Ultraviolet Absorption Spectra, Solvent Effect and Non-Linear Optical Properties of 2-Amino-4,6-dimethylpyridine by Hartee-Fock and Density Functional Theory

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In the present work, the ultraviolet absorption spectrum of 2-amino-4,6-dimethylpyridine has been carried out experimentally (in water, *n*-hexane, ethanol, methanol and MgO) and theoretically (in water, ethanol and methanol) in the range 3500-2300 cm^{-1} in the solution phase. Predicted electronic absorption spectra from time dependent density functional theory (TD-DFT) calculation have been analyzed and compared with the experimental UV-visible spectrum. The effects of amino and methyl group substituent in pyridine ring have been analyzed. The electronic properties such as excitation energy, wavelength corresponding to absorption maxima (λ_{max}), oscillator strength (f), HOMO and LUMO energies are calculated by time-dependent density functional theory (TD-DFT) using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) as basis sets. The electric dipole moment (μ), polarizability (α) and the first hyperpolarizability (β) have been computed to evaluate the non-linear optical (NLO) response 2-amino-4,6-dimethylpyridine by Hartee-Fock (HF) and density functional theory (DFT) (B3LYP) with already mentioned basis sets. In addition, Mulliken atomic charges of the atoms are also calculated.

Keywords: Ultraviolet spectrum, 2-Amino-4,6-dimethylpyridine, Hartee-Fock, Density functional theory.

INTRODUCTION

Electronic spectroscopy is concerned with electron transition between orbital of different energy, usually from the occupied orbital of highest energy to vacant orbital of lowest energy. The excitation is as a result of absorption of light, the quantum energy (E) of which is a function of frequency (ν). However, not all absorption of radiation by organic molecules result in electronic excitation, the probability of excitation depends on the wave functions of both the ground and excited states of orbital concerned. The rules about which a transition is allowed or forbidden, is a function of symmetry and multiplicity of the ground and excited state of the orbital concerned. The electronics excitation in a molecule is accompanied by change in vibrational and rotational quantum numbers; therefore what supposes to be absorption lines becomes a broad peak containing vibrational and rotational fine structures. However, the interaction of solute and solvent molecules blurred out the fine structures and a smooth curve is observed [1-4].

As an extension of the earlier works on the ultraviolet absorption spectra of some substituted pyridine compounds [5-13] the present investigation is confined to the study of the UV

absorption spectrum of 2-amino-4,6-dimethylpyridine (Fig. 1). There is no earlier report on the UV absorption spectrum of this molecule.
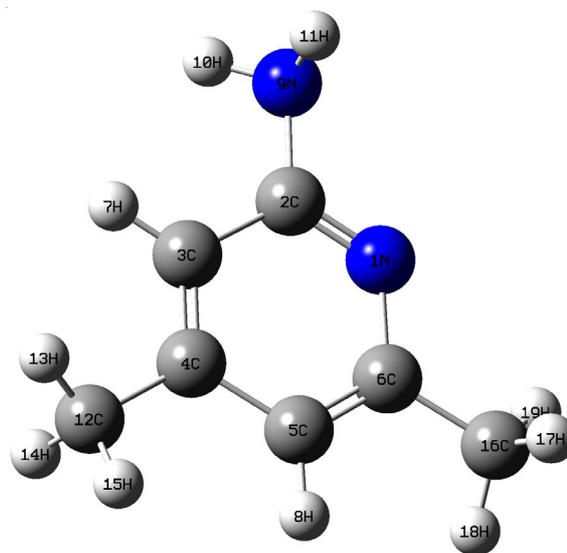
Fig. 1. Optimized geometric structure with atoms numbering of 2-amino-4,6-dimethylpyridine (2,4,6-ADMP)

As part of this investigation on spectroscopy, the electronic absorption spectra have been carried out. The aim of present investigation is to study the effect of solvents and substituents on the absorption spectra of 2-amino-4,6-dimethylpyridine. The aim of present study is twofold namely: (i) To record the electronic absorption spectra for the substituted pyridines in different solvents and to study the effect of these solvents on the absorption spectra. (ii) To study the effect of substituents on the absorption spectra.

EXPERIMENTAL

The compound 2-amino-4,6-dimethylpyridine (2,4,6-ADMP) was purchased from Sigma Aldrich Chemical Pvt. Ltd., Germany with purity of more than 99 % and was used as such without further purification. UV/visible spectra of 2,4,6-ADMP was recorded in solvents water, *n*-hexane, ethanol, methanol and MgO of different polarity as shown in Fig. 2. The solvents were distilled several times to spectro quality grade, while the solute was used without further purification.
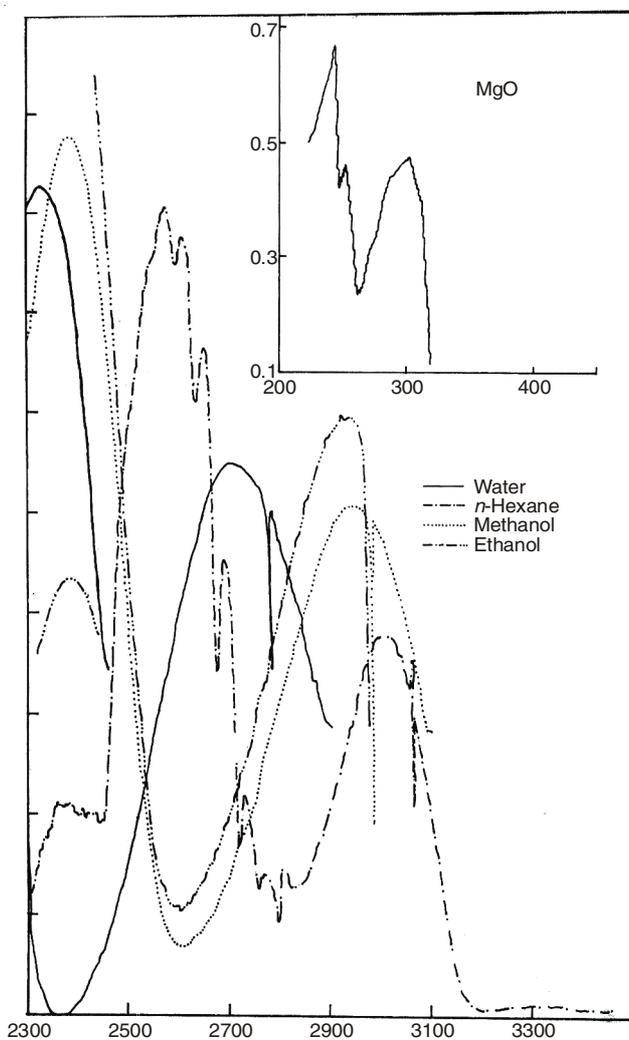
Fig. 2. Electronic absorption spectra of 2,4,6-ADMP in different solvents

Computational details

The computational work was done to determine the optimized geometry of the title compound. The HF (Hartree Fock) and DFT (hybrid B3LYP: the Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional) [14,15] method was chosen for compound 2,4,6-ADMP. The entire calculations were performed by using the Gaussian 09 program package on a personal computer [16]. The electronic absorption spectra for optimized molecule calculated with the time dependent density functional theory (TD-DFT) at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. The time-dependent HF and DFT (TD-HF and TD-DFT) proved to be a powerful and effective computational tool for the study of ground and excited state properties by comparison to the available experimental data. Hence, we used TD-B3LYP to obtain excitation energy, wavelengths (λ_{max}), oscillator strengths and compare with the experimental results of 2,4,6-ADMP. The HOMO and LUMO energies are calculated by using HF and DFT methods with the same basis sets. The non-linear parameters (dipole moment, polarizability and first order hyperpolarizability), Mulliken atomic charges of the atoms are calculated by using HF and DFT methods with the same basis sets.

RESULTS AND DISCUSSION

UV-visible absorption spectra

Shift of O-O band: Kasha [17], Sponer and Rush [18] have shown that π-π* system of pyridines appears at 38350 cm^{-1} in vapour phase. In the present study the spectra was studied in different solvents and in solid phase. The O-O band has been observed at 41660 cm^{-1} in 2,4,6-ADMP. It shows that band system is shifted towards shorter wavelength (2400 Å) in 2,4,6-ADMP. The blue shift is observed at 3310 cm^{-1} in 2,4,6-ADMP. When the shift is observed with different solvents a blue shift was observed under present study as shown in Table-1.

TABLE-1
SHIFT OF O-O BAND (π-π* SYSTEM) OF 2-AMINO-4,6-DIMETHYL PYRIDINE IN DIFFERENT SOLVENTS WITH RESPECT TO PYRIDINE (O-O BAND OF PYRIDINE 38350 cm^{-1})

Solvent	2,4,6-ADMP	
	π-π* band (cm^{-1})	Shift (cm^{-1})
Water	42010	3660
Methanol	41320	2970
Ethanol	41490	3140
n-Hexane	38750	400
MgO	41660	3310

Solvent effect: As suggested by Ram *et al.* [19] in pyridines the introduction of –N= group in place of –CH in benzene exhibit a blue shift in transition 2600 Å band (π-π*). In the present study the near ultraviolet spectra of the molecule 2,4,6-ADMP was observed in different solvents *viz.* water, methanol, ethanol, *n*-hexane and MgO (Fig. 2). The bands as higher absorption are taken to be O-O band. The band system which corresponds to 1_{Alg} -1_{B2u} 2600 Å (π-π*) transition of benzene has been observed between 2580-2380 Å in 2,4,6-ADMP for different solvents. The shift of absorption band occurring upon a change from one solvent to another is due to the salvation energy of the solute in the ground and excited state and is equal to $\Delta v = v_{sol1} - v_{sol2}$. According to Finar [20], polar solvents and those which can form hydrogen bonds tend to

interact electrostatically with various chromophores which changes the charge distribution in the molecule and results in increased delocalization. For π-π* system both ground and excited states are stabilized and absorption maxima moves towards longer wavelength as the polarity of the solvent increases.

The n-π* transition (3100 Å) shift towards shorter wavelength with the increase in the polarity of the solution because in this transition ground state is more stabilized than the excited state. In the present study of 2,4,6-ADMP the π-π* and n-π* system shift towards the shorter wavelength with the increase of the polarity of the solvent while going from ethanol to water (Table-2) with the exception in case of methanol. The wavelength also shifts towards shorter wavelength in case of *n*-hexane *i.e.* non-polar solvent. Similar trend is also observed in case of inorganic solid solvent MgO. From these, it seems that ground state is more stabilized than excited state in both π-π* and n-π* transitions.

In the spectra of monocyclic azynes the absorption band due to transition of an electron from a lone pair orbital to a π orbital of the ring is shifted towards red region by *meta* directing group. Stephensen [21] and Goodmen & Harrell [22] have observed a blue shift in *ortho* halogenated pyridine and pointed out the substitution in *ortho* position exerted an influence through interaction with the non bonding electron of the nitrogen. Therefore, as observed in present case the π-π* system is observed blue shifted to *meta* directing 2,4,6-ADMP. In 2,4,6-ADMP the blue shift from *n*-hexane to water is in the order of decreasing refractive index of the solvents (Table-2), which is in accordance with the work of Mataga and Kubota [23].

On the basis of fully optimized ground-state structure, calculations have been performed to determine the low-lying excited states of 2,4,6-ADMP using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets. The calculated result

involving the vertical excitation energies, oscillation strength (f) and wavelength (λ_{max}) are carried out as shown in Table-3 and compared with measured experimental wavelength listed in Table-2.

For 2,4,6-ADMP, the transitions for HF/6-311++G(d,p) basis set are observed at wavelengths 228, 213 and 202 nm in ethanol at 226, 213 and 202 nm in methanol and at 225, 213 and 202 nm in water solvent. The transitions for B3LYP/6-311++G(d,p) basis set are observed at wavelengths 274, 251 and 243 nm in ethanol, at 274, 251 and 243 nm in methanol and at 273, 250 and 243 nm in water solvent. There are three values of wavelengths for each solvent. For each solvent the first wavelength corresponding to n→π* and another two corresponding to π→π* transitions. The results obtained in B3LYP are nearer to experimental results and are better than those obtained in HF method.

HOMO–LUMO energy: The HOMO (highest occupied molecular orbital) energy characterizes the ability of electron giving, the LUMO (least unoccupied molecular orbital) characterizes the ability of electron accepting and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gap between the HOMOs and LUMOs is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. Both HOMO and LUMO are the main orbitals that take part in chemical stability. The energy values of LUMO and HOMO and their energy gap determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness–softness of a molecule [24]. The molecule having a large energy gap is known as hard and having a small energy gap is known as soft molecule. The hard molecule is not more polarizable than the soft ones because they need big energy to excitation [25,26]. The decrease in the HOMO and LUMO energy explains the intramolecular charge transfer (ICT) interaction taking place within the molecule which is responsible for the activity of the molecule. The HOMO–LUMO energy separation has served as a simple measure of kinetic stability. A molecule with a small or no HOMO–LUMO gap is chemically reactive. Pearson showed that the HOMO–LUMO gap represents the chemical hardness of the molecule [27]. Another parameter that is calculated is electrophilicity index, which measures the energy lowering of a ligand due to maximal electron flow between donor and acceptor [28]. The energies of HOMO, LUMO, HOMO$_{-1}$ (second highest occupied molecular orbital) and

TABLE-2
EFFECT OF SOLVENTS ON n-π* AND π-π* TRANSITION IN 2-AMINO-4,6-DIMETHYL PYRIDINE

Solvent	Refractive index	2,4,6-ADMP	
		n-π*	π-π*
Water	1.3380	2900	2380
Methanol	1.3773	3030	2420
Ethanol	1.3362	2940	2410
n-hexane	1.4500	3010	2580
MgO	–	3000	2400

TABLE-3
ELECTRONIC ABSORPTION SPECTRA OF 2,4,6-ADMP [ABSORPTION WAVELENGTH (λ_{max}, nm), EXCITATION ENERGY (eV) AND OSCILLATOR STRENGTH (f)] USING TD-DFT WITH HF/6-311++G(d,p) AND B3LYP/6-311++G(d,p) BASIS SETS

Solvents	HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)			Assignments
	λ_{max}	E	f	λ_{max}	E	f	
Ethanol	228	5.45	0.0477	274	4.53	0.0395	n-π*
	213	5.84	0.0332	251	4.94	0.0174	π-π*
	202	6.15	0.1093	243	5.11	0.0352	π-π*
Methanol	226	5.49	0.0478	274	4.53	0.0400	n-π*
	213	5.84	0.0319	251	4.95	0.0167	π-π*
	202	6.15	0.1072	243	5.11	0.0344	π-π*
Water	225	5.52	0.0491	273	4.54	0.0430	n-π*
	213	5.84	0.0367	250	4.96	0.0162	π-π*
	202	6.15	0.1038	243	5.12	0.0349	π-π*

LUMO$_{+1}$ (second least unoccupied molecular orbital) and corresponding energy gap in different solvents for 2,4,6-ADMP are calculated with the TD-DFT method and same basis sets and presented in Tables 4 and 5.

The complete equations for calculating ionization potential, electron affinity, chemical potential, global hardness, global softness, electronegativity and electrophilicity index are as follows (Table-6): Ionization potential (I) = –E$_{HOMO}$; Electron affinity (A) = –E$_{LUMO}$; Chemical potential (μ) = (E$_{LUMO}$ + E$_{HOMO}$)/2; Global hardness (η) = (E$_{LUMO}$ – E$_{HOMO}$)/2; Global softness (S) = 1/η; Electronegativity (σ) = – μ; Electrophilicity index (ω) = μ^2/2η.

These values will be same for the solvents ethanol, methanol and water for each basis set since the values of E$_{HOMO}$ and E$_{LUMO}$ are same in all the solvents as shown in Tables 4 and 5.

The contours of the occupied and unoccupied molecular orbitals in different solvents using HF/6-311++G(d,p) basis set is shown in Fig. 3 and using B3LYP/6-311++G(d,p) basis set is shown in Fig. 4.

Mulliken charges: Mulliken charges estimates partial atomic charges calculated from the Mulliken population analysis [29,30]. Here HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets in solvents methanol, ethanol and water are used to calculate mulliken charges. The calculations are carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbitals and are routinely used as variables in linear regression procedures. The mulliken charges of 2,4,6-ADMP is shown in Fig. 5. The figure shows positive and negative charges of atoms of 2,4,6-ADMP.

TABLE-4
CALCULATED ENERGY VALUES (eV) OF 2,4,6-ADMP BY USING TD-DFT/HF/6-311++G(d,p)

Solvents	E$_{HOMO}$	E$_{LUMO}$	E$_{HOMO-1}$	E$_{LUMO+1}$	E$_{LUMO}$ – E$_{HOMO}$	E$_{LUMO+1}$ – E$_{HOMO-1}$	E$_{Total}$ (Hartree)
Ethanol	-0.33	0.04	-0.37	-0.05	0.37	0.32	-379.87
Methanol	-0.33	0.04	-0.37	-0.05	0.37	0.32	-379.87
Water	-0.33	0.04	-0.37	-0.05	0.37	0.32	-379.87

TABLE-5
CALCULATED ENERGY VALUES (eV) OF 2,4,6-ADMP BY USING TD-DFT/B3LYP/6-311++G(d,p)

Solvents	E$_{HOMO}$	E$_{LUMO}$	E$_{HOMO-1}$	E$_{LUMO+1}$	E$_{LUMO}$ – E$_{HOMO}$	E$_{LUMO+1}$ – E$_{HOMO-1}$	E$_{Total}$ (Hartree)
Acetone	-0.25	-0.03	-0.26	-0.02	0.22	0.24	-382.4
Diethyl ether	-0.25	-0.03	-0.26	-0.02	0.22	0.24	-382.4
CCl$_4$	-0.25	-0.03	-0.26	-0.02	0.22	0.24	-382.4

HOMO-Ethanol   HOMO-Methanol   HOMO-Water

LUMO-Ethanol   LUMO-Methanol   LUMO-Water
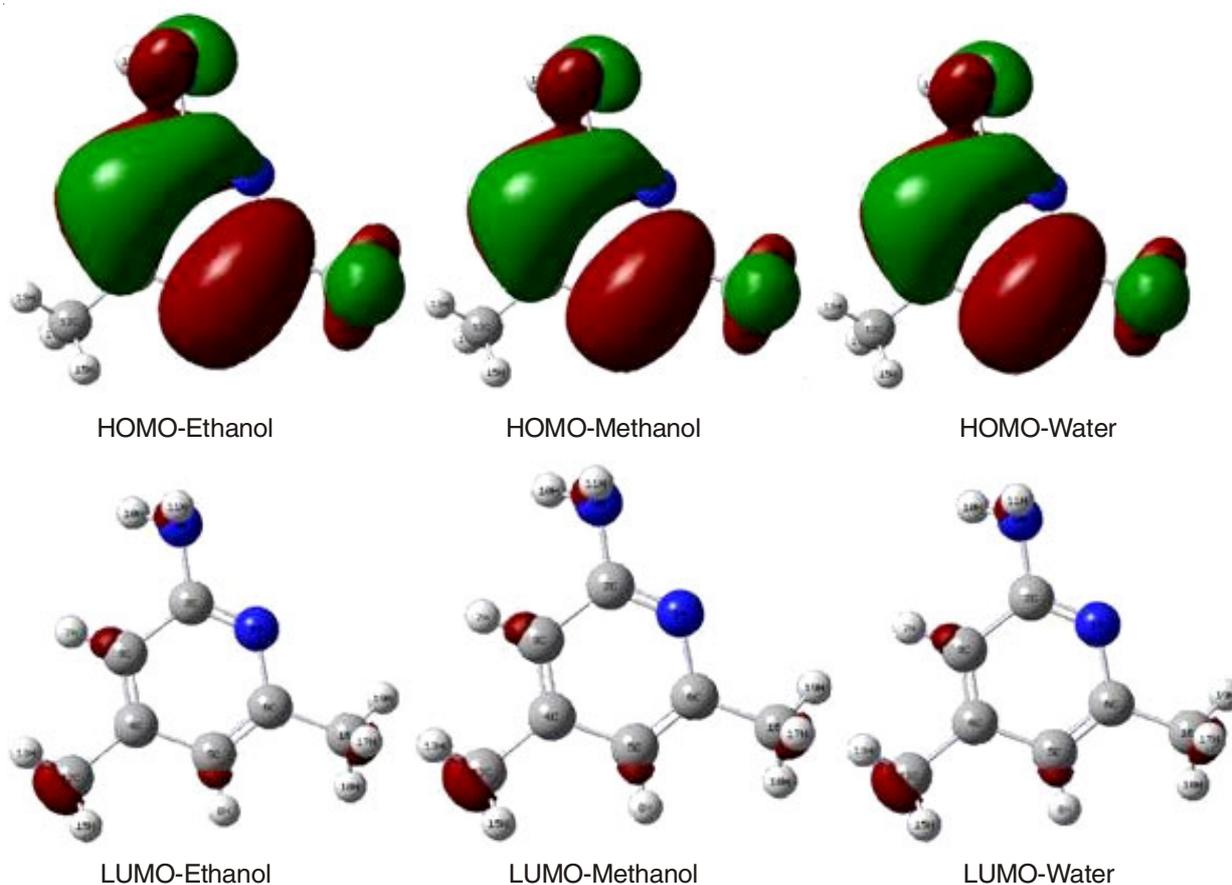
Fig. 3. Contours of the occupied and unoccupied molecular orbitals in different solvents using HF/6-311++G(d,p)
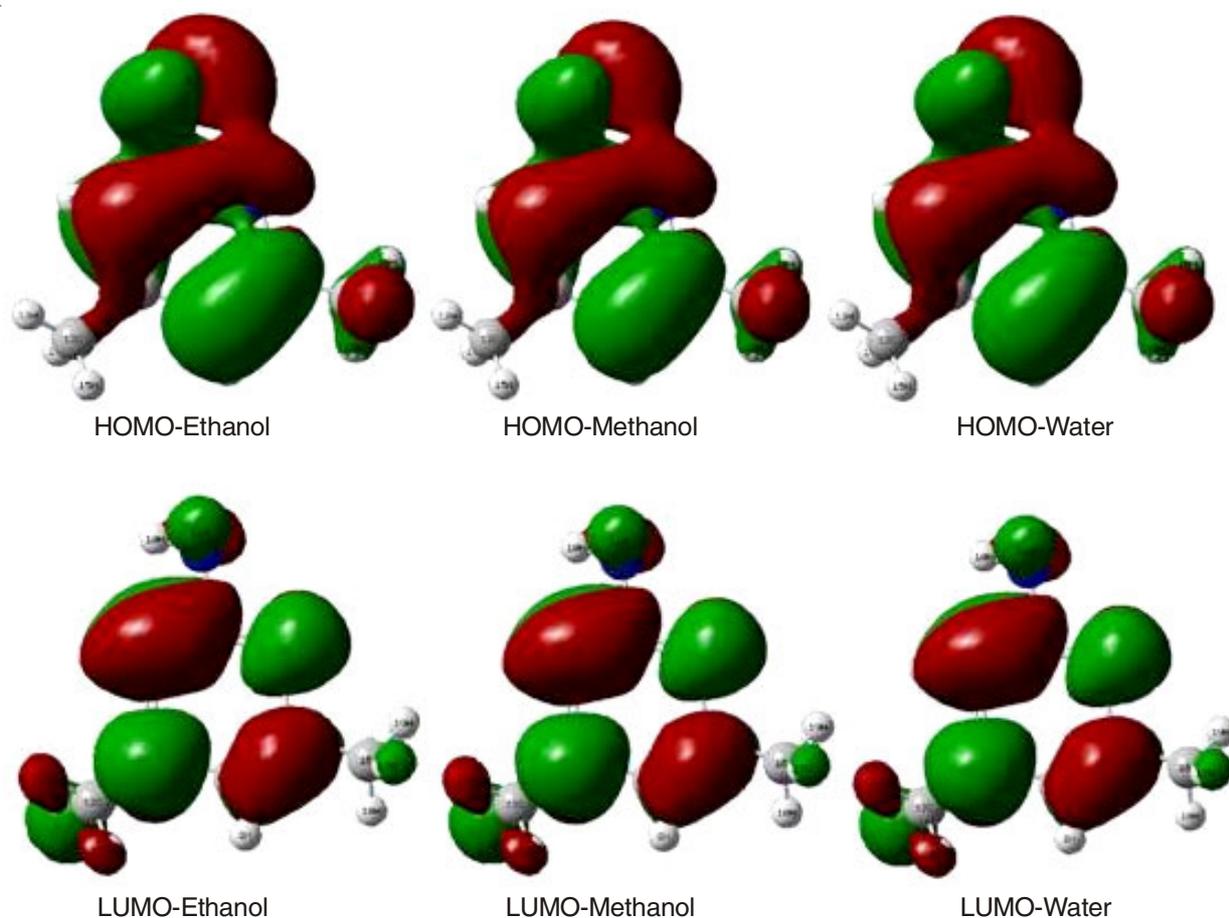
Fig. 4. Contours of the occupied and unoccupied molecular orbitals in different solvents using B3LYP/6-311++G(d,p)

TABLE-6
COMPUTED IONIZATION POTENTIAL (I), ELECTRON
AFFINITY (A), CHEMICAL POTENTIAL (μ), GLOBAL
HARDNESS (η), GLOBAL SOFTNESS (S, eV^{-1}), ELECTRO-
NEGATIVITY (σ) ND ELECTROPHILICITY INDEX (ω)
USING HF/6-311++G(d,p) AND B3LYP/6-311++G(d,p)
BASIS SETS IN THREE SOLVENTS

Parameters	HF/6-311++G(d,p) values (eV)	B3LYP/6-311++G(d,p) values (eV)
E$_{HOMO}$	-0.33	-0.25
E$_{LUMO}$	0.04	-0.03
Ionization potential (I)	0.33	0.25
Electron affinity (A)	-0.04	0.03
Chemical potential (μ)	-0.145	-0.14
Global hardness (η)	0.185	0.11
Global softness (S)	5.4	9.1
Electronegativity (σ)	0.145	0.14
Electrophilicity index (ω)	0.057	0.09

Fig. 5. Mulliken charges of 2,4,6-ADMP computed by HF/6-311++G(d,p) and B3LYP/6-31+G(d,p) basis sets in ethanol, methanol and water [N-nitrogen, C-carbon, H-hydrogen]

Non-linear optical (NLO) properties: Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. Non-linear optical is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for emerging technologies in the areas such as telecommunications, signal processing and optical interconnections [31-33].

The dipole moment (μ), polarizability (α) and second-order polarizability or the first hyperpolarizability (β), are calculated using HF and DFT with 6-31+G(d,p) and 6-311++G (d,p) basis sets on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment (μ), the mean polarizability ⟨α⟩, the anisotropy of the polarizability (Δα) and the mean first hyperpolarizability β$_{Total}$, using the x, y, z components from Gaussian 09W output is as follows:

$$\text{Dipole moment } (\mu) = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \qquad (1)$$

The mean polarizability and anisotropy of polarizability respectively are defined by

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\Big[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 +$$

$$(\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xx}^2 + \alpha_{xy}^2 + \alpha_{yz}^2)^2 \Big]^{\frac{1}{2}} \qquad (3)$$

The mean first-order hyperpolarizability (β_{Total}) is defined as:

$$\beta_{Total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \qquad (4)$$

where, $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$; $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$; $\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$.

It is well known that the higher values of dipole moment, molecular polarizability and hyperpolarizability are important for more active NLO properties. The calculated value of dipole moment was found to be 4.83 Debye [HF/6-311++G(d,p)] and 4.71 Debye [B3LYP/6-311++G(d,p)] for 2,4,6-ADMP. The highest value of dipole moment is observed for component μ_x for 2,4,6-ADMP at all levels of theory. The calculated values of dipole moment with all components are shown in Table-7. The polarizabilities and first hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted

in to electrostatic units (esu) (α: 1 a.u = 0.1482×10^{-24} esu, β: 1 a.u = 8.6393×10^{-33} esu) [33].

The mean polarizabilities $\langle \alpha \rangle$ and anisotropy of polarizability ($\Delta\alpha$) are also included in Table-7 (molecules are in the xy plane). It is observed that the B3LYP/6-311++G(d,p) level of theory leads to higher $\langle \alpha \rangle$ in comparison to other method. The calculated values of $\langle \alpha \rangle$ are -7.74×10^{-24} esu [HF/6-311++G(d,p)] and -7.75×10^{-24} esu [B3LYP/6-311++G(d,p)]. Additionally, the anisotropy of the polarizability ($\Delta\alpha$) has been determined using *ab initio* and DFT methods. The calculated values are 2.88×10^{-24} esu at HF levels and 2.80×10^{-24} esu at B3LYP level for 2,4,6-ADMP. The first static hyperpolarizability calculated values are presented in Table-7. The values of β_{Total} is 3.49×10^{-31} esu at HF/6-311++G(d,p) and 3.46×10^{-31} esu at B3LYP/6-311++G(d,p). The large value of β calculated by the HF and B3LYP methods show that the studied compound is a good NLO material. The theoretical calculation of β components is very useful as this clearly indicates the direction of charge delocalization.

Conclusion

In the present work, an attempt has been made on the experimental and theoretical UV-visible spectral studies, HOMO-LUMO energies, Mulliken charges and NLO properties of industrially important 2,4,6-ADMP. Equilibrium geometries, electronic parameters and thermodynamic parameters of 2,4,6-ADMP have been analyzed at HF and DFT/B3LYP using 6-311++G(d,p) basis set. The TD-DFT calculations on the molecule provided deep insight into their electronic structures and properties. In addition, the calculated UV-visible results are all in good agreement with the experimental data. The lowering of HOMO–LUMO band gap supports bioactive property of the molecule. The predicted NLO properties show that the title compound is a good candidate as non-linear optical material. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non-linear optics.

TABLE-7
NON-LINEAR OPTICAL PARAMETERS (DIPOLE MOMENT, POLARIZABILITY AND FIRST ORDER HYPERPOLARIZABILITY) OF 2,4,6-ADMP

Parameters	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Dipole moments (Debye)		
μ_x	-4.04	-3.90
μ_y	-2.47	-2.48
μ_z	0.96	-0.94
μ_{Total}	4.83	4.71
Polarizability (a.u.)		
α_{xx}	-49.30	-49.78
α_{xy}	-9.97	-9.85
α_{yy}	-50.84	-51.30
α_{xz}	0.90	0.92
α_{yz}	3.40	3.34
α_{zz}	-56.48	-55.86
$\langle \alpha \rangle$	-52.21 = -7.74 × 10⁻²⁴ esu	-52.31 = -7.75 × 10⁻²⁴ esu
$\Delta\alpha$	19.45 = 2.88 × 10⁻²⁴ esu	18.89 = 2.80 × 10⁻²⁴ esu
Hyperpolarizability (a.u.)		
β_{xxx}	-11.08	-11.51
β_{xxy}	-6.20	-5.75
β_{xyy}	-25.86	-24.85
β_{yyy}	-5.40	-6.43
β_{xxz}	-0.95	-0.92
β_{xyz}	1.82	1.80
β_{yyz}	12.0	11.76
β_{xzz}	-0.84	-0.93
β_{yzz}	5.66	5.02
β_{zzz}	2.02	2.0
β_x	-37.78	-37.29
β_y	-5.94	-7.16
β_z	13.07	12.84
β_{Total}	40.41 = 3.49 × 10⁻³¹ esu	40.08 = 3.46 × 10⁻³¹ esu

REFERENCES

1. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley, New York (2004).
2. P.S. Kalsi, Spectroscopy of Organic Compounds, New Age International, New Delhi (2005).
3. E.A. Braude, UV and Visible Light Absorption in Determination of Organic Structures by Physical Methods, Academic Press, New York (1955).
4. Y.R. Sharma, Elementary Organic Spectroscopy, Principle and Chemical Applications, S. Chand and Company Ltd., India (1998).
5. R.N. Medhi, R. Barman, K.C. Medhi and S.S. Jois, *Spectrochim. Acta A*, **54**, 623 (1998).
6. K.C. Medhi and R.N. Medhi, *Spectrochim. Acta A*, **49**, 1024 (1993).
7. K.C. Medhi and R.N. Medhi, *Spectrochim. Acta A*, **47**, 1061 (1991).
8. K.C. Medhi and R.N. Medhi, *Spectrochim. Acta A*, **46**, 1333 (1990).
9. D. Shoba, S. Periandi, S. Boomadevi, S. Ramalingam and E. Fereyduni, *Spectrochim. Acta A*, **118**, 438 (2014).
10. M. Arivazhagan and D.A. Rexalin, *Spectrochim. Acta A*, **107**, 347 (2013).
11. R. Mathammal, N. Sudha, L. Guru Prasad, N. Ganga and V. Krishnakumar, *Spectrochim. Acta A*, **137**, 740 (2015).
12. B.S. Yadav, R. Kumar, M.K. Singh and J. Teotia, *Int. Trans. Appl. Sci.*, **1**, 581 (2009).
13. Vinita, J. Teotia, Seema and M.K.Yadav, *Int. Trans. Appl. Sci.*, **6**, 205 (2014).

14. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).

15. C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, **37**, 785 (1988).

16. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, Gaussian 09 Program, Revision A.02, Gaussian, Inc., Wallingford CT (2009).

17. M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).

18. J.H. Rush and H. Sponer, *J. Chem. Phys.*, **20**, 1847 (1952).

19. K. Ram, B.R. Pandey and R.S. Tripathi, *Spectrosc. Lett.*, **10**, 893 (1977).

20. I.L. Finar, Organic Chemistry: Stereochemistry and the Chemistry of Natural Products, vol. 2 (1975).

21. S. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

22. L. Goodman and R.W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).

23. N. Mataga and T. Kubota, Molecular Introductions and Electronic Spectra, Marcel Dekkar Inc., New York (1970).

24. J.L. Reed, *J. Phys. Chem. A*, **101**, 7396 (1997).

25. C.W. Kwon, A. Poquet, S. Mornet, G. Campet, M.H. Delville, M. Treguer and J. Portier, *Mater. Lett.*, **51**, 402 (2001).

26. R. Kumar, S. Kumar and J. Teotia, *J. Adv. Phys.*, **8**, 2122 (2015).

27. R.G. Pearson, *J. Chem. Sci.*, **117**, 369 (2005).

28. R.G. Parr, L.V. Szentpaly and S. Liu, *J. Am. Chem. Soc.*, **121**, 1922 (1999).

29. R.S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

30. I.G. Csizmadia, Theory and Practice of MO Calculations on Organic Molecules, Elsevier, Amsterdam (1976).

31. M.G. Papadopoulos, A.J. Sadlej, J. Sadley and J. Leszczynski, Non-Linear Optical Properties of Matter, In: Challenges and Advances in Computational Chemistry and Physics, Springer, ISBN:978-1-4020-4849-4 (2006).

32. D.S. Chemla, *Rep. Prog. Phys.*, **43**, 1191 (1980).

33. R. Rajendran, T.H. Freeda, U.L. Kalasekar and R.N. Peruma, *Adv. Mater. Phys. Chem.*, **1**, 39 (2011).