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Time Dependent-Density Functional Theory Calculations on Frequency-dependent Photophysical Properties of 2, 3-diphenylcyclopropenone

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Abstract

Time Dependent Density Functional Theory (TD-DFT/B3LYP/6-31G*) calculations have been performed on the optimized structure of 2, 3-diphenylcyclopropenone (DPCP) in the UV region of the spectra; giving energies, oscillator strength, dipole moment, μ and polarizability, α in solvents of different polarities. The study was also extended to the number of transitions, frontier orbital energy gaps (E_{LUMO} - E_{HOMO}) analysis of this strained ring donor–acceptor (D-A) molecular system to calculate its ionization potential (I), electron affinity (EA) and global hardness (η) in the solvent of choice. This aids in understanding the relationship between the structure and properties of this molecule.TD-DFT/B3LYP/6-31G* calculation results, when compared with the reported experimental studies results of the solvatochromic shift properties of this molecule, showed ten excited singlet states for DPCP in the UV region. This indicates minimum overlap of the electronic transition bands computationally. The increased $\Delta E_{LUMO-HOMO}$ (4.09 - 4.31eV), I and η, the lower dipole moments and polarizability values as solvent polarity increased, suggests high stability of this compound in polar solvents. The excess polarizabilities obtained for its singlet excited states show that the excited state of this compound is more polar than its ground state, and that, the molecule is chemically active.

Keywords: Excited states, Polarities, Optimized structure, Diphenylcyclopropenone, Oscillator strength, Polarizabilities, Dipole moment

Introduction

2, 3-diphenylcyclopropenone (DPCP), a highly basic amphiphilic, three-membered strained ring donor–acceptor (D-A) molecular system, have attracted significant attention due to its participation in a wide variety of synthetically useful reactions and its application in medicine (Ashraf , Alaa, Mohsen and El-Sheref, 2007; Damian and Thompson, 2007). This molecule reacts readily with both nucleophilic and electrophilic reagents, forming a ring opening products with the possibility of carbonyl or conjugate addition. Although, it reaction pattern towards dipolar reagents and compounds having a reactive system is sometimes complex, but investigations have established the utility of this molecule as building blocks for the construction of

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larger molecules. Thus, accurate determination of its structural properties, such as; dihedral angles, bond angles bond length, molecular vertical excitation energies, dipole moment and polarizability in different solvent are essential (Ashraf , Alaa, Mohsen and El-Sheref, 2007). These properties determine the solubility of the compound and relate its structure and activities to its usefulness; and predict other structures with desired optical properties (Udhayakala, Jayanthi, Rajendiran and Gunasekaran, 2011). Changes in dipole moment and polarizability usually alter the electrostatic interaction of molecules with the solvent in the ground and excited state, which causes a shift in the absorption maximum (Grozema, Telesca, Jonkman, Siebbeles and Snijders). A prior knowledge of the dipole moments of electronically excited species is also often useful in the design of non-linear optical materials, the elucidation of the nature of excited states and the course of any photochemical (Borbulevych et al., 2002; Raikar , Tangod, Mastiholi and Sreenivasa, 2010; Joshi and Pant, 2012).

Moreover, investigation of Intra-molecular Charge Transfer (ICT) molecules has always been very important in chemistry and biochemistry. This has been focus on systems in which donor and acceptor groups are directly connected through a single σ or π-bond, with the interaction through single bond focused on through-space interaction (hyper-conjugation) between the donor and acceptor, and the interaction through π-bond concentrated on orbital overlap (conjugation) between donor and acceptor groups (Wang and Ho, 2000). The ICT from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both molecular dipole moments and molecular polarizabilities (Raikar , Tangod, Mastiholi and Sreenivasa, 2010). The efficiency of the charge transfer is reflected in the molecular geometry of the ground state of molecules and, in principle, may be an indicator of different electron conjugation effects. Thus, it may be a measure of the contribution of the resonance forms to the ground electronic structure of a molecule (Joshi and Pant, 2012).

The qualitative acceptable description of excited states and properties of any system is much more challenging than its analogous ground state calculation. Thus, many theoretical treatment/computational techniques and experimental procedures have been proposed regarding solvent spectral frequency shifts (Solvatochromic Shift) of organic molecules to estimate the electrostatic properties of molecules in their electronically excited states (Raikar , Tangod, Mastiholi and Sreenivasa, 2010; Adeoye, Obi-Egbedi, and Iweibo). The present work reports the molecular orbital calculations: Time Density Functional Theory (TD-TDFT) of the excited state dipole moments (μ*), excited state polarizability (α*), transition dipole moment (Δμ), frontier molecular orbital energies (E_{HOMO} and E_{LUMO}) and their corresponding energy gaps (E_{LUMO} - E_{HOMO}), absorption wavelength, oscillator strength and vertical excitation energies of DPCP in its first electronically excited in solvent of different polarities.

The inclusion of solvation effect via a Polarisable Continuum Model (PCM) reduces the excitation energies, due to stabilization of the LUMO orbital (Gerlings, De-Proft and Langeneaker, 2003; Shubing, 2005). Moreover, the UV stability, electron distribution and reactivity of this system, based on the Qualitative Structure Property Relationship (QSPR) parameters (Gerlings, De-Proft and Langeneaker, 2003; Shubing, 2005): energy gap, ionization potential (IP), electron affinity (EA), global hardness (η), global electrophilicity (ω) and chemical potential (κ) which a measure of the escaping tendency of electrons from equilibrium are discussed; the results obtained are compared with earlier reports based on the modified Solvatochromic Shift Equation (SSE) (Adeoye, Obi-Egbedi and Iweibo, 2012).

Methodology

Time Density Functional Theory (TD-TDFT) calculation was carried out with Gaussian'03 (Frisch, et al., 2004) using Becke-Lee-Young-Parr composite exchange correlation functional (B3LYP) and 6-31G* basis set for the geometry optimized structure of 2, 3-DPCP in different solvent (methanol, dichloromethane and n-hexane), leading to the energy minima, the determination of the convergence properties of the molecules with the imposition of Cs

point group symmetry it modelled structures (Arivazhagan., Subhasini and Austine, 2012) (Kosar B, 2012). This method was also employed to calculate and analyze the spectral shifts and the absorbance measurements in the Ultra violet (UV) range. The electronic transitions, absorption wavelength, HOMO (Highest Occupied Molecular Orbital), and energies, oscillator strength, and other absorption parameters was also reported.

These absorption spectra parameters obtained provide valuable data base for comparison with the previous experimental results obtained using the modified Solvatochromic Shift Equation (Adeoye, Obi-Egbedi and Iweibo, 2012) and for further future computational studies. Quantum chemical computation of the ground and excited state molecular geometry, dipole moments, polarizabilities, energies and frontier orbital energies were carried out in these media while the frontier orbital energies related molecular parameters were calculated using the following equations:

$$\kappa = {}^{1}/_{2}\,(E_{HOMO} + E_{LUMO}) \quad \text{I}$$

$$\eta = \left(\frac{\delta^2 E}{\delta N^2}\right)_{v(r)} = \left(\frac{\delta \chi}{\delta N}\right)_{v(r)} = \frac{I-EA}{2} = {}^{1}/_{2}\,(E_{LUMO} - E_{HOMO}) \quad \text{II}$$

$$\omega = {}^{\kappa^2}/_{2\eta} \quad \text{III}$$

$$EA = -E_{LUMO} = I - 2\eta \quad \text{IV}$$

$$S = {}^{1}/_{2\eta} \quad \text{V}$$

$$\chi = -(\delta E/\delta N)_{v(r)} = \frac{I+EA}{2} = -\kappa \quad \text{VI}$$

$$I = -E_{HOMO} = \kappa + \eta \quad \text{VII}$$

LUMO (Lowest Unoccupied Molecular Orbital) energies have been calculated. Further, UV stability of the molecules has been discussed in the light of absorption wavelength and electronic transition oscillator strength (*f*). The effect of different solvent media (methanol ε = 33), (dichloromethane ε = 9.1) and (n-hexane ε = 0.00) on the transition

Although, the possibilities of verification of the calculated geometrical structures by the corresponding data are limited, but it has been reported that TD-DFT B3LYP/6-31G* optimization correctly reproduces experimental structures of molecules (Foresman and Frisch, 1996; Deperasinska, 2007). In the light of this finding, it is believed that geometry of the studied molecule as used were correct.

Results and Discussion

The major photo excitation responsible for the optical properties of most studied molecule corresponds to an excitation of an electron from the HOMO to LUMO. The theoretical computed singlet state excitations for 2, 3-diphenylcyclopropenone in methanol, DCM and n-heptane using TD-B3LYP/6-31G* on the optimized structure of the molecule are as shown in Table 1, while the theoretically computed transition dipole moment μ (D) of the compounds are also presented in the Table 2. The HOMO, LUMO, E_{LUMO} - E_{HOMO} and the calculated related molecular parameters which help to predict the types of chemical reactivity for many compounds are presented in Table 3.

Table 1: TD-B3LYP/6-31G//B3LYP/6-31G computed singlet state excitations for 2, 3-diphenylcyclopropenone

		EXCITED STATES									
Solvent		1	2	3	4	5	6	7	8	9	10
Methanol	v(cm^{-1})	28,267	32,116	36,332	36,409	37,873	41,076	44,024	44,305	44,685	45,078
	f	0.0081	0.8892	0.0222	0.0157	0.0003	0.0003	0.0070	0.0297	0.0016	0.0037
	EE(eV)	3.5047	3.9819	4.5047	4.5140	4.6956	5.0929	5.4583	5.4903	5.5402	5.5889
DCM	v(cm^{-1})	27682	31,852	36,390	36,471	37,460	41,078	33,436	43,995	44,216	44,555
	f	0.0071	0.9083	0.0230	0.0150	0.0003	0.0002	0.0067	0.0182	0.0022	0.0189
	EE(eV)	3.4321	3.9492	4.5118	4.5218	4.6445	5.0930	5.4123	5.4546	5.4820	5.5242
n-heptanes	v(cm^{-1})	25,712	31,523	36,054	36,645	36,739	41,088	41,339	41,754	43,636	43,912
	f	0.0038	0.8755	0.0004	0.0189	0.0126	0.0002	0.0012	0.0013	0.0249	0.0424
	EE(eV)	3.1879	3.9083	4.4702	4.5433	4.5550	5.0942	5.1255	5.1757	5.4102	5.4444

f: Oscillator strength, v*: Absorption maximum (in wave number), EE: Excited state energy

Table 2: Theoretically computed transition dipole moment (D) of the compounds

	TRANSITION STATES									
Solvent	1	2	3	4	5	6	7	8	9	10
Methanol	0.306	3.019	0.449	0.377	0.050	0.049	0.228	0.470	0.110	0.164
DCM	0.291	3.064	0.458	0.368	0.050	0.042	0.225	0.370	0.128	0.374
n-heptane	0.220	3.024	0.062	0.412	0.336	0.361	0.981	0.445	0.434	0.564

Table 3: HOMO, LUMO, energy gaps (eHOMO–LUMO), and related molecular properties of 2, 3-diphenyl cyclopropenone

Solvent	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{HOMO-LUMO}$ (eV)	κ (eV)	ω (eV)	I (eV)	EA (eV)	η (eV)	S (eV)	μ (D)	α ($Å^3$)
Methanol	-6.323	-2.022	4.301	-4.173	4.048	6.323	2.022	2.151	0.232	6.031	85.640
DCM	-6.305	-2.024	4.281	-4.165	4.051	6.305	2.024	2.141	0.234	7.033	85.890
n-heptane	-6.142	-2.043	4.099	-4.093	4.088	6.142	2.043	2.049	0.244	7.335	86.881

Electronic properties: Mulliken population distribution and molecular electrostatic potential surfaces.

The optimized structure of DPCP (Figure 1) has planar (C1) geometry. Both HOMO and LUMO of DPCP has π character which is delocalized on the whole molecule. But, the electron densities are more at the carbon (7C and 8C) of the cyclopropenone moiety for LUMO. This leads to the intra-molecular charge separation upon excitation (push-pull effect) (Ramegowda, 2013). The carbonyl carbon (9C) and carbonyl oxygen (O1) has the highest and lowest Mulliken charges based on the calculated Mulliken populations respectively (Figure 3), attesting to the position of high electron densities in the molecule. The electrostatic potential and the Mulliken charges of DPCP predicts that the site of protonation will be the oxygen atom (Figures 3 and 4), which is to be expected as the orbital that contains the electron pair that the proton seeks should be the HOMO. Color red represents the area of high electron density i.e. partially negative charge (oxygen atom due to the presence of two lone pairs of electrons) while the blue area represents area of low electron density (partially positive charge) (Gotwals and Sendlinger, 2006). These attest to the fact that stable molecule of this compound has aromatic character and reacts with both electrophilic and nucleophilic reagents which inform its use in the preparation of a plethora of heterocyclic systems (Breslow, Haynie and Mirra, 1965; Bo, Chang, and Qingwei, 2011).

Spectra Properties

Ten singlet excited states were recorded on the UV-absorption spectra of this molecule as opposed to two or three bands observed in the experimental result. These show that, computationally, the extent of overlap of the transition bands is low. Hypsochromic shifts were observed for virtually all the transitions except the excited states 4 and 6 which were slightly shifted towards the red region of the spectra in polar solvent. Associated with the red shift is the decrease in absorption intensity in both polar and non-polar solvents. For the excited states that are shifted towards the blue region of the spectrum, there are increase in excitation

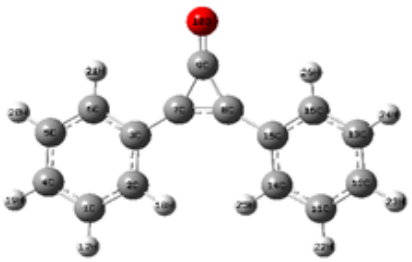
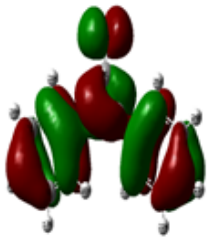
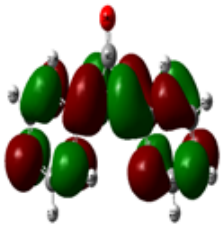


Figure 1: The optimized molecular structure of 2, 3-diphenylcyclopropenone



HOMO



LUMO

Figure 2: Frontier molecular orbital diagrams of DPCP by the TD-DFT/6-3IG* level of theory

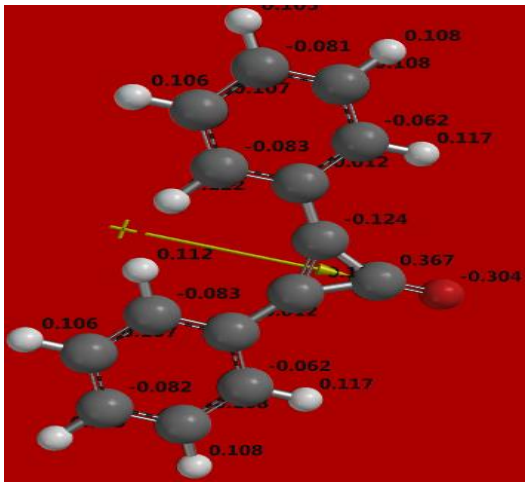


Figure 3: Mulliken charges with the dipole vector of 2, 3- diphenylcyclopropenone

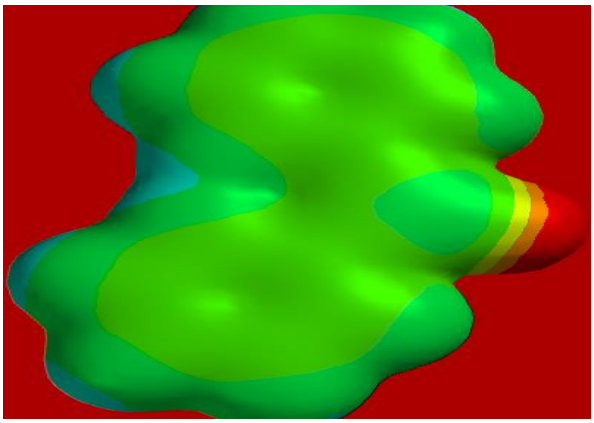


Figure 4: Electrostatic surface potential of 2, 3-diphenylcyclopropenone. Region of high electron density is shown in red and of lower electron density in light blue energy, showing that the ground states of this molecule at this region is more solvated and more polar than its corresponding excited states. This is also supported by the experimental results (Adeoye, Obi-Egbedi and Iweibo, 2012).

The calculated vertical excitation energy level with highest oscillator strength occurred at n=2 in both polar and non-polar solvents. This agrees with the earlier reported experimental absorption spectra with the lowest allowed transitions of DPCP which appears around at 32,516cm^{-1} (Adeoye, Obi-Egbedi and Iweibo, 2012). This can be assigned the HOMO-LUMO transition due to its very strong value of oscillator strength. The calculated transition dipole moment values (Δμ) for the different transitions from the computational results are functions of the oscillator strength (*f*). The higher the *f*, the larger the dipole moment for the compound as confirmed by the experimental results (Adeoye, Obi-Egbedi, & Iweibo) and supported by the approximate theory (Potts and Baum, 1974; Udhayakala, Jayanthi, Rajendiran and Gunasekaran, 2011). From the values of the excited states dipole moment and polarizability presented in Tables 2 and 3, the excited state dipole moment values (μ*) varies with solvent polarity and the lowest value was recorded for the molecule in methanol, the excited state polarizability (α*) also decreases with increasing solvent polarity.

In comparison with experimental estimation Adeoye, Obi-Egbedi and Iweibo (2012), calculated increase in μ in non-polar solvent indicates strong activity of this

compound in non-polar solvent relative to polar solvent. The presence of ICT character of the singlet state is also reflected by the increase in the dipole moment and lower values of its optical gap and excitation energy. The large differences observed between the experimental (Adeoye, Obi-Egbedi, & Iweibo) and calculated values of μ and larger $\Delta\mu_e$ may be due to the various assumptions and simplifications made in the derivation of the solvatochromic shift equations used.

Also, in this strained-ring compound, there is intra-molecular donor-acceptor charge transfer in which there is shift of electron from the phenyl ring through the cyclopropenyl ring to the oxygen atom of the carbonyl carbon (CO) or second phenyl ring of the compound. Moreover, the observed positive values for the transition polarizabilities (Δα) show that the excited states of the compound studied were more polar than their corresponding ground states and that the molecule is highly active (Adeoye, Obi-Egbedi and Iweibo, 2012).

Frontier Molecular Orbital energy gaps and related molecular properties

The HOMO - LUMO energy gap reflects the chemical activity of the molecules (Iweibo, 1991; Bo, Chan and Qingwei, 2011). This property enables the determination of the strength of molecular interactions (e.g., long range intermolecular induction, dispersion forces etc.), the cross-sections of different scattering and collision processes and the optical properties of a system (Eric, Amy and Lisa, 2007). The LUMO is an electron acceptor and represents the ability of any molecule to obtain an electron (or electrons) whereas the HOMO represents the ability to donate electron Ya-Ying, Fu-Ming and Eddy (2008) since it is the outermost molecular orbital with electrons. Consequently, a HOMO→LUMO interaction implies the movement of electrons to or from the aromatic parts of this molecule, the substituents on the ring system of it and the carbonyl C or O atoms on the molecule.

Associated within the frame work of Self Consistent Field Molecular Orbital (SCF-MO) theory, other molecular properties can be obtained through the E_{HOMO} and E_{LUMO} (optical gaps) as expressed in the previous section (Equations III-VI). The larger the optical band gaps, the harder the molecules and electron charge transfer is most when the optical band gap is low (Bo, Chan, & Qingwei, 2011; Obi-Egbedi, Targema, Adeoye and Gbangban, 2015). Thus, the calculated values of ς , A, I, η , χ ω and S expressed through HOMO and LUMO energy values for the molecules are as presented in Table 3. The values of the calculated molecular descriptors/ structure-activity relationship properties slightly depend on the solvent dielectric constant (polarity). The electrotronegativity (χ) values of these molecules in the representative solvents follow the trend $\chi_{\text{n-heptane}} < \chi_{\text{DCM}} < \chi_{\text{methanol}}$ (i.e. increases with increasing solvent polarity). Thus, the selected molecular descriptors vary systematically with the solvent polarity. For this molecule, HOMO, LUMO and optical band gaps has been found to be closer in methanol and dichloromethane, but differ on changing to n-heptane. This shows that these properties are greatly influenced by solvent polarity.

Conclusions

The effect of solvents on the frequency-dependent photo-physical properties of 2, 3-diphenylcyclopropenone in its first electronically excited states was analyzed by Time Dependent Density functional theory with B3LYP/6-31G* level. This theory has been found to provide support for the earlier experimental reported electronic properties of the systems studied in this work, when the experimental errors, solvent interactions and various assumptions and simplifications made in the derivation of the modified solvatochromic shift equations whose consistency was earlier determined were considered. This also confirms the reliability of the method employed.

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