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Molecular Optimized Structure, NLO Applications Like Frequency Doubling and SHG, Fock Matrix of NBO Analysis, HOMO and LUMO Frontier Orbital Energies Analysis, Different Thermochemsitry Properties of 4-Fluoro-3-Methylbenzonitrile Based on Quantum Chemical Calculations

Shajikumar[1], Arockiasamy Ajaypraveenkumar[2] and R. Ganapathi Raman[3*]
[1,2]Nano Computational Laboratory, Department of Nano Technology, Noorul Islam Centre for Higher Education, Kumaracoil - 629 180, Kanyakumari District, Tamilnadu, India
[3]Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil - 629 180, Kanyakumari District, Tamilnadu, India

***Corresponding Author Email ID: ganapathiraman83@gmail.com**

ABSTRACT

The optimized structure of 4-fluoro-3- methylbenzonitrile (4F3MBN) was predicted theoretically. Geometrical parameters (atomic distances, angles and dihedral angels) are predicted by means of Density Functional Theory (DFT) levels employing the B3LYP/ 6-311++G (d, p), cc-pvdz and Aug- cc-pvdz basis set. Function of the electronic transitions is the root of electronic structure of the investigated molecules and draws the absorption spectra was find out nearly 300nm in the visible region. Frequency doubling and SHG applications are exist in the title molecule, so that the NLO are calculated using DFT with the different basic sets. NBO analysis are predicted by computational method and listed. The FMOs (frontier molecular orbitals) always reports energies and properties of many electron states. These FMOs is crucial for visual as well as electric properties. The thermochemsitry properties like Entropy, Enthalpy, Gibbs free energy, elevated heat energy and minimum energy have been calculated. At last Electrostatic potential derived charges identified using theoretical calculations.

KEYWORDS: 4-Fluoro-3-Methylbenzonitrile, Natural Bond Analysis, Atomic Charges and Electrostatic Potential Derived Charges

1. INTRODUCTION

Benzonitrile is a multi-discipline compound in global industry. In the sub components of the benzontriles are applicable in industry and medical fields. In medical field which is the best urinary sterile in the appearance of powder and steam for issuing bronchial tube. In the industry, this is the one of the leading dye like blue aniline and preserving food items (Sundaraganasan, 2009)). Benzonitrile and its components has easiest and adoptable compound with others, structural simplicity and used for various fields like medical, industrial dye, DSSC etc. So numbers of studies were investigated. The detail interpretation of crystal structure, vibrational frenquecy compared experimental and theoretical of 2-Fluro-5-Methylnezonitrile has been studied. The potential energy allocation values of 2-Fluro-6-Methylnezonitrile was studied by (Murugan, 2012). The bond-antibond stabilization energies were deliberated by applying the Natural Bond Orbital (NBO) psychiatry. Molecular stability calculations, vibrational analysis, electronic transitions and energy eigenvalues of 2-Bromo-4-Methylnezonitrile done by (Muhammad Shahid, 2009).

Reported UltraViolet-Visible (UV-Vis) spectrum of 4-methoxybenzonitrile. In the paper, Electronic amalgamation spectra and sensitized device are determined using gaseous state and solvent as Acetonitrile. And he had drawn the isodensity plots of frontier molecular spectra. The position of nitro cluster in 4-methoxybenzonitrile in geometries, electronic structures in addition to spectral properties was analyzed (Prakasam et al., 2013).

Mohan et al., (1992) reported total energy distribution of both spectrum of 2-chloro-6-methylbenzonitrile.

Rabia'tun Hidayah Jusoh et al., 2015 reported three new compounds, N-(2-methybenzoyl)-N'-(3-methyl-2-pyridyl) thiourea (I), N-(3-methylbenzoyl)-N'-(6-methyl-2-pyridyl) thiourea (II) are isomers and N-(2-methylbenzoyl)-N'-(6-methylpyridine-2-yl)thione (III) typical spectroscopic techniques, vibrational frequency, Electronic absorption spectra, 13C and 1H NMR chemical shift assignment and CHNS analysis.

2. MATERIALS AND METHODS

Computational details: Atomic coordinates of optimized molecule and all computational physics calculations had been evaluated through Gaussian 09 original pack up (Alen, 2015) using DFT-B3LYP well-designed with the dynamic basis sets using the software and results were visualized using many output soft ware's like Gass view, Gass sum, VEDA, chemcraft etc. UV-Vis spectra and electronic properties for instance HOMO and LUMO energies were resolute by time-dependent DFT (TD-DFT), along with the output of the UV-Vis spectra taken from Gaussian and the spectra were drawn by Gauss sum program. Electrostatic Potential map draw by MOLKEL program. Bond interactions and electron high density were analyzed using NBO in Gaussian09 DFT B3LYP level. The polarizability and hyperpolarizibility are calculated to understand the frequency doubling and SHG behavior of 4F3MBN.

3. RESULTS AND DISCUSSION

Molecular Geometry: The geometry optimized molecular structure of 4F3MBN has 16 atoms with 42 normal modes of vibration. It belongs to the C1 point group symmetry. Fig. 1 shows the optimized geometry of the particle and Table 1 presents the optimized values obtain for bond lengths and bond angles. The various bond lengths and bond angles are found to be almost the same at B3LYP/ 6-311++G(d, p), cc-pvdz and Aug- cc-pvdz methods. Thus the investigation merged experimentally and theoritically (4-Fluro-benzonitrile) in the solid phase by (Kuppusamy Sambathkumar, Vibrational spectra, 2015).

The bond length between C1-C2 in above three methods are found to be 1.540, 1.540, 1.540 respectively, And its microwave data value 1.399 and 1.387 respectively. The bond length between C7-F8 in B3LYP three basic sets and microwave data are 1.350, 1.350, 1.350 and 1.354 respectively. The bond length between C9-N10 in theoretical optimized values using B3LYP three basic sets and microwave data are 1.149, 1.147, 1.149 and 1.159 respectively.

The bond angle between C1-C2-C3 in computerized parameter values of different basic sets and microwave data are 119.9, 119.9, 119.9 and 120 respectively. The bond angle between C2–C3–C4 in three basic sets already used and experimental data are 119.9, 120, 119.9 and 120.2 respectively.

Calculate the parameter values of different basic sets of the fluro and nitrile (C7-F8, C9-N10) atomic distances, angles and dihedral angels (C2–C3–C4) are coincided with microwave data. It gives the fruitful agreement with DFT calculations. The premeditated geometric optimized parameters can be applicable for settle on the additional parameters of 4F3MBN.

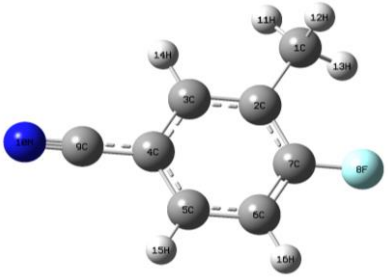

Fig.1.Optimized Geometrical Structure of 4-Fluoro-3-Methylbenzonitrile

HOMO–LUMO Analysis: The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) interactions are held between acid-base. In general, when the orbital reacts with one another is produced another two orbitals which has the filled-empty interaction for the stabilization. Those interactions are most welcomed orbitals in molecules for reactivity and kinetic stability. The HOMO is the orbital that possibly will serve as fulfilled electron pair, most available for bonding, most weakly held electrons and characteristic for nucleophilic component. The LUMO is the orbital that might be used as the empty and characteristic for electrophilic component. These orbitals are placed in a final boundary level of electron of the molecule, so it is called the frontier orbitals (FMO's). HOMO energy, LUMO energy and chemical potential analyzed by different basic sets and listed in Table 2. The bond between atomic orbital compositions is described by the HOMO and LUMO diagram shown in Fig. 2. Both orbitals have the higher standard value (Sambathkumar K, et at., 2015) and (Prasad MVS, et at., 2015)

The 3D images of the orbitals computed for the 4F3MBN molecules are illustrated in Fig. 2. The energy hole projected the equalized charge relocate relations enchanting position surrounded by the particle (Zeynep Demirciog Lu et at, 2014)) furthermore it is also can be supported with NLO results, as described later.

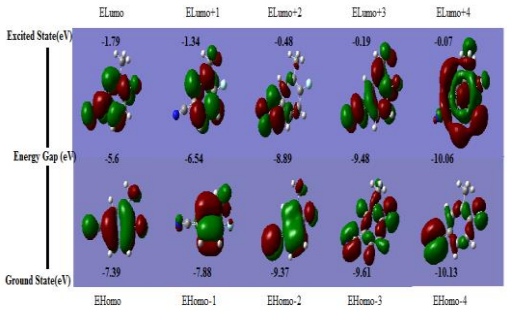

Fig.2.Energy Gap Plot of 4-Fluoro-3-Methylbenzonitrile

NLO Properties: During the fields designed for example communiqué, indication dispensation and visual interconnections, NLO enhance the functions for frequency shifting, optical modulation, optical switching and optical logic for the developing technologies (Balachandran V et al., 2013). The first hyperpolarizability (β), dipole moment (μ) and polarizability (α) of 4F3MBN is calculated using DFT with the different basic sets for the NLO applications like frequency doubling and SHG. Base on top of the finite-field move toward, the non-linear visual constraint for instance dipole moment, polarizability, and first order hyperpolarizability of 4F3MBN molecules are deliberate via the various origin sets for extra dependability. The arithmetical values of more than mention parameters

are scheduled in Table.3. In the being there of an exterior electric field (E), the energy of the structure is a role of the electric field. First hyperpolarizability is a third-rank tensor that is able to describe by a 3x3x3 matrix.

Table.1.Theoretically Optimized Geometrical Parameters of 4F3MBN Obtained

Parameters	B3LYP			Microwave Data(Benzonitrile)
Bond Length(Å)	**6-311++G(d,p)**	**cc-pvdz**	**Aug-cc-pvdz**	
C1-C2	1.540	1.540	1.540	1.399
C1-H11	1.070	1.070	1.070	
C1-H12	1.070	1.070	1.070	
C1-H13	1.070	1.070	1.070	
C2-C3	1.540	1.401	1.540	1.387
C2-C7	1.355	1.401	1.355	
C3-C4	1.355	1.401	1.355	1.391
C3-H14	1.070	1.070	1.070	
C4-C5	1.540	1.401	1.540	1.391
C4-C9	1.539	1.401	1.539	
C5-C6	1.355	1.401	1.355	1.387
C5-H15	1.070	1.070	1.070	
C6-C7	1.540	1.401	1.540	
C6-H16	1.070	1.070	1.070	
C7-F8	1.350	1.350	1.350	1.354
C9-N10	1.149	1.147	1.149	1.158
Parameters	**B3LYP**			**Microwave Data(Benzonitrile)**
Bond Angle(°)	**6-311++G(d,p)**	**cc-pvdz**	**Aug-cc-pvdz**	
C2-C1- H11	109.477	109.471	109.477	
C2- C1- H12	109.470	109.471	109.470	
C2- C1-H13	109.476	109.471	109.476	
H11- C1- H12	109.477	109.471	109.477	
H11- C1- H13	109.477	109.471	109.477	
H12- C1- H13	109.451	109.472	109.451	
C1- C2- C3	120.000	120.000	120.000	119.9
C1- C2- C7	119.999	120.000	119.999	
C3-C2- C7	120.001	120.000	120.001	
C2-C3- C4	119.994	120.000	119.994	120.2
C2-C3-H14	119.988	120.000	119.988	
C4-C3-H14	120.018	120.000	120.018	
C3-C4-C5	119.993	120.000	119.993	120.1
C3- C4-C9	120.050	120.001	120.050	
C5-C4-C9	119.957	119.999	119.957	
C4-C5-C6	120.006	120.000	120.006	120.2
C4-C5-H15	119.957	120.000	119.957	
C6-C5-H15	120.037	120.000	120.037	
C5-C6- C7	119.992	120.000	119.992	
C5-C6- H16	120.030	120.000	120.030	
C7-C6-H16	119.978	120.000	119.978	
C2-C7- C6	120.015	120.000	120.015	
C2-C7- F8	120.015	120.000	120.015	
C6-C7- F8	119.970	120.001	119.970	
Parameters	**B3LYP**			**Microwave Data(Benzonitrile)**
Dihedral Angle(°)	**6-311++G(d,p)**	**cc-pvdz**	**Aug-cc-pvdz**	
H11-C1-C2-C3	-30.04	-30.00	-30.04	
H11-C1-C2-C7	149.96	150.00	149.96	
H12-C1-C2-C3	89.97	90.00	89.97	
H12-C1-C2-C7	-90.03	-90.00	-90.03	
H13-C1-C2-C3	-150.05	-150.00	-150.05	
H13-C1-C2-C7	29.95	30.00	29.95	

C1-C2-C3-C4	-179.95	180.00	-179.95	
C1-C2-C3-H14	0.04	0.00	0.04	
C7-C2-C3-C4	0.05	0.00	0.05	
C7-C2-C3-H14	-179.96	-180.00	-179.96	
C1-C2-C7-C6	179.95	-180.00	179.95	
C1-C2-C7-F8	-0.03	0.00	-0.03	
C3-C2-C7-C6	-0.05	0.00	-0.05	
C3-C2-C7-F8	179.97	-180.00	179.97	
C2-C3-C4-C5	0.00	0.00	0.00	
C2-C3-C4-C9	180.00	180.00	180.00	
H14-C3-C4-C5	-179.99	180.00	-179.99	
H14-C3-C4-C9	0.00	0.00	0.00	
C3-C4-C5-C6	-0.06	0.00	-0.06	
C3-C4-C5-H15	179.97	180.00	179.97	
C9-C4-C5-C6	179.95	-180.00	179.95	
C9-C4-C5-H15	-0.03	0.00	-0.03	
C4-C5-C6-C7	0.06	0.00	0.06	
C4-C5-C6-H16	-179.95	180.00	-179.95	
H15-C5-C6-C7	-179.97	-180.00	-179.97	
H15-C5-C6-H16	0.02	0.00	0.02	
C5-C6-C7-C2	-0.01	0.00	-0.01	
C5-C6-C7-F8	179.98	180.00	179.98	
H16-C6-C7-C2	-180.00	-180.00	-180.00	
H16-C6-C7-F8	-0.01	0.00	-0.01	

Table.2.Calculated Energies of the Frontier Orbital Energies for the Title Compound by Reference From (Julio Casado, 1971)

Basic Set	B3LYP/6-311++G(d,p)	B3LYP/cc-pvdz	B3LYP/Aug-cc-pvdz
SCF Energy(a.u)	-463.060	-463.066	-463.101
Dipole Moment (Debye)	3.579	3.550	3.678
LUMO (eV)	-1.790	-1.500	-1.790
HOMO (eV)	-7.400	-7.180	-7.400
ENERGY GAPc(eV)	-5.610	-5.680	-5.610
Electronegativity (χ)	-4.595	-4.340	-4.595
Chemical Potential (μ)	4.595	4.340	4.595
Global Hardness (η)	2.805	2.840	2.805
Global Softness (s)	0.357	0.352	0.357
Electrophilicity Index (ω)	6.444	6.163	6.444
EHOMO-1(eV)	-7.820	-7.630	-7.820
ELUMO+1(eV)	-1.360	-1.050	-1.360
EHOMO-1 - ELUMO+1(eV)	-6.460	-6.580	-6.460

Table.3.Functions of the Optical Using Different Basic Level of the 4f3mbn

Parameters	**B3LYP**		
	6-311++G(d,p)	**cc-pvdz**	**Aug-cc-pvdz**
μx	-1.062	-1.060	-1.116
μy	-0.009	0.012	0.008
μz	-0.866	-0.830	-0.883
μ=	1.369Debye	1.346Debye	1.423Debye
αxx	120.990	111.686	125.070
αxy	0.048	-0.040	-0.043
αyy	54.156	39.297	58.753
αxz	19.075	16.890	18.622
αyz	0.446	-0.209	-0.316

Parameters	B3LYP		
	6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz
αzz	114.095	107.117	119.333
α0	213.177×10-33 esu	186.688×10-33 esu	223.600×10-33 esu
α=	1841.706×10-33 esu	1612.855×10-33 esu	1931.751×10-33 esu
βxxx	199.546	92.953	175.627
βxxy	7.971	-15.204	-5.679
βxyy	-9.978	-5.620	-3.836
βyyy	-6.453	19.280	4.841
βxxz	131.538	79.044	125.250
βxyz	-1.250	0.396	0.219
βyyz	6.263	-28.193	12.122
βxzz	61.084	24.393	55.302
βyzz	-5.712	-6.355	0.836
βzzz	91.360	53.242	61.993
β0	2934.296×10-33 esu	1319.389×10-33 esu	2610.687×10-33 esu

Table.4.Thermodynamic Functions of 4-Fluro-3-Methylbenzonitrile Obtained by b3lyp Level with the Basis Sets

Thermodynamic Functions of DMAP	B3LYP		
	6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz
Self Consistent Field Energy (a.u)	-463.175	-463.073	-463.101
Zero Point Vibrational Energy (kcal/mol)	74.071	74.206	73.957
Rotational Constant (GHz)	2.988	2.986	2.970
	0.879	0.872	0.873
	0.682	0.677	0.677
Rotational Temperature (K)	0.143	0.143	0.143
	0.042	0.042	0.042
	0.033	0.033	0.033
Thermal Energy (kcal/mol)			
Total	79.526	79.634	79.404
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	77.749	77.857	77.626
Specific Heat Capacity at Constant Volume (cal/mol˚K)			
Total	32.222	32.153	32.354
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	26.260	26.192	26.393
Dipole moment (Debye)	3.490	3.602	3.421
Homo(eV)	-7.390	-7.180	-7.400
Lumo(eV)	-1.790	-1.500	-1.790
Energy gap(eV)	5.600	5.600	5.600
Entropy(S) (cal/mol˚K)			
Total	91.651	91.365	91.337
Translational	40.614	40.614	40.614
Rotational	29.575	29.590	29.594
Vibrational	21.462	21.161	21.130
Gibbs Free Energy	0.084	0.084	0.084
Enthalpy	0.128	0.128	0.127

Table.5.Calculated Net Charges by Mulliken Population Method

Atoms	B3LYP		
	6-311++G(d, p)	cc-pvdz	Aug-cc-pvdz
C1	-0.353	0.084	0.908
C2	1.526	-0.153	0.251
C3	-1.564	0.087	1.243
C4	2.433	0.048	1.059
C5	-0.910	0.075	0.838
C6	0.582	0.044	0.735
C7	-1.224	0.135	-0.036
F8	-0.157	-0.151	-0.625
C9	-1.227	-0.119	-0.899
N10	-0.165	-0.080	-0.045
H11	0.148	0.026	-0.289
H12	0.181	0.048	-0.127
H13	0.165	0.029	-0.309
H14	0.173	-0.035	-1.029
H15	0.180	-0.025	-0.890
H16	0.212	-0.012	-0.785

Table.6.Second order Perturbation Theory Analysis of FOCK Matrix in NBO Basis for 4f3mbn at b3lyp/6-311++g (D, P) Level

Donor (i)	Type	Ed/e	Acceptor (j)	Type	Ed/e	E(2)	E(i)- E(j)	f(i,j)
C1-C2	σ	1.979	C3-C4	σ*	0.025	2.76	1.17	0.05
	σ	1.979	C6-C7	σ*	0.026	2.65	1.20	0.05
C1-H11	σ	1.987	C2-C7	σ*	0.035	3.02	1.06	0.05
C1-H12	σ	1.977	C2-C3	π*	0.313	3.82	0.53	0.04
C1-H13	σ	1.987	C2-C3	σ*	0.018	3.19	1.08	0.05
C2-C3	σ	1.972	C3-C4	σ*	0.025	3.14	1.27	0.06
	σ	1.972	C4-C9	σ*	0.032	3.09	1.26	0.06
	σ	1.972	C7-F8	σ*	0.032	3.79	0.97	0.05
	π	1.666	C4-C5	π*	0.390	19.80	0.28	0.07
	π	1.666	C6-C7	π*	0.347	20.69	0.28	0.07
C2-C7	σ	1.976	C2-C3	σ*	0.018	2.59	1.29	0.05
	σ	1.976	C3-H14	σ*	0.012	2.09	1.17	0.04
	σ	1.976	C6-C7	σ*	0.026	4.87	1.31	0.07
	σ	1.976	C6-H16	σ*	0.012	2.24	1.17	0.05
C3-C4	σ	1.965	C4-C5	σ*	0.025	4.45	1.26	0.07
	σ	1.965	C4-C9	σ*	0.032	3.42	1.26	0.06
	σ	1.965	C9-N10	σ*	0.012	4.59	1.66	0.08
C3-H14	σ	1.979	C2-C7	σ*	0.035	3.97	1.08	0.06
	σ	1.979	C4-C5	σ*	0.025	3.93	1.09	0.06
C4-C5	σ	1.967	C3 - C4	σ*	0.025	4.60	1.26	0.07
	σ	1.967	C4-C9	σ*	0.032	3.44	1.26	0.06
	σ	1.967	C9-N10	σ*	0.012	4.59	1.66	0.08
	π	1.661	C2-C3	π*	0.313	20.09	0.29	0.07
	π	1.661	C6-C7	π*	0.347	17.93	0.28	0.06
	π	1.661	C9-N10	δ*	0.079	19.44	0.38	0.08
C4-C9	σ	1.978	C3-C4	σ*	0.025	2.92	1.29	0.06
	σ	1.978	C4-C5	σ*	0.025	2.94	1.29	0.06
	σ	1.978	C9-N10	σ*	0.012	9.79	1.69	0.12
C5-C6	σ	1.972	C4-C9	σ*	0.032	3.22	1.26	0.06
	σ	1.972	C7-F8	σ*	0.032	4.70	0.96	0.06
C5-H15	σ	1.981	C3-C4	σ*	0.025	4.07	1.09	0.06
C6-C7	σ	1.980	C2-C7	σ*	0.035	5.01	1.29	0.07

	π	1.662	C2-C3	π*	0.313	18.91	0.30	0.07
	π	1.662	C4-C5	π*	0.390	19.86	0.30	0.07
C6-H16	σ	1.976	C2-C7	σ*	0.035	4.08	1.08	0.06
C7-F8	σ	1.996	C2-C3	σ*	0.018	1.39	1.59	0.04
	σ	1.996	C5-C6	σ*	0.013	1.24	1.58	0.04
C9-N10	σ	1.993	C4-C9	σ*	0.032	8.46	1.60	0.11
	π	1.987	C3-C4	σ*	0.025	3.17	0.89	0.05
	π	1.987	C4-C5	σ*	0.025	3.20	0.89	0.05
	δ	1.959	C4-C5	π*	0.390	8.69	0.35	0.05
C4-C5	π*	0.390	C9-N10	δ*	0.079	21.29	0.10	0.09
LP								
F8	σ	1.990	C2-C7	σ*	0.035	1.15	1.59	0.04
	σ	1.990	C6-C7	σ*	0.026	1.07	1.64	0.04
	π	1.971	C2-C7	σ*	0.035	6.08	0.97	0.07
	π	1.971	C6-C7	σ*	0.026	5.93	1.02	0.07
	δ	1.923	C6-C7	π*	0.347	18.55	0.44	0.09
N10	σ	1.972	C4-C9	σ*	0.032	11.46	1.05	0.10

[a]E(2) resources energy of hyper conjugative dealings (stabilization energy).
[b]Energy disparity linking donor and acceptor i and j NBO orbitals.
[c]$F_{(i;j)}$ is the Fock matrix element flanked by i and j NBO orbitals.

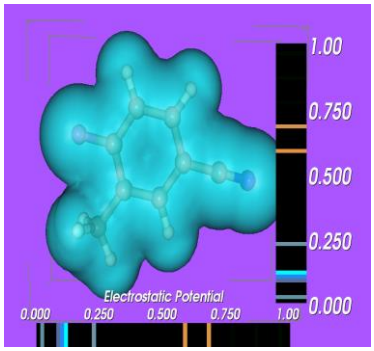

Fig.3.Electrostatic Potential Surface of 4F3MBN

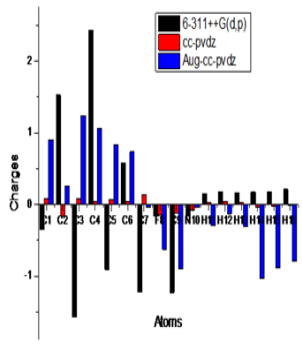

Fig.4.Mulliken's Graph Done by B3LYP with Dynamic Basic Sets

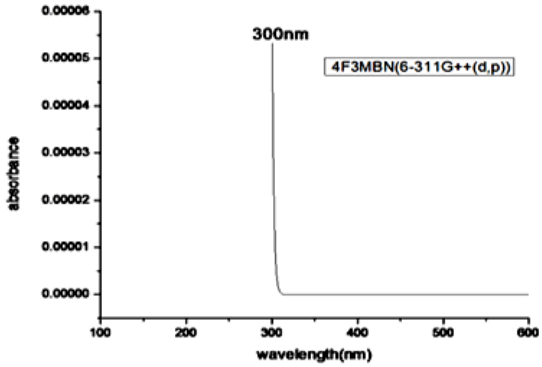

Fig.5.Calculated Electronic Amalgamation Spectra of 4F3MBN

In this research paper, 4F3MBN compound has been computed and tabulated the polarizability. The hyperpolarizability tensors were predicted only on the software with different basic sets and results obtained from the equations already programmed by software. However, values should be on electronic units (esu), which are into modúlate the atomic units (Balachandran & Parimala, 2013). It is fine acknowledged that the elevated values of dipole moment, molecular polarizability, and hyperpolarizability are imperative for further vigorous NLO properties. The premeditated dipole moment is equal to 1.369 Debye, 1.346 Debye and 1.423 Debye in 4F3MBN. The calculated polarizability aij are subjugated by the slanting components while have non-zero and zero values. The value of α equated as 1841.706×10--33esu, 1612.855×10-33esu and 1931.751×10-33esu for heading compounds. And the values β of the title compounds with our basic sets 2934.296×10-33esu, 1319.389×10^{-33} esu and 2610.687×10-3esu respectively.

The calculated values of polarisibility (α) and first hyperpolarisibility (β) comes out to be as 213.185a.u, 186.694a.u, 223.608a.u and 339.656a.u, 152.724, 302.197. Threshold values for NLO effects is that of Urea used for comparison purposes whose polarisibility and first hyperpolarisibility values are compared with our title compound values. It has the enhancing NLO property (Diwaker C S, 2015). Above results of three basics sets, the cc-pvdz is something different while compare with other two. Since from the computed results, the values are 6 times that of standard values. So it is proposed that the compound under investigation is a strong potential material for NLO applications like frequency doubling and SHG.

Further molecular properties:

Thermodynamic Functions: A number of intended thermodynamic parameters are specified in Table.4. Level factors have been suggested (Hubert Joe I, 2009)) for an precise predication in formative the zero-point vibration energies (ZPVE), and the entropy(S) vib (T) and they can be used with the morals of this Table 4 (Senthil Kumar J, et al., 2015) On the other hand, the accurate prediction of Entropy, Enthalpy, Gibbs free energy, elevated heat energy and minimum energy had been calculated. The margin values of 4F3MBN at room temperature at dissimilar method, which gives the changes in the total entropy. The total energies and the change in the total entropy and Self consistent field energy of 4F3MBN at breathing space dissimilar basic sets are also tabulated in Table 4.

Electrostatic Potential: Molecular Electrostatic Potential (ESP) surface plotted the optimized electronic structure of 4F3MBN, intended for predicting hasty sites of the molecules by using the B3LYP/6-311++G (d, P) basis set with the computer software Molekel. To comprehend the qualified polarity of the molecules threw the visual technique. Learn association among the molecular structures as well as the physiochemical properties (Yufeng Chen, 2016)). Significant of the electrostatic potential is based on the gratitude of one molecule by another used for medicine-receptor and enzyme-substrate interactions by Ertu grul Gazi Saglam et al., 2015). In the MEP, generated a charge distribution gap around the molecule, which is exceedingly useful in accepting the reactive sites for nucleophilic and electrophilic attack in studies of biological identification and hydrogen bonding interactions Sharmi Kumar, 2016) and (Murray, 1996). The province among red color is regard as most electronegative (electrophilic) province and the province with blue color is most positive (nucleophilic) region, where as the bluish green color surrounded by the ring system of APN is related to less positive region. The electrophilic and nucleophilic have red and blue color respectively. Red color is regarded as most electronegative region and blue color is most positive region. For the zero regions represent the color of green. This Figure provides a visual representation of the chemically active sites and comparative reactivity of atoms.

Mulliken Population Analysis: The Mulliken psychoanalysis is the oldest and finest population analysis method. The electron population of each atom of the molecules is identifying, because of calculating the mulliken charges as explained by the density functional methods. The charge distribution of the 4F3MBN gives the Carbon and Hydrogen charges had both signs. It has positive charge as well as negative with different basic sets. Fluruo and Nitrile atoms have negative charges in all basic sets, which are donor atoms. Mulliken atomic charge computation has a vital position in the relevance of quantum chemical calculation to molecular system because of atomic charge effect, dipole moment, molecular polarizabiliy, electronic structure and a lot of properties of molecular systems. We write the Gaussian output shown in the Table.5. We find the title molecule has different charge distribution with respect to the dynamic basic sets and quantum calculations. The predicted atomic charges are explained through graphical representation (Fig. 4.). In order to change the every basic set, the charge distribution should be change by (Renjith R., 2014). The charge change with origin set due to polarization For illustration, the charge of H(15) and H(16) atoms are 0.180e, 0.212e at B3LYP/6-311++G(d,p), -0.025e, -0.012e at B3LYP/cc-pvdz and -0.890e -0.785e at B3LYP/cc-pvdz in the title compound 4F3MBN.

Natural Bond Orbitals: The high electron density in orbital bonding is predicted Natural Bond Orbital (NBO) analysis. In the natural localized orbital sets, NBOs is the one of the sequence. Natural localized orbital calculate the electron density in atom and bonding of the atoms. The molecular systems investigating charge transfer or conjugative interaction in a convenient basis. To evaluate the interactions of the orbitals in the NBO analysis the second order Fock matrix should be carried out. The micro disturbance theory also is reported for resulting the electron donor orbital, acceptor orbital and the interacting stabilization energy. The perfect Lewis structure into an empty non-Lewis orbital predicting the solution of relations is a defeat of habitation from the attentiveness of electron NBO. For each donor and acceptor, the stabilization energy E (2) coupled with the delocalization i-j is estimated as

$$E(2) = -n_\sigma \frac{\langle\sigma|F|\sigma\rangle^2}{\varepsilon_\sigma^* - \varepsilon_\sigma} = -n_\sigma \frac{F_{ij}^2}{\Delta E} \qquad (1)$$

The larger is the E (2) value, the more intensive is the interaction between electron donors and electron acceptors, i.e., the additional donating propensity from electron donors to electron acceptors and the superior the degree of conjugation of the entire structure. Delocalization of electron density among engaged Lewis type (bond or lone pair) NBO orbital and officially vacant non-Lewis NBO orbital correspond to a stabilizing donor–acceptor dealings. The NBO psychiatry has been perform on the compound by means of NBO 3.1 series as implement in the

Gaussian 09W package at the DFTB3LYP/ 6-311++G(d,p) level of theory with the intention of make clear the intermolecular dealings, hybridization and delocalization of electron density within the molecule, which are presented in Table 6. The ICT (Intra molecular charge transfer) causing stabilization of the system, because of the intramolecular hyperconjugative interactions are formed by the orbital overlap between σ(C–C)-σ*(C–C), π(C–C) - π*(C–C). NLO activity ICT is one of the strongest causes (Veeraiah, 2015). These exchanges are experimental as augment in electron density (ED) in C–C antibonding orbital that weaken the own bonds. The stabilization energy (18.55kJ/mol) of lone pair F8 (3) with that of anti-bonding C6-C7 is the most valuable interactions in the whole molecule. The resulting stabilization (21.29kJ/mol) energy transfer occurs from C4-C5 with antibonding C9–N10, which one is the very largest delocalization. The resulting stabilization energy of (1.15 and 1.07 kJ/mol) the reactions between the F8 (3) with that of anti-bonding C2-C7 and C6-C7, these are the smallest delocalization, respectively as listed in Table.6. In the substitution, least energy transfer is exist only on carbon-carbon interactions, C7-C8 (σ) to C2-C3 (σ*) (1.39 kJ/mol) and C7-C8 (σ) to C5-C6 (σ*) (1.24 kJ/mol).

UV-Visible: UV–vis spectrum of 4F3MBN is drawn in Fig. 5. In the electronic transition spectra cut off wavelength is the most important parameters. In our title compound has high delocalization of π -electrons which absorbed 300 nm and these band is due to the electronic transition of π- π*. The benzonitrile Dyes have the electron injection. While inject the electron from the excited dye to semiconductor surface. Computational calculations with basic level to observe the electronic transitions of 4F3MBN and electronic absorption spectra were graphed. The UV-Vis region is the stronger region while compare with the absorption in the visible region, which results have a red-shift. This result indicates the excited state of 4F3MBN molecule has the good absorption value, so we can use on DSSC applications and the other NLO applications, which enhancing well.

4. CONCLUSION

B3LYP level with the B3LYP parallel basis sets are utilized to carry out a exhaustive study of the structures, optimized parameters, molecular electrostatic potential map and thermodynamic parameters of 4F3MBN. The extensive changes in bond lengths of the 4F3MBN are explained with the aid of NBO analysis. Analysis expound the intermolecular interaction, hybridization and delocalization of electron density within the molecule. The ICT (Intra molecular charge transfer) causing stabilization of the system, because of the intermolecular hyper conjugative relations are fashioned by the orbital overlap between σ(C–C)-σ*(C–C), π(C–C) -π*(C–C).The lowering of the HOMO–LUMO energy gap value has substantial influence on the ICT and bioactivity of the molecules. ICT is one of the strongest causes for the NLO activity. Mulliken atomic charge calculation shows the atomic charge effect, dipole moment, molecular polarizabiliy, electronic structure and a lot of properties of molecular systems. Threshold values for NLO effects is that of Urea used for comparison purposes whose polarisibility and first hyperpolarisibility values are compared with our title compound. And values are 6 times that of standard values. The size, shape, charge density and site of chemical reactivity of the molecules are depends upon the electron density iso-surface mapped with electrostatic potential surface depicts. And which colors changes represents the potential differences of the molecules. The thermo chemical parameters are predicted for find the property changes of the title compound. So we propose that the compound under investigation is a strong potential material for NLO applications like frequency doubling and SHG.

REFERENCES

Alen S, Sajan D, Job Sabu K, Tom Sundius, Chitanya K, Frank Blockhuys, Bena Jothy V, Vibrational Spectral Analysis, electronic Absorption and Non-Linear Optical Behavior of (E)-1-(2,4,6-Trimethoxyphenyl)Pent-1-en-3-one, Vibrational Spectroscopy, 79, 2015, 1–10.

Balachandran V and Parimala K, Molecular Structures, FT-IR and FT-Raman Spectra, NBO Analysis, NLO Properties, Reactive Sites and Quantum Chemical Calculations of Keto-Enol Tautomerism (2-amino-4-Pyrimidinol and 2-Amino-Pyridine-4(1H)-One)", Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy", 102, 2013, 30–51.

Diwaker, C.S. Chidan Kumar, Ashish Kumar, Siddegowda Chandraju, Hoong-Kun Fun, Ching Kheng Quah, 2015, "Synthesis, Spectroscopic Characterization and Computational Studies of 2-(4-Bromophenyl)-2-Oxoethyl 3-Methylbenzoate by Density Functional Theory", Journal of Molecular Structure, 1092, 192–201.

Ertu Grul Gazi Saglam, Ahmet Ebinç, Celal Tugrul Zeyrek, Hüseyin Ünver, Tuncer H€okelek, 2015, Structural Studies on some Dithiophosphonato Complexes of Ni(II), Cd(II), Hg(II) and Theoretical Studies on a Dithiophosphonato Ni(II) complex Using Density functional Theory, Journal of Molecular Structure, 1099, 490-501.

I Hubert Joe; I Kostova; C Ravikumar; M Amalanathan; S C Pinzaru, 2009, "Journal of Raman Spectroscopy", 40, 1033-1038.

Julio Casado, Lise Nygaard and G Ole sorensen, Microwave Spectra of Isotopic Benzonitriles. Refined Journal of Molecular Structure, 8(211), 1971, 1971.

Kuppusamy Sambathkumar, Vibrational Spectra, NBO, HOMO–LUMO and conformational stability studies of 4-hydroxythiobenzamide, Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy, 147, 2015, 51–66.

Mohan S, Murugan R & Srinivas S, Proction of Natural Academicals Science India, 62A (121), 1992.

Muhammad Shahid, Munawar Ali Munawar, Sohail Nadeem, Waqar Nasir and Muhammad Salim, 2-Bromo-4-Methylbenzonitrile, Acta Crystallographica Section E, 2009.

Murray JS, Sen K, Molecular Electrostatic Potentials Concepts and Applications, Elsevier, Amsterdam, 1996.

Murugan M, Balachandran V and Karnan M, Vibrational Spectra and Electrostatic Potential Surface of 2-Fluoro-6-Methoxybenzonitrile Based on Quantum Chemical calculations, Journal of Chemical and Pharmaceutical Research, 4(7), 2012, 3400-3413

Prakasam A, Sakthi D, Anbarasan PM, DFT Studies on the Electronic Structures of 4-Methoxybenzonitrile Dye for Dye-Sensitized Solar Cell, International Letters of Chemistry, Physics and Astronomy, 12, 2013, 8-22.

Prasad MVS, Udaya Sri N, Veeraiah V, 2015, "A Combined Experimental and Theoretical Studies on FT-IR, FT-Raman and UV–Vis spectra of 2-Chloro-3-Quinolinecarboxaldehyde", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 148 163–174

Ravindra Kumar Singh, Ashok Kumar Singh, Synthesis, Molecular Structure, Spectral Analysis, Natural Bond Order and Intramolecular Interactions of 2-Acetylpyridine Thiosemicarbazone: A Combined DFT and AIM Approach, Journal of Molecular Structure, 1094, 2015, 61–72.

Renjith R, Vibrational Spectra, Molecular structure, NBO, HOMO–LUMO and First Order Hyperpoalarizability Analysis of 1,4-Bis (4-Formylphenyl) Anthraquinone by Density Functional, Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy, 131, 2014, 225–234.

Sambathkumar K, Jeyavijayan S, Arivazhagan M, Electronic Structure investigations of 4-Aminophthal Hydrazide by UV–Visible, NMR Spectral Studies and HOMO–LUMO Analysis by Ab Initio and DFT Calculation, Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy, 147, 2015, 124–138.

Senthil Kumar J, Arivazhagan M, Thangaraju P, Vibrational Spectra, NLO analysis, and HOMO-LUMO Studies of 2-Chloro-6-Fluotobenzoic Acid and 3,4-Dichlorobenzoic Acid by Density Functional Method", Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy , 147, 2015, 235–244.

Sharmi Kumar J, Renuga Devi TS, Ramkumaar GR, Bright A, Ab initio and Density Functional Theory Calculations of molecular Structure and Vibrational spectra of 4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid, Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy, 152, 2016, 509–522.

Sundaraganasan N, Elango G, Sebastian S & Subramani P, Molecular Structure, vibrational Spectroscopic Studies and Analysis of 2-Fluoro-5-methylbenzonitrile, Indian Journal of Pure & Applied Physics, 47, 2009, 481-490.

Veeraiah A, FT-IR, FT-Raman, UV/Vis Spectra and Fluorescence Imaging Studies on 2-(Bromoacetyl) Benzo (b) Furan by AB Initio DFT Calculations, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 147, 2015, 212–224.

Yufeng Chen, Jin Yang, Zonglong Li, Ran Li, Weidong Ruan, Zhiping Zhuang, Bing Zhao, 2016, Experimental and Density Functional Theory Study of Raman and SERS spectra of 5-Amino-2-Mercaptobenzimidazole, Spectrochimica Acta Part A: Molecular and Bio Molecular Spectroscopy, 153, 344–348.

Zeynep Demirciogˇlu, Cigˇdem Albayrak, Orhan Buyukgungor, Experimental (X-Ray, FT-IR and UV–Vis Spectra) and Theoretical Methods (DFT Study) of (E)-3-methoxy-2-[(p-Tolylimino) Methyl] Phenol", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 128, 2014, 748–758.