



ISSN 0973-3450

(Print)

JUC Vol. 13(2), 50-59 (2017). Periodicity 2-Monthly

(Online)



ISSN 2319-8036

9 772319 803009



Estd. 2005

JOURNAL OF ULTRA CHEMISTRY

An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering

website:- www.journalofchemistry.org

Quantum chemistry calculations of 2-aminopyrimidine-5-carbonitrile Dye Sensitizer for Solar Cells

S. ARUL¹ and T. SENTHILNATHAN²¹Assistant Professor, Department of Physics, GRT Institute of Engineering and Technology, Tiruttani-631209²Professor, Department of Physics, Velammal Engineering College, Chennai – 600 066Email: senphy@yahoo.comEmail address of Corresponding Author:- arulvenkt@gmail.com<http://dx.doi.org/10.22147/juc/130206>

Acceptance Date 20th Feb., 2017,

Online Publication Date 2nd March, 2017

Abstract

Quantum chemistry calculations of energies, geometries, electronic structures, polarizabilities, and hyperpolarizabilities of organic dye sensitizer 2-aminopyrimidine-5-carbonitrile were studied based on ab initio HF and Density Functional Theory (DFT) using the hybrid functionals B3LYP. Ultraviolet-visible (UV-Vis) spectrum was investigated by Time Dependent DFT (TDDFT). Features of the electronic absorption spectrum in the visible and near-UV regions were assigned based on TDDFT calculations. The electronic absorption bands are assigned to $\pi \rightarrow \pi^*$ transitions. Calculated results suggest that the three excited states with the lowest excited energies in 2-aminopyrimidine-5-carbonitrile is due to photo induced electron transfer processes. The interfacial electron transfer between semiconductor TiO_2 electrode and dye sensitizer 2-aminopyrimidine-5-carbonitrile is due to an electron injection process from excited dye to the semiconductor's conduction band. The role of amine and nitrile group in 2-aminopyrimidine-5-carbonitrile geometries, electronic structures, and electronic absorption spectra were analyzed in Dye sensitizer solar cell (DSSC) give good conversion efficiency.

Keywords: Dye sensitizer, Density functional theory, Electronic structure, Absorption spectrum.

1. Introduction and preliminaries

The Dye-Sensitized Solar Cell (DSSC) have attracted a great deal of interest rapidly in the attention of many research groups during the recent year¹. Since the first developed and reported by M. Gratzel *et al.* in the 1991². The advantages of the DSSC are that it uses the widely abundant and non-toxic TiO_2 material. The sensitizer is capable of absorbing light and inducing an electron transfer to the conduction wide-band gap of the TiO_2 semiconductor. An electrolyte, *i.e.* organic solvent

containing an iodide/trioxide redox couple (I/I-3), is in charge of the regeneration of the photo oxidized dye molecules. For the operation of the photochemical device, the counter electrode is sealed to the working photo electrode with a spacer and the volume between the electrodes, as well as the voids between the TiO_2 nanoparticles, are filled with the electrolyte solution. Ru-based sensitizers have attracted much attention because they exhibit impressive solar energy conversion efficiencies of ~11.1 %^{4, 5}. However, the depletion of Ru and its toxicity have prompted research into metal-free organic sensitizers that are inexpensive, abundant, ecofriendly, have high molar

absorption coefficients, and most importantly, have tunable spectral and electrochemical properties⁶⁻⁸. Although the DSCs show excellent energy conversion, their commercial applications are still limited because of stability and long-term operation problems, such as solvent evaporation or leakage, as well as degradation of the electrolyte or of the dye. In order to overcome these disadvantages it is of high interest to replace the liquid electrolyte with solid state materials. Carbonitrile is an important class of high performance dyes, which are easily processable, and display good mechanical properties, outstanding thermal and thermal-oxidative stability. Nitrile dyes were used for aerospace, marine, and electronic packaging applications. By thermal treatment of nitrile derivatives at elevated temperatures (generally high up to 350 °C) for an extended period of time. In this work the performance of 2-aminopyridine-5-carbonitrile metal free dye that can be used in DSSC is analyzed.

2. Computational methods :

The computations of the geometries, electronic structures, polarizabilities and hyperpolarizabilities, as well as electronic absorption spectrum for dye sensitizer 2-aminopyridine-5-carbonitrile was done using ab initio HF and DFT with Gaussian03 package⁹. The DFT was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP)¹⁰⁻¹², and all calculations were performed without any symmetry constraints by using polarized split-valence 6-311G++ (d, p) basis sets. The electronic absorption spectrum requires calculation of the allowed excitations and oscillator strengths. These calculations were done using TD-DFT with the same basis sets and exchange-correlation functional in vacuum and solution, and the non-equilibrium version of the polarizable continuum model (PCM)^{13, 14} was adopted for calculating the solvent effects.

3. Results and Discussion

3.1 The geometric structure :

The optimized molecular structure of 2-aminopyrimidine-5-carbonitrile was obtained from Gaussian 03 and Gauss view programs were shown in Fig. 1 The optimized structural parameters (the bond length, bond angle and dihedral angle) calculated by B3LYP with 6-311++G (d, p) basis set are shown in the Table 1. Since the crystal structure of the exact title compound is not available till now, the optimized structure can be only be compared with other similar systems for which the crystal structures have been solved. From the theoretical values we can find that most of the optimized bond lengths, bond

angles and dihedral angles. The optimized bond lengths of C1-C2 and C3-C4 is 1.35 and 1.08 Å respectively at B3LYP/6-311G++ G (d, p) and also well matched with HF/6-311G++ G (d, p)

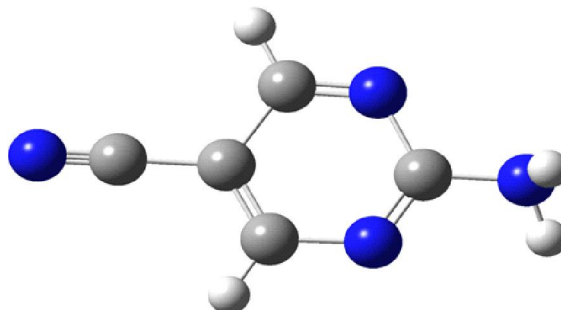


Fig. 1: Optimized geometrical structure of dye 2-aminopyrimidine-5-carbonitrile

3.2 Comparative Vibrational frequency analysis :

The IR and Raman spectra calculated by ab initio HF of 2-aminopyrimidine-5-carbonitrile is HF/6311++G (d, p) and B3LYP/6311++ (d, p) basic set. The strongest value of IR absorption for 2-aminopyrimidine-5-carbonitrile corresponds vibrational mode 28 near about 1614 cm⁻¹, which corresponds to stretching mode of C=C bonds. From the Figure 2 and 3, it is found that the calculated frequencies by B3LYP/6311++ (d, p) basic set are closer to the HF/6311++G (d, p) basic set. These values obtained by HF and DFT methods are strongly underestimated. In small difference of the calculated vibrational mode is observed. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with experimental values. Any way not with standing the level of calculations it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. In our study we have followed two different scaling factors B3LYP/6-311G++(d,p) and HF/6-311G++(d,p). IR and Raman spectra observed frequency shown in Fig: 2 and Fig: 3. The frequencies strongest of IR absorption for 2-aminopyrimidine-5-carbonitrile B3LYP/6-311G++ (d, p) 1712 cm⁻¹ and HF/6-311G++ (d, p) 1744 cm⁻¹ respectively. The frequencies of strongest Raman activity for 2-aminopyrimidine-5-carbonitrile B3LYP/6-311G++ (d, p) 2448 cm⁻¹ and HF/6-311G++ (d, p) 2416 cm⁻¹ respectively.

3.3 Polarizability and hyperpolarizability :

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field¹⁵. They determine not only the strength of molecular interactions (long-range intermolecular induction, dispersion

Table 1. Bond lengths (in Å), bond angles (in degree) and dihedral angles (in degree) of the dye 2-aminopyridine-5-carbonitrile

S.No.	Bond length(Å) bond angles (in degree) and dihedral angles (in degree)	B3LYP/6311G+(d,p)	HF/6-311G++(d,p)
1.	C1-C2	1.35	1.30
2.	C1 -N6	1.35	1.31
3.	C1- C9	1.32	1.34
4.	C2-C3	1.40	1.35
5.	C3- C4	1.08	1.38
6.	C3-C10	1.40	1.07
7.	C4- C5	1.42	1.3
8.	C4- C7	1.32	1.43
9.	C4- C6	1.08	1.07
11.	C7- C8	1.16	1.35
12.	C9- C12	1.00	1.13
13.	C9-C1	1.00	0.99
14.	C2-C1-C6	126.16	0.99
15.	C2-C1-C9	116.92	115.83
16.	C6-H1-C9	116.45	122.05
17.	C1-C2-C3	116.32	122.05
18.	C2-C3-C4	122.67	125.39
19.	C2-C3-C10	116.83	117.77
20.	C4-C3-C10	120.08	123.70
21.	C3-C4-C5	115.83	118.52
22.	C3-C4-C7	122.08	117.85
23.	C5-C4-C7	122.08	121.08
24.	C4-C5-C6	122.68	117.67
25.	C4-C5-C11	120.49	123.76
26.	C6-C5-C11	116.82	121.06
27.	C1-C6-C5	116.32	118.56
28.	C1-C9-C12	119.59	125.46
29.	C1-C9-C13	119.59	117.67
30.	C12-C9-C13	120.80	117.66
31.	C4-C7-C8-C5-C-1	180.02	118.34
32.	C4-C7-C8-C5-C-2	179.99	180.01
33.	C6-C1-C2-C3	-0.00	180.05
34.	C9-C1-C2-C3	179.98	-177.77
35.	C2-C1-C6-C5	0.00	-0.88
36.	C9-C1-C6-C5	-179.98	177.91
37.	C2-C1-C9-C12	-0.04	-14.78
38.	C2-C1-C9-13	180.01	-166.47
39.	C6-C1-C9-C12	-180.05	-166.49
40.	C6-C1-C9-C13	0.00	14.80
41.	C1-C2-C3-C4	-0.00	-0.82

42.	C1-C2-C3-C10	180.00	179.10
43.	C2-C3-C4-C5	0.00	0.43
44.	C2-C3-C4-C7	-179.98	-179.89
45.	C10-C3-C4-C5	-179.99	-179.46
46.	C10-C3-C4-C7	0.00	0.17
47.	C3-C4-C5-C6	-0.00	-0.31
48.	C3-C4-C5-C11	179.99	179.47
49.	C7-C4-C5-C6	179.99	180.01
50.	C7-C4-C5-C11	-0.00	-0.19
51.	C4-C5-C6-C1	0.00	0.57
52.	C11-C5-C6-C1	179.99	-179.23

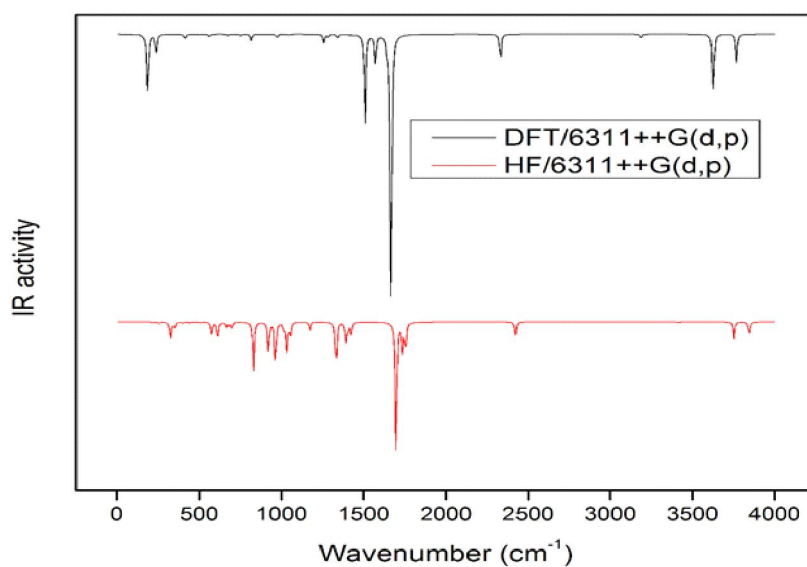


Fig: 2 Observed IR spectra in 2-aminopyridine-5-carbonitrile

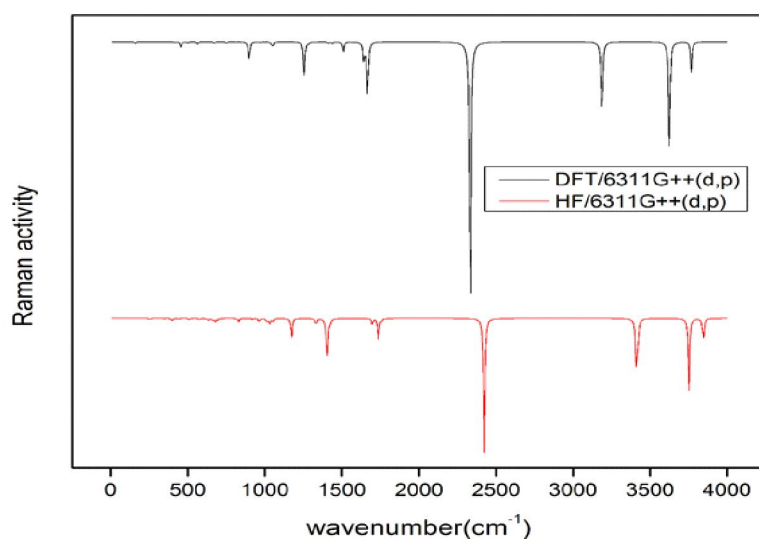


Fig: 3 Observed Raman spectra in 2-aminopyridine-5-carbonitrile

forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties (NLO) of the system¹⁶. It has been found that the dye sensitizer hemicyanine system, which has high NLO property, usually possesses high photoelectric conversion performance. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of 2-aminopyridine-5-carbonitrile was calculated.

The polarizabilities and hyperpolarizabilities could be computed via finite field (FF) method, sum-over state (SOS) method based on TDDFT, and coupled-perturbed HF (CPHF) method. However, the use of FF, SOS, and CPHF methods with large sized basis sets for 2-aminopyridine-5-carbonitrile is too expensive. Here, the polarizability and the first hyperpolarizabilities are computed as a numerical derivative of the dipole moment using B3LYP/6-31G (d,p). The definitions for the isotropic polarizability is

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

The polarizability anisotropy invariant is

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

and the average hyperpolarizability is

$$\beta_{\square} = \frac{1}{5}(\beta_{iiz} + \beta_{izi} + \beta_{zii})$$

Where, α_{xx} , α_{yy} , and α_{zz} are tensor components of Polarizability; β_{iiz} , β_{izi} , and β_{zii} (i from X to Z) are tensor components of hyperpolarizability.

Tables 2 and 3 list the values of the polarizabilities and hyperpolarizabilities of the dye 2-aminopyridine-5-carbonitrile. In addition to the individual tensor components of the polarizabilities and the first hyperpolarizabilities, the isotropic polarizability, polarizability anisotropy invariant and hyperpolarizability are also calculated. The calculated isotropic polarizability of 2-aminopyridine-5-carbonitrile is -78.0044 a.u. However, the calculated isotropic polarizability of JK16, JK17, dye 1, dye 2, D5, DST and DSS is 759.9, 1015.5, 694.7, 785.7, 510.6, 611.2 and 802.9 a.u., respectively. The above data indicate that the donor-conjugate p bridge-acceptor (D-p-A) chain-like dyes have stronger response for external electric field. Whereas, for dye sensitizers D5, DST, DSS, JK16, JK17, dye 1 and dye 2, on the basis of the published photo-to-current conversion efficiencies, the similarity and the difference of geometries, and the calculated isotropic polarizabilities, it is found that the longer the length of the conjugate bridge in similar dyes, the larger the polarizability of the dye molecule, and the lower the photo-to-current conversion efficiency. This may be due to the fact that the longer conjugate-p-bridge enlarged the delocalization of electrons, thus it enhanced the response of the external field, but the enlarged delocalization may be not favorable to generate charge separated state effectively. So it induces the lower photo-to-current conversion efficiency.

3.4 Electronic absorption spectra and sensitized mechanism:

The calculated electronic absorption spectra of 2-aminopyridine-5-carbonitrile in vacuum and solvent, as determined using TD-DFT (B3LYP)/6-311++ G(d,p) calculations and the result shown in Fig: 4. It is observed that 2-aminopyridine-5-carbonitrile for the absorption in the visible region is much weaker than that in the UV region. These show three major absorption bands at 244, 207, and 186 nm in solvent and five absorption bands at 202, 213, and 169 nm in vacuum, respectively. As compared to the bands calculated for the molecule in vacuum, the absorption

Table 2: Polarizability (α) of the 2-aminopyrimidine-5-carbonitrile (in a.u)

	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	α	$\Delta\alpha$
DFT/6311G++(d,p)	57.98	0.00	50.53	0.00	0.00	52.94	53.82	6.58
HF/6-311++G(d,p)	59.73	0.00	4.70	2.56	0.00	0.88	57.03	3.22

Table 3: Hyperpolarizability (β) of the dye 2-aminopyrimidine-5-carbonitrile (in a.u.).

	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{ii}
DFT/6-311+G(d,p)	152.3	0.00	-4.17	-0.00	0.02	-0.00	0.00	1.48	-0.00	0.00	149.70
HF/6-311++G(d,p)	150.8	0.01	-6.29	0.38	9.42	-0.00	0.43	1.65	0.00	0.44	146.58

bands of 2-aminopyridine-5-carbonitrile in solvent are stronger and slightly red shifted, which is due to solvent effects. Generally, UV spectra of sensitizers in solvents are reported. Therefore, we carried out our computational calculations assuming that the sensitizer was in a solvent. The reported UV spectrum in solvent also includes solvent effects that cause the absorption spectra to be slightly red shifted. This is quite consistent with the observations made in vibrational studies, and we expect that the selected architectural unit of the dye sensitizer will exhibit a high open circuit voltage. The TD-DFT calculations are capable of describing the spectral features of 2-aminopyridine-5-carbonitrile because of the agreement of line shape and relative strength as compared with the vacuum and solvent.

The HOMO-LUMO gap of 2-aminopyridine-5-carbonitrile in acetonitrile at B3LYP/6-31G (d, p) theory level is smaller than that in vacuum. This fact indicates that the solvent effects stabilize the frontier orbitals of 2-aminopyridine-5-carbonitrile. So it induces the smaller intensities and red-shift of the absorption as compared with that in vacuum.

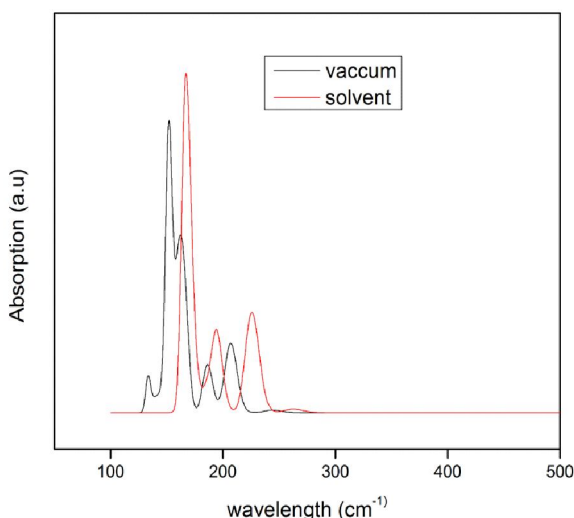


Figure 4. Calculated electronic absorption spectra of the dye 2-aminopyridine-5-carbonitrile in acetonitrile.

3.5 Electronic Structures and Charges :

Electronic Structure analysis was performed in order to analyze the charge populations of the dye 2-aminopyridine-5-carbonitrile. Charge distributions in C, N and H atoms were observed because of the different electro-

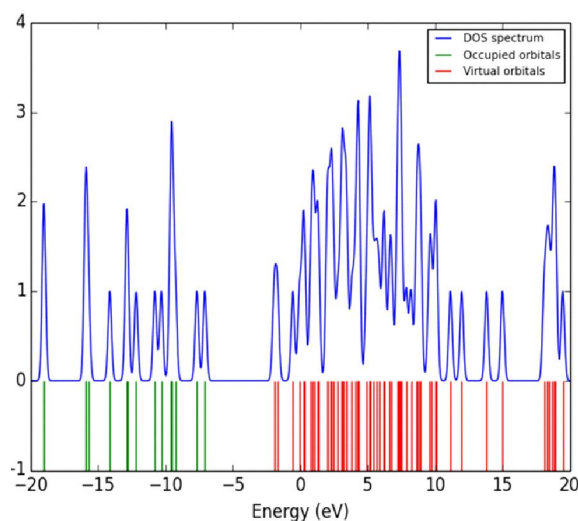


Fig. 5. The frontier molecular orbital energies and corresponding DOS spectrum of the dye 2-aminopyridine-5-carbonitrile.

negativity, the electrons transferred from C atoms to C, N atoms, C atoms to H and N atoms to H atom. The natural charges of different groups are the sum of every atomic natural charge in the group. These data indicate that the cyanine groups are donors and amide groups is acceptor and the charges were transferred through chemical bonds. The frontier molecular orbitals (MO) energies and corresponding density of state of the dye 2-aminopyridine-5-carbonitrile Dye is shown in Fig. 6. The HOMO-LUMO gap of the dye 2-aminopyridine-5-carbonitrile Dye in vacuum is 5.14 eV.

The visible and near-UV regions are the most important regions for photocurrent conversion, so only the 19 lowest singlet/singlet transitions associated with absorption bands in the visible and near-UV regions for 2-aminopyridine-5-carbonitrile are listed in Table 5. The data shown in Table 4 and Fig. 6 were obtained using TD-DFT/6-311++G (d, p) with solvent effects included. While the calculated HOMO and LUMO energies of the bare $\text{Ti}_{38}\text{O}_{76}$ cluster as a model for nanocrystalline are -6.55 and -2.77 eV, respectively, resulting in a HOMO-LUMO gap of 3.78 eV, the lowest transition is reduced to 3.20 eV according to TDDFT, and this value is slightly smaller than typical band gap of TiO_2 nanoparticles with nm size. The above data also reveal the interfacial electron transfer between semiconductor TiO_2 electrode and the dye sensitizer 2-aminopyridine-5-carbonitrile Dye is electron injection processes from excited dye to the semiconductor conduction band. This is a kind of typical interfacial electron transfer reaction.

Table 4. Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with $f > 0.01$ of the absorption bands in visible and near- UV region for the dye 2-aminopyridine-5-carbonitrile in acetonitrile.

State	Configurations composition (corresponding transition orbitals)	Excitation energy (eV/nm)	oscillator strength (f)
1	30 -> 32 30 -> 33 31 -> 32 31 -> 33	3.74/330.6	0.00
2	30 -> 33 31 -> 32 31 -> 33	3.78/327.76	0.00
3	29 -> 32 30 -> 32 30 -> 33 31 -> 32 31 -> 33	4.51/274.40	0.01
4	29 -> 33 30 -> 32 30 -> 33 31 -> 33	4.62/267.99	0.09
5	27 -> 32 28 -> 32 29 -> 32 29 -> 33	5.62/220.50	0.01
6	27 -> 32 28 -> 32 28 -> 33 29 -> 32 29 -> 33	5.65/219.16	0.02
7	27 -> 32 28 -> 32 28 -> 33 29 -> 33	5.88/210.72	0.00
8	27 -> 32 27 -> 33 28 -> 32 28 -> 33 29 -> 32 29 -> 33 31 -> 34	6.17/200.64	0.11
9	27 -> 32 27 -> 33 29 -> 32 31 -> 34	6.66/185.92	0.04
10	26 -> 32 26 -> 33 26 -> 35 31 -> 35	6.77/183.10	0.00
11	27 -> 32 29 -> 34 30 -> 34 31 -> 34 31 -> 35	6.95/178.21	0.01
12	26 -> 32 30 -> 34 30 -> 35 31 -> 35	7.00/176.93	0.00
13	24 -> 32 24 -> 33 27 -> 32 27 -> 33 29 -> 33 30 -> 34 31 -> 34	7.04/175.94	0.14
14	24 -> 32 25 -> 32 27 -> 32 27 -> 33 30 -> 35 31 -> 34	7.31/169.57	0.08
15	24 -> 32 25 -> 32 26 -> 33 27 -> 32 27 -> 33 30 -> 35 31 -> 34	7.32/169.26	0.08
16	26 -> 32 26 -> 33 27 -> 33	7.34/168.69	0.01
17	24 -> 32 26 -> 34 27 -> 33 30 -> 35 31 -> 34 31 -> 35	7.58/163.57	0.08
18	25 -> 33	7.60/162.93	0.00
19	24 -> 32 26 -> 34 27 -> 33 29 -> 34 31 -> 36	7.67/161.52	0.04
20	24 -> 32 24 -> 33 24 -> 34 28 -> 34 29 -> 34	7.76/159.74	0.02
	30 -> 34 30 -> 36 31 -> 36		

Table: 5 Theoretically computed zero-point vibrational energy (Kcal mole), rotational constants (GHz), rotational temperatures (Kelvin), thermal energy (Kcal mol⁻¹), and molar capacity at constant volume (Cal mol⁻¹ Kelvin⁻¹), dipole moment (Debye) and vibrational temperatures (Kelvin) for 2-aminopyridine-5-carbonitrile.

Parameter	B3LY3	HF
Zero-point vibrational energy	57.78	59.79
Rotational constant (GHZ)	5.88	5.65
	1.03	0.94
	0.88	0.81
Rotational temperature (Kelvin)	0.28	0.27
	0.04	0.04
	0.04	0.03
	62.51	63.96
Energy total	0.88	0.88
Translational	0.88	0.88
Rotational	60.73	62.18
Vibrational	5.10	3.43
Dipole moment	132.04	302.52

Vibrational temperature	217.77	353.39
	257.39	458.68
	331.19	492.25
	583.51	566.06
	595.27	624.52
	646.72	724.60
	712.64	820.03
	796.17	871.85
	803.28	904.57
	805.12	945.10
	961.38	968.97
	1072.59	994.48
	1166.10	1186.66
	1284.13	1317.44
	1391.29	1376.74
	1430.82	1448.73
	1490.32	1477.17
	1505.48	1504.64
	1799.79	1511.00
	1838.32	1682.26
	1921.22	1909.40
	2026.01	1993.83

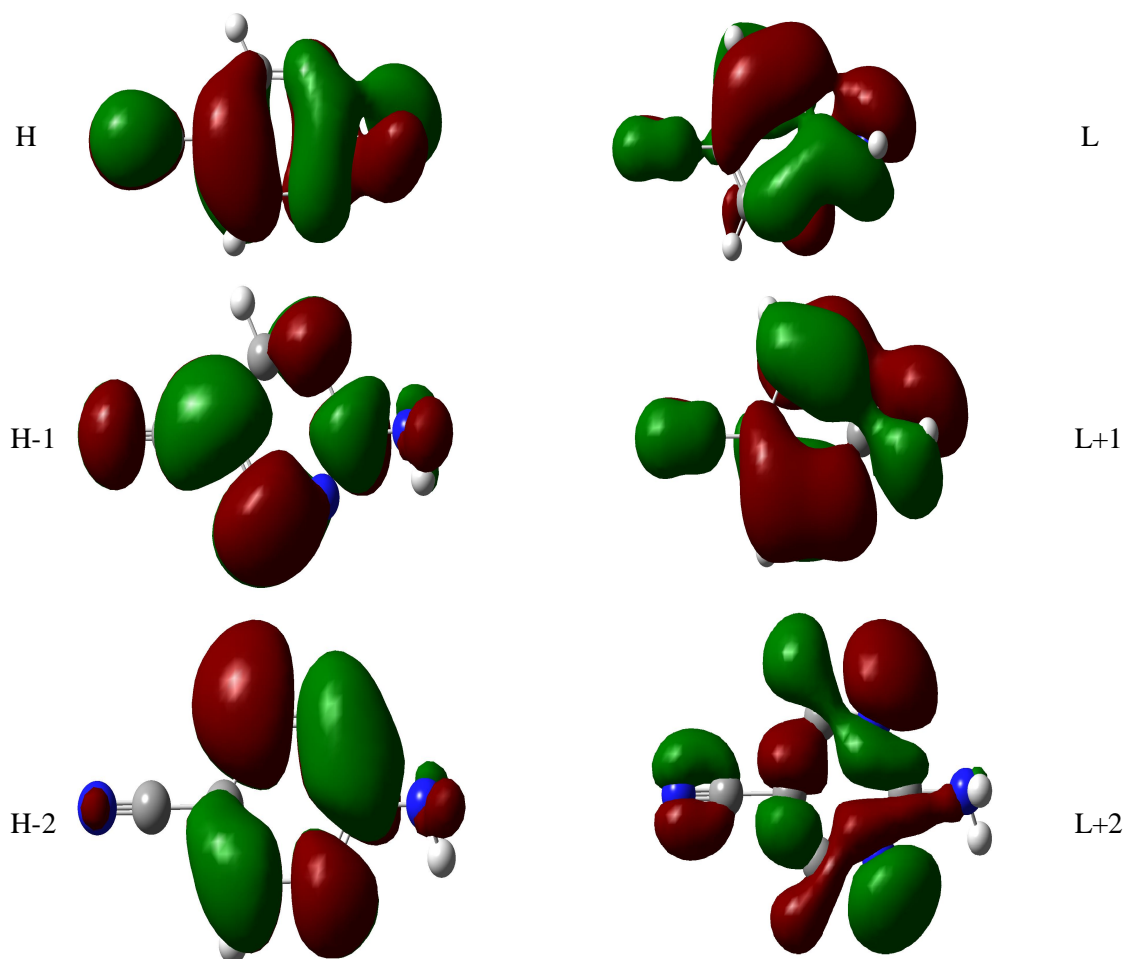


Fig: 6 Isodensity plots (is density contour = 0.02 a.u.) of the frontier orbitals of 2-aminopyridine-5-carbonitrile.

3.6 Mulliken population analysis :

The natural population analysis of 2-aminopyridine-5-carbonitrile obtained by Mulliken¹⁷ population analysis with HF and B3LYP using same basis set 6-311++G (d, p). Calculation of effective atomic charges plays an important role in the application of quantum chemical calculations to molecular systems. Our interest here is in the comparison of different methods to describe the electron distribution in 2-aminopyridine-5-carbonitrile as broadly as possible, and assess the sensitivity, the calculated charges to changes in (a) the choice of the basis set; (b) the choice of the quantum mechanical method. Mulliken charges, calculated the electron population of each atom defined in the basic functions. The Mulliken charge calculated different

levels and at same basis set listed in Table 6. The results can, however, better represent in graphical form as given Fig. 7. The charge depending on basis set and are changed due to polarizability. The C1 atom has more positive charge both HF/6-311++G (d, p) and B3LYP/6-311++G (d, p), whereas the C7 atom has more negative charge than the other atoms. The result suggests that the atoms bonded to H atom and all N atoms are electron acceptor and the charge transfer takes place from H to N. The H13 and H14 atoms by HF/6-311++G (d, p) and B3LYP/6-311++G (d, p) methods are more positive than the other atoms due to electron accepting substitutions at that position in 2-aminopyridine-5-carbonitrile.

Table 6. Mulliken atomic charges

Atoms	Atomic charges	
	DFT/B3LYP	HF
C	0.244	0.01
N	-0.29	-0.20
C	0.15	0.05
C	0.78	1.66
C	0.14	-0.01
N	-0.29	-0.18
C	-0.92	-2.00
N	-0.51	-0.17
N	-0.40	-0.30
H	0.201402	0.30
H	0.20	0.29
H	0.35	0.28

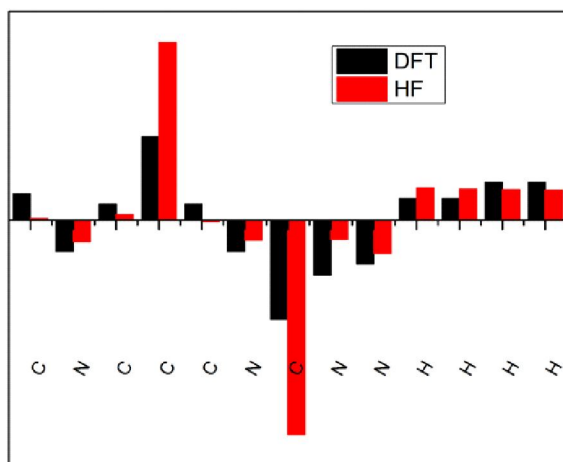


Fig: 7. Mulliken population analysis chart of 2-aminopyridine-5-carbonitrile.

3.7 Thermodynamic properties :

Thermodynamic parameters, rotational constants, rotational temperature, vibrational temperature and dipole moment have been presented in Table 5. Scale factors have been recommended for an accurate prediction in determining the Zero-Point Vibration Energies (ZPVE) and the entropy¹⁸, Svib (T) and the molar capacity at constant volume were calculated. The variations in the ZPVEs seem to be significant. The ZPVE is much lower by the DFT (B3LYP) method than by HF method. The biggest value of ZPVE 2-aminopyridine-5-carbonitrile is 59.79052 Kcal/mole obtained at HF/6-311+G (d, p) whereas the smallest value

is 57.78035Kcal/mole obtained at B3LYP/6-311++G (d, p). The total energies are found to decrease with the increase of the basis set dimension and the change in the total entropy of 2-aminopyridine-5-carbonitrile at room temperature at different basis set are only marginal. The dipole moment of the molecule was also calculated with HF/B3LYP/6-311+G (d, p) basis set. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation.

4. Conclusions

Using density functional theory with hybrid function B3LYP calculations, the geometries, electronic structures, polarizabilities, hyperpolarizabilities and the UV-Vis spectra, vibrational properties by FT-IR and FT-Raman spectroscopies and were performed SQM force field method of dye 2-aminopyridine-5-carbonitrile were investigated. The NBO result suggest that 2-aminopyrimidine-5-carbonitrile is a (D- π -A) system. The calculated isotropic polarizability of 2-aminopyrimidine-5-carbonitrile is 6.587170a.u and hyperpolarizabilities of 2-aminopyrimidine-5-carbonitrile are 149.70874 a.u respectively.

The frequencies strongest value of IR absorption for 2-aminopyrimidine-5-carbonitrile B3LYP/6-311++G (d, p) 1712 cm⁻¹ and HF/6-311G++ (d,p)1744 cm⁻¹ and the frequencies of strongest Raman activity for 2-aminopyrimidine-5-carbonitrile B3LYP/6-311++G (d, p) 2448 cm⁻¹ and HF/6-311G++(d,p) 2416 cm⁻¹ respectively. The electronic absorption spectral features in visible and near-UV region were assigned based on the qualitative agreement to TD- DFT calculations. The absorptions are all ascribed to $\pi \rightarrow \pi^*$ transition. The three major absorption bands at 244, 207, and 186 nm in solvent and three absorption bands at 202, 213, and 169 nm in vacuum, respectively. The excited states with the lowest excited energies of 2-aminopyrimidine-5-carbonitrile is photoinduced electron transfer processes that contributes sensitization of photo-to-current conversion processes. The electron transfer between semiconductor TiO₂ electrode and dye sensitizer 2-aminopyrimidine-5-carbonitrile is electron injection process form excited dyes as donor to the semiconductor conduction band. This property of dye 2-aminopyrimidine-5-carbonitrile the role of amide group's is as follow: it enlarged the distance between electron donor group and semiconductor surface, and decreased the

timescale of the electron injection rate, result in giving lower conversion efficiency. This indicates that the choice of the appropriate conjugate bridge in dye sensitizer is very important to improve the performance of DSSC.

References

1. B. O'Regan, M. Gratzel, *Nature* **353**, 737-739 (1991).
2. M. Gratzel, *Nature* **414**, 338-344 (2001).
3. Nazeeruddin MK, Kay A, Rodicio L, Humphry-Baker R, Muller E, Liska P, Vlachopoulos N, Gratzel M, *J. Am Chem Soc* **115**, 6382-6390(1993).
4. Nazeeruddin MK, Pechy P, Renouard T, Zakeeruddin SM, Humphry-Baker R, Comte P, Liska P, Cevey L, Costa E, Shklover V, Spiccia L, Deacon GB, Bignozzi CA, Gratzel M, *J Am Chem Soc* **123**, 1613-1624 (2001).
5. N.G. Park, K. Kim, *Phys. Status Solidi a*. **205**, 1895-1904 (2008).
6. Hara K, Sayama K, Ohga Y, Shinpo A, Suga S, Arakawa H *Chem Commun* 569-570 (2001).
7. Wang Z S, Cui Y, Hara K, Dan-oh Y, Kasada C, Shinpo A *Adv Mater* **19**, 1138-1141 (2007).
8. Horiuchi T, Miura H, Sumioka K, Uchida S, (2004) *J Am Chem Soc* **126**, 12218-12219.
9. Yang HY, Yen YS, Hsu YC, Chou HH, Lin JT (2010) *Org Lett* **12**, 16-19.
10. M.J. Lundqvist, M. Nilsing, P. Persson, S. Lunell, *Int. J. Quantum Chem.* **106**, 3214-3234 (2006).
11. D.F. Waston, G.J. Meyer, *Annu. Rev. Phys. Chem.* **56**, 119-156 (2005).
12. C. R. Zhang, H. S. Chen, and G. H. Wang, *Chem. Res. Chin. U.* **20**, 640-646 (2004).
13. Y. Sun, X. Chen, L. Sun, X. Guo, W. Lu, *Chem. Phys. Lett.* **381**, 397-403 (2003).
14. O. Christiansen, J. Gauss, J. F. Stanton, *Chem. Phys. Lett.* **305**, 147-155 (1999).
15. Z. S. Wang, Y. Y. Huang, C. H. Huang, J. Zheng, H.M. Cheng, S. J. Tian, *Synth. Met.* **14**, 201-207 (2000).
16. K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *J. Phys. Chem. B.* **107**, 597-606 (2003).
17. C.R. Zhang, Z.J. Liu, Y.H. Chen, H.S. Chen, Y.Z. Wu, L.H. Yuan, *J. Mol. Struct. (THEOCHEM)* **899**, 86-93 (2009).
18. R.S. Mulliken, *J. Chem. Phys.* **23**, 1833-1840 (1995).
19. M. Alcolea Palafox, *Int. J. Quantum Chem.* **77**, 661-684 (2000).