

To Investigate Specific and Non-specific Interactions Effects of Solvents on COXD-Perchlorate Molecule

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Abstract: The electronic absorption and emission spectra of COXD-Perchlorate polar laser dye in distinct organic solvents have been analyzed, to understand the relationship exhibited between absorption spectrum (λ_{max}) and solvatochromic constants, through non-specific and specific interactions effects on the intensities, peak positions of both absorption and emission spectrum. The electronic absorption in distinct solvent exhibits a feeble and broad spectrum domain as a result of $\pi-\pi^*$ transits. Spectral regression techniques were used for the qualitative chemical analyses of a COXD-Perchlorate compound which provide an opportunity to get an insight of solvent ability to form the Hydrogen-coupling with the solute particles besides the electric dipole interactions and electrical-optical molecular parameters in the excited states. The HOMO and LUMO energy band gap suggest compound is softer and highly reactive.

INTRODUCTION

Solvatochromism¹ is one amongst the few existing techniques, that lets to calculate the localized electric field within the core of liquids, eventually by the strength of the intermolecular interactions. Few models merely take account of extended field interactions, ignoring the availability of specific interactions to the overall shift confined to a prone solvent (in Bakshiev's hypothesis)¹. In Bakshiev hypothesis the overall spectral shift confined in electronic spectrum of the molecule is articulated by the means of the relation of the form:

$$\tilde{\nu}_{max} = \tilde{\nu}_{max,0} + a_1 F[\epsilon] + a_2 F[n] \quad (1)$$

Where, $\tilde{\nu}_{max}$ - maximum absorption wavenumber, $\tilde{\nu}_{max,0}$ - maximum absorption wavenumber reported for the gaseous condition of the solute. Functions $F[\epsilon] = \frac{\epsilon-1}{\epsilon+2}$ and $F[n] = \frac{n^2-1}{n^2+2}$ depends on dielectric permittivity and index of refraction of solvent respectively, a_1, a_2 - coefficients. In models like Catalan and Kamlet-Taft^{2,3}, solvent polarity scale is explained by the form

$$\Delta\tilde{\nu}_{sp} = a_3\alpha + a_4\beta + a_5\pi^* \quad (2)$$

Where $\Delta\tilde{\nu}_{sp}$ - specific interactions, α - hydrogen bond donor, β -hydrogen bond acceptor and π^* - polarizability, a_3, a_4, a_5 - coefficients. Computational techniques are also performed. The influence of all kind of interaction is accustomed by the goodness of the coefficients of regression, $a_i, i = 1,2,3,4,5$. The significance of determining the coefficients of regression is because of their usage in an electrical-optical parameter inclusive of dielectric constant or dipole moment in the molecular excited states. In the solvation mechanism, the solvent surroundings decide crucial changes in optoelectrical characteristics of the spectral energetic dye molecules than to the ones in its vaporous stage²⁻⁷.

MATERIALS AND METHODS

The laser dye 9-Cyano-2,3,6,7,12,13,16,17-octahydro-1H,5H,11H,15H-xantheno[2,3,4-ij:5,6,7-i'j'] diquinolizin-4-ium perchlorate (CODX-Perchlorate) is purchased from Exciton Company USA. The solvents used are commercially available S-D Fine Chemicals Ltd, India and all are of spectroscopic grade, laser dye and solvents are used without further purification. The UV-VIS absorption studies were carried out on a Shimadzu UV-1800 spectrometer and steady-state fluorescence studies on Hitachi F-2700 Fluorescence Spectrophotometer (Table 1). All the measurements were performed at 25°C temperature with solutions concentration range 10⁻⁵-10⁻⁶ mol.dm⁻³. Theoretical TD-DFT quantum mechanical computations which were executed in GAMESS to acquire supplementary knowledge of molecular arrangement and electronic properties for CODX-Perchlorate. Molecular orbitals (HUMO, LUMO) and orbital contributions and oscillator energy towards the minimum ten levels of singlet-singlet transits were theoretically calculated in vacuum and ethanol with 6-31G basis set.

THEORETICAL CONTEXT

In elucidating their spectral behavior, solvents effects and specific interactions between solvent and solute particles are of key factors. For regression studies⁸, the equation is of the form,

$$I = a_0 + a_1J_1 + a_2J_2 + a_3J_3 + a_4J_4 + \dots \dots \dots \quad (3)$$

Where a₁, a₂, a₃ and a₄ are distinct coefficients of regression and a₀ –is the invariable regression intercept. The λ_{max} of assigned peak is treated as dependent variable (I), and independent variables (J₁, J₂, J₃, J₄...) of solvent interaction parameters (ε, n, E) or (E, P, Q, R) (Table.1) ε- Dielectric constant, n –refractive index, E- experimental solvent polarity susceptible to solute-solvent and H-coupling interaction. P=[(ε-1)/(2ε+1)] measures solvent polarity agent, Q = [(n²-1)/(2n²+1)] measures solvent induced dipole-solute permanent dipole interaction. R = {[(ε-1)/(ε+2)]-[(n²-1)/(n²+2)]} measures stable dipole-stable dipole interaction. Multiple regression analysis techniques were executed for every situation using Origin 8.5 software (Tables 2).

RESULTS AND DISCUSSION

ELECTRONIC ABSORPTION AND EMISSION SPECTRUM

A λ_{abs} and solvent parameters (Table.1) reveals that cleared redshifts in the absorption maxima with the increase in dielectric constant of solvents. The electronic absorption spectra for CODX-Perchlorate in the domain 250-280nm. The shift is essentially a result of π-π* transits, solvent-solute interactions such as H-bonding and dipolar interaction accounts steadiness of π* orbitals more than the π orbitals. The widespread character of few groups is apparently because of blending of the lowest electronic condition of the hydrogen reinforced complex with distinct electronic states, due to charge exchange from the electron giver particle. The electronic emission spectra in the domain 410-480nm (Fig.1), the shift is essential a result of n-π* transits, sharpening of peaks is least in solvent hexane, propanol, and butanol this may be attributed to electron donating property of perchlorate.

Table I. Solvent parameters and UV absorption and emission spectral data used in the study.

Solvent	n	ε	E	P	Q	R	λ _{abs}	λ _{ems}
Hexane	1.48	1.89	31	0.186	0.221	-0.055	253.5	437.98
Dioxane	1.420	2.210	36.0	0.223	0.202	0.034	274.1	444.37
Ethyl acetate	1.370	6.020	38.1	0.385	0.184	0.400	276.7	458.51
Butanol	1.400	17.51	49.7	0.458	0.195	0.604	268.6	479.09
Propanol	1.380	20.45	50.7	0.464	0.188	0.635	260.9	423.78
Acetone	1.360	20.56	42.2	0.464	0.181	0.646	272.8	456.35
Methanol	1.330	32.66	55.4	0.477	0.169	0.709	265.5	459.42
Acetonitrile	1.340	35.94	45.6	0.479	0.173	0.711	271.6	469.21

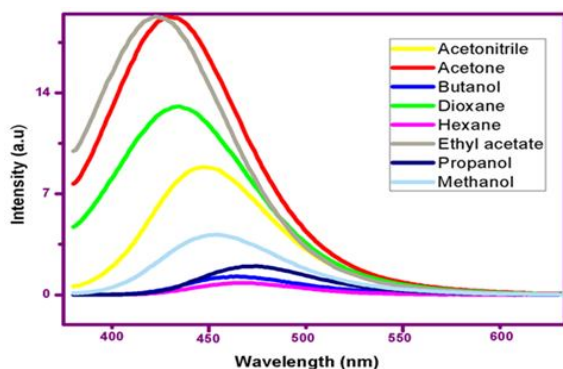


Fig 1. Fluorescence spectra for CODX-Perchlorate in solvents

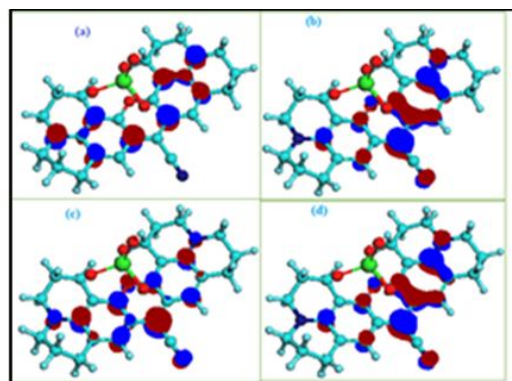


Fig. 2 HOMO and LUMO a) & c) in vacuum b) & d) in Ethanol

SOLVATOCHROMIC ABSORPTION – MULTIPLE REGRESSION RELATIONS ANALYSIS

For a thorough explanation of the solute spectral variations, multi-parameter analysis of λ_{abs} had been considered. Employing the multiple linear coefficient regressions methods numerous one constants forms were accustomed to relate the spectral shifts with distinct experimental solvent polarity. One constant relation λ_{abs} CODX-Perchlorate with ϵ , n or E reveals a high dependence of E (M.C.C = 0.809) than ϵ and n . The relations of E f or dye suggests the solvatochromic role for the transits CODX-Perchlorate is specially governed through the solvent ability to create the Hydrogen-coupling with the solute particles besides the electric dipole interactions. Low MCC value for ϵ and n implies that there is no significant contribution to the spectral shifts, suggests no much non-specific interactions are involved in spectral changes, henceforth combinations are needed. Correlations with two solvent constants for (ϵ , n) and (ϵ , E) with MCC = 0.724 and 0.766 respectively shows the better influence of those constants on the position maxima wavelength than (n , E) with MCC = 0.619. However, the MCC values accomplished when employing different constants E is 0.809 intimates that Hydrogen coupling plays an important task in spectral shift together with ϵ and n .

Relations amongst λ_{abs} of dye with each solvatochromic parameter P , Q , and R in Table.2 exhibits dependency of λ_{abs} of laser dye. One constant relation among λ_{abs} -for dye with either P , Q or R reveals a high dependency of dielectric constant, index of refraction. Correlations with two constants for dye (P , R) and (Q , R) with MCC values of 0.812 and 0.8219 respectively suggests the greater influences of solvent polarity, which is a measure of solute permanent electric dipole- solvent induced electric dipole interaction and permanent electric dipole- permanent electric dipole interaction on particular λ_{abs} -positions. Thus, for CODX-Perchlorate, solute permanent dipole - solvent permanent dipole interactions accumulated with solvent H-bonding ability and/or dipolar interactions and index of refraction is rendering primarily to the empiric solvatochromism. In a lot of events, the distinct three constants combining, suggests that specific solvent-solute interaction especially H-coupling⁸⁻¹⁰ and non-specific solvent-solute interactions inclusive of dispersive and dipolar consequences.

MOLECULAR ORBITALS STUDY

Since, molecular orbital^{11,12} plays a vital role in electro-optical properties, in addition, chemical reaction and UV-visible spectrum. HOMO indicates the variously distinguished donor orbitals, renders the capability to donate an electron and LUMO suggests that of prominent acceptor orbitals, explain the capability to obtain electron. HOMO-1, LUMO+1, renders different donor and acceptors levels, such orbitals specify the way molecule interacts with different species. Molecular orbitals for HOMO-1, HOMO, LUMO, LUMO+1 for laser dye are pictured in Fig. 2. Tables 3 reveals the HOMO-LUMO energy details for in vacuum and ethanol media. For CODX-Perchlorate HOMO and LUMO in a vacuum, electrons are least localized on nitrogen atoms (N5, N15) and carbon atoms (C28, C19, C20, C11, C9, C10, C1, C22,). In ethanol HOMO and LUMO, the electron is localized least localized on (N5) than (N30, N15) nitrogen atoms, (C26, C27, C28) are most localized than carbon atoms (C21, C11, C20, C26, C27, C28C10, C23, C24, C25). Change in dipole moments and oscillator strength is due to the transfers of charges within the molecules which is attributed to Molecular orbitals studies. Dipole moments and oscillator strength are tabulated

in Table 3. It can be inferred from Tables 3, there is a minor change in the values of dipole moments within the vacuum whereas the large change in ethanol during transitions between energy levels for the compound.

Table 2. Multiple linear regression Correlation Coefficients (MCC) for samples using ϵ , n , E and P , Q and R and their combinations solvent parameters for λ_{\max} .

Parameter	a_1	a_2	a_3	MCC	Parameter	a_1	a_2	a_3	MCC
ϵ	2.561			0.432	P	716.2			0.7312
n	-1152.3			0.513	Q	-321.6			0.5762
E	2.521			0.809	R	65.12			0.7641
ϵ, n	2.112	-791.57		0.619	P,Q	14.12	-1187		0.741
ϵ, E	0.175	3.587		0.766	P,R	912.12	-69.96		0.812
n, E	-302.12	3.129		0.724	Q,R	-843.0	271.83		0.8219
ϵ, n, E	0.1791	-313.3	3.001	0.829	P,Q,R	4328.1	-3205	-1419	0.8522

Table 3. HOMO and LUMO energy details for CODX-Perchlorate in Vacuum and Ethanol media.

Orbital	Energy in eV		Oscillator strength		Dipole in Debye	
	Vacuum	Ethanol	Vacuum	Ethanol	Vacuum	Ethanol
H-1	-0.3119	-0.3107	0.5127	0.1621	12.5697	19.0008
H	-0.2613	-0.2167	0.0027	0.0509	15.2025	28.1136
L	-0.0891	-0.0659	0.3218	0.0014	12.8182	45.5025
L+1	-0.0175	-0.0298	0.1198	0.3084	14.4157	39.4514

CONCLUSIONS

The electronic spectra of CODX-Perchlorate have been resolved in different solvents having totally distinct solvatochromic parameters. The absorption and fluorescence spectra of the dye display a key dependency of non-specific and specific solvent-solute interactions. Multi-parameter correlation linear regression studies on absorption spectrum gave different coefficients correlation values, which suggests that observational formulations utilized are advantageous for assessing solvents influences on the electronic absorption and fluorescence spectrum of laser dye. One constant relation λ_{abs} CODX-Perchlorate reveals a high dependence of experimental solvent polarity than dielectric constant and refractive index, suggests the solvatochromic role for the transits CODX-Perchlorate is specially governed through the solvent ability to create the Hydrogen-coupling with the solute particles besides the electric dipole interactions.

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