29(0.0291)	H+1→L(72.04%)	405.27(0.0331)	H+1→L(87.01%)
369.79(0.0831)	H-2→L(81%)		H-1→L(49.25%)		H-1→L(35.58%)
335.69(0.0918)	H-5→L(55%)		H→L(45.20%)		H→L(29.26%)
	H-3→L(38%)	374.74(0.0917)	H+1→L(55.84%)	373.00(0.0835)	H-1→L(65.94%)
328.08(0.0159)	H-4→L(80%)		H-2→L(43.05%)		H→L(41.63%)
315.39(0.4693)	H-3→L(47%)		H-3→L(34.86%)	348.05(0.0251)	H-3→L(84.28%)
	H-5→L(28%)	363.01(0.0194)	H-2→L(75.54%)	325.35(0.4021)	H-4→L(63.14%)
	H-4→L(16%)	329.99(0.8028)	H-3→L(65.50%)		H-2→L(53.89%)
			H-2→L(42.76%)		H-3→L(37.84%)
			H→L(39.91%)	315.91(0.4062)	H-4→L(73.34%)
			H-1→L(23.52%)		
			H-4→L(95.02%)		
		303.09(0.0195)			

Table 6: Calculated infrared absorption bands of functional groups in 4-[(Z)- phenyldiazenyl]-2H-Chromen-2-one dye (cm⁻¹)

Vibrations	DFT/B3LYP/6-31+G*	Expt. (cm ⁻¹)
C-H _{str} (aromatic)	3230-3188	3080
C-H _{str} (aromatic)	3251	
C=O _{str} (lactone)	1796	1628
C=C _{str} (aromatic)	1659-1601	1483
N=N _{str}	1554	1522
C-O _{str} (lactone)	1279	1101
C-N _{str}	1078	1333
C-Hd _{ef} (aromatic)	779-874	

Expt. value [40]

Conclusion

In this study we carried out a detailed DFT/TDDFT calculations on new 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one in gas and in solvents (ethanol and diethyl ether). Vertical excitation calculations shows red-shift of the absorption maximum in the presence of a polar solvent and it suggests an intra-molecular charge transfer feature of the excited state. We have also studied using DFT to give better insight into the electronic properties and the global local reactivities; from the results obtained it suggests that 4-[(Z)-phenyldiazenyl]-2H-Chromen-2-one can be used in solar cell applications and as DSSC sensitizers. We hope that our results may provide a reference for further experimental and theoretical work on this particular dye as there is no much information about it so far.

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