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Spectroscopic Analysis, Electronic, Optical and Thermodynamical Properties of 2-amino-5-fluorobenzonitrile by *Ab Initio* Methods

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ABSTRACT

2-Amino-5-fluorobenzonitrile (2A5FBN), a novel molecule has been reported after mutually experimental and theoretical approaches on molecular atomic structure, vibrational spectra, Non-linear Optics (NLO) properties, Natural Bond Orbital (NBO) analysis and Molecular Electrostatic Potential (MEP). The Fourier Transform Infrared Spectroscopy (FTIR) (400-4000 cm^{-1}) and FT-Raman spectra (50-3500 cm^{-1}) of 2A5FBN were recorded. The density functional Hybrid functional Becke, three-parameter, Lee-Yang-Parr (HF/B3LYP) methods with 6-311++G (2d, p) as higher basis set was determined the molecular geometry, harmonic vibrational frequencies and bonding features of 2A5FBN in the ground state. Time-dependent Density Functional Theory (TD-DFT) has produced the calculated energy and oscillator strength. The calculated Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies show that charge transfer occurs within the molecule. Mulliken Population Analysis (MPA) and Natural Population Analysis (NPA) on charges also have been evaluated. Eventual investigation on thermodynamic parameters like enthalpy, Gibbs free energy, zero point energy, entropy, heat capacity, dipole moment and atomic charges have also been conducted. Finally, spectra of the title compound have good complement while compared with the calculation results were applied to simulate infrared and Raman spectra.

Keywords: 2-amino-5-fluorobenzonitrile, NBO, Molecular atomic charges, Molecular electrostatic potential, HF/B3LYP

INTRODUCTION

Benzonitrile is the child molecule to the parent molecule ammonia to toluene, which had the enormous changing with the consequence of the particular ratio [1]. Benzonitrile has the nick names like phenyl cyanide or cyanobenzone, these are very sensitive in air, skin and eye nuisance. The fragrances, cosmetics, steroid, aromatic alcohols for color removers, solvents for fatty acids, hydrocarbons and oils are used with benzonitrile as a chemical broker. The existence of Vitamin B-complex in plants and animal tissues helps to increase the salicylate level in blood. This complex is used in cholocystrographic tests, urology media, miticides and medicine productions [2]. In this compound produce medical, pharmaceuticals, antiseptics, bioactive sensors react with ammonia. This ammonia benzonitrile derivative had widespread applications that exist in the commercial and scientific world [3]. These ammonia benzonitrile molecules mainly focus the electronic and optical properties like di-fluorescence, Intramolecular Charge Transfer (ICT) in intense excited state and space between the states. The medical world introduces a term neuromodulator and the derivative act as this and identifies the biogenic amine in the human brain [4]. Vasoconstriction is fabricated of using ammonia benzonitrile as well as it has an activity of cardiovascular [5]. From the derivatives produced the biologically active components, perform like a radio defensive mediators and in arthrobacter which is the induction of nitrilase activity. In the metal ions, this compound has coordinated the metals in the course of dissimilar modes in the chemistry [6].

The computational word and research change its phase using the theoretically and computational methods. Observed and calculated methods of molecules had enormous applications in the number of fields including science and technology. The computational investigations are augmenting the less expansive, time consuming, accuracy of the research which turns on to the qualifications of the theoretical methods instead of experimental. This method makes sure that the big molecule interactions, electronic, optical, thermodynamically properties of the molecules. Aminobenzonitile molecules had lot of reviews between the observed and calculated as denoted below. Subashini and Periandy [7] investigated the Fourier Transform Infrared Spectroscopy (FTIR), FT-Raman, Nuclear Magnetic Resonance (NMR) and UV analysis using experimentally by the molecule (R)-2-amino-1-phenylethanol as well as the electronic energy gap, Natural Bond Orbital (NBO), Molecular Electrostatic Potential and thermo analysis are calculated computational hybrid methods. Sudha et al. [3], reported the theoretical and experimental studies on optimized structure, vibrational spectra and NBO analysis of 2-Amino-4-chlorobenzonitrile (2A4CBN). Sundaraganesan et al. [8] have recorded the IR and Surface-enhanced Raman Scattering (SERS) of 2-amino-5-bromopyridine and assigned the vibration values.

Sebastian et al. [9] have tested the vibrational frequencies; find the potential energy distributions and some of the quantum mechanical calculation of the molecule 4-Amino-3-hydroxy-1-naphthalenesulfonicacid (4A3HNSA). Ramalingam et al. [10], have established the spectra of infrared and Raman spectra of the 5-Amino-2-nitrobenzoic acid (ANB) and calculated the geometry optimized on the potential energy surface at Hartree–Fock (HF), Møller–Plesset perturbation theory (MP) (MP2) and Becke, three-parameter, Lee-Yang-Parr (B3LYP) levels. Lago et al. [10] have compared the studies of the p-aminobenzoic acid and predicted many properties using computational methods. The present letter 2-Amino-5-fluorobenzonitrile (2A5FBN) have inspected both observed and calculations method. The literature review concluded that, there are no publications of the title compound 2A5FBN using the theoretical methods. From the equilibrium molecular structure, parameters and vibrational assignments help to determine the results of the interior properties of the molecules. Electronic transitions, molecular orbital gap, visual representation of charges, Intra charge Interactions, hyperpolarizability and thermodynamical properties are predicted using the HF/DFT methods using the hybrid basis sets.

EXPERIMENTAL DETAILS

The compound 2A5FBN provided a sturdy purity of larger than 99% and used as such without any additional refinement by Sigma-Aldrich Chemical Company, the USA. The FT-Raman spectrum of 2A5FBN has been recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 50-3500 cm^{-1} on a EZ Raman, Enwave optronics, USA IFS 66 V spectrometer. The FTIR spectrum was recorded using 8400S Bruker, Alpha T and Germany infrared spectrophotometer using pellet technique in the region 4000-400 cm^{-1}. At the room temperature with scanning speed of 30 $cm^{-1}.min^{-1}$ the spectra are traced. The Figures 1 and 2 shows the association of both observed and calculated IR and Raman spectra of 2A5FBN. The above spectra are conceded out at the Department of Nanotechnology, Noorul Islam Centre for Higher Education (NICHE), Kumaracoil, Thackalay, and Kanyakumari District.

The spectra are computerized using the HF/B3LYP with 6-311++G (2d, p) basic set and the output spectra are monitored threw Gauss sum program, which gives the Raman intensities spectra directly. This program equating the intensity theory of Raman scattering derived relationship and produces the modified Raman intensities data. The assignments give the same results while compared with the three basic sets. The Raman intensity data also merged with the dynamic basic sets which confirmed the formation of methylbenzonitrile.

Computational details

The GAUSSIAN 09W program is used for predicted the quantum computational calculations of 2A5FBN with the original version with three parameter functional by way of applying *Ab initio* B3LYP method in correlations [11-17] level with different basis sets on Intel Core i3 1.9 GHz processor personal computer to derive the complete geometry optimization [18]. Gaussian software is a super positioning tool for developing fields of computational physics like structural analysis, reaction mechanisms, potential energy values, charge distributions and excitation energies of the compound [18]. The single point energy calculation is computing the energies of specific molecular structures and the allied molecular properties are predicted initially. Geometry optimizations calculating equilibrium structure of molecules, optimizing transition structures and energy minimizations at dynamic basic sets. From the second derivatives the energy has been calculated the FTIR, Raman frequency computing and intensities plots are done by the Gauss sum program. The vibrational assignments with Total Electron Density (TED) are calculated and explained using the Scaled quantum mechanical program using VEDA 4.0. Software [19,20]. An elevated degree of precision at the customarily considerations along with obtainable linked by the GAUSSVIEW program are made by the molecules vibrational frequency assignments. The electronic oscillatory frequency and electronic properties such as Higher Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) orbital energy distribution, Mulliken atomic charge distribution, Natural Population Analysis (NPA) and thermo dynamical parameters are resolute by the Time-dependent DFT (TD-DFT) [21]. The energy absorption spectra and energy gap plot drawn from Gauss view 5.0 programs [22]. Electrostatic Potential map had been drawn by MOLEKEL. Bond interactions and electron high density delocalization are analyzed using NBO in Gaussian09 DFT with same basic sets. The polarizability and hyperpolarizability is calculated to understand the frequency doubling of the Self Help Groups (SHGs) behavior of 2A5FBN. At last, investigations are conducted to find the density of states of different atoms, total density of states and band gap studies are found using theoretical replicas.

RESULTS AND DISCUSSION

Molecular geometry

Cs point group symmetry molecule equilibrium structure of 2A5FBN has been constructed and displayed in the Figure 3. The research compound optimized by the dissimilar basis sets on both HF and DFT methods. From the results, the Ab initio HF and DFT B3LYP methods with 6-311++G (2d, p) predicted a good and minimum energy of 2A5FBN as -476.45413244 and -479.23468930 Hartree, respectively. The length, angle and dihedral angel for bonding of each atoms of the compound has computed and tabulated in Table 1. 2A5FBN has the fluorine atom, benzonitrile group and amino group substituent and so this is called as a tri-substituted aromatic compound. In the compound, benzene ring hybrid by the equal length, angle of the carbon atoms between the bonds. The hydrogen atoms connected to the ring because of the electron valance distribution is the mainly reason for the change of the chemical and physical properties of the molecules [20]. The nitrile group and fluorine atoms occupy the hydrogen atoms placed in the ring. This changing of atoms, modify the angles in faultless structure of hexagonal [3]. The molecule has seven carbons bonds, three C–H, two N–H, two C–N and one C-F bonds. There is no crystal structure for the 2A5FBN, the carbons bonding decreased as C4-C5=1.405 Å, C8-C9=1.401 Å, C2-C3 and C7-C8=1.400 Å, C2-C8=1.398 Å, C3-C4 & C5-C7=1.357 Å. From that result, it is found that the benzene ring has almost the same length of the all carbons bond and deviation should be around 0.005 Å it only corresponds with the earlier reports. The bond between the N-H and C-H are also predicted and compared with the observed microwave data. The length of the C≡N bond had 1.147 Å is computed by both basic sets and 1.158 Å is observed for the benzonitrile in early results. Both results had good correlation and the minimum deviation level is 0.011Å, whose result is shorter than the single bond carbon and amino group as valued is 1.138 Å for both the basis sets. At last, the length of the carbon fluorine bond is calculated and merged with the observed value as 1.350 Å which is reported by Bak et al. [19]. The angles between the bonds have been predicted by an atom that has tae corresponding results while comparing with the microwave data.

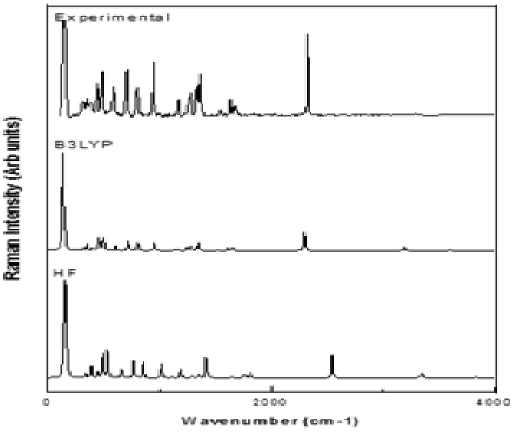

Figure 1: Experimental and calculated FTIR spectrum of 2A5FBN

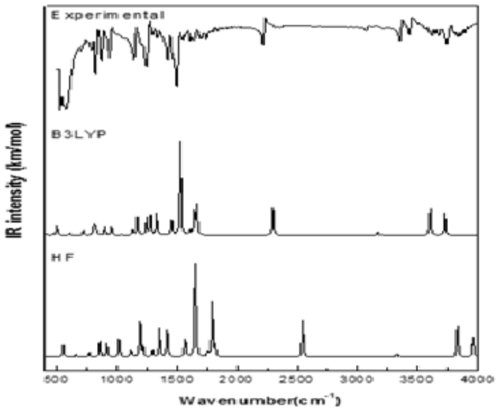

Figure 2: Experimental and calculated FT-Raman spectrum of 2A5FBN

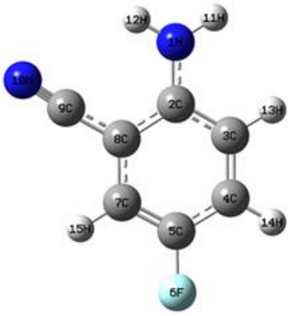

Figure 3: Optimized structure of 2A5FBN

Vibrational analysis

The FTIR and FTR spectra are predicted based on the observed values by the computational physics methods using HF basis set and interpreted the vibrational assignments with TED, polarization ratio, reduced mass and forced constant as tabulated in Table 2. The 15 atom 2A5FBN has 39 (3N-6) normal vibrations that separated the 12 in-plane and 27 out-of-plane vibrations in A′ & A″ species, while regarding the symmetric planer and asymmetric non-planar vibrations, respectively. All FTIR and FTR spectra have all activate vibrations. The observed frequencies, intensities, scaled, activities values 2A5FBN are calculated and the graphical comparisons of the both methods are drawn in Figures 2 and 3.

C-H vibrations

The 2A5FBN is the substituted aromatic system. The 2A5FBN has 9 modes of carbon hydrogen vibration in 39 (3N-6) normal vibrations is separated by three in-plane bending vibrations, three torsion, three stretching (mode no.3-5). The three bending of in-plane vibrations (mode no.18-20) slouch in the region 1000-1300 cm^{-1} [20,21]. The title compound modes are calculated and the wavenumbers 804, 859, 916, 1117, 1219, 1296 and 1354 cm^{-1} are compared with the observed values of the 819, 870, 935, 1137, 1245, 1294, 1331 cm^{-1} and 798, 948, 1172, 1284, 1334 cm^{-1} at the FTIR and FTR, respectively. The 3 torsion vibrations (mode no. 30-32) slouches in the region 495,456 and 448 cm^{-1} are calculated. The mode no. 4 had the vibration of stretching at 3355 cm^{-1} and 3352 cm^{-1} for both the calculated and observed methods, respectively.

Table 1: Optimized geometrical parameters of 2A5FBN

Parameters	6-311++G (2d,p)			Parameters	6-311++G (2d,p)			Parameters	6-311++G (2d,p)	
Bond length (Å)	**B3LYP**	**HF**	**A**	**Bond angle (°)**	**B3LYP**	**HF**	**A**	**Dihedral angle (°)**	**B3LYP**	**HF**
N1-C2	1.338	1.338		C2-N1-H11	120	120		H11-N1-C2-C8	180	180
N1-H11	1.000	1.000		C2-N1-H12	120	120		H12-N1-C2-C3	180	180
N1-H12	1.000	1.000		H11-N1-H12	120	120		C1-N2-C3-C4	180	180
C2-C3	1.400	1.398		N1-C2-C3	120.22	120.44		C8-C2-C3-H13	180	180
C2-C8	1.398	1.395	1.4	N1-C2-C8	120.22	120.44		N1-C2-C8-C7	180	180
C3-C4	1.357	1.359		C3-C2-C8	119.56	119.12		C3-C2-C8-C9	180	180
C3-H13	1.070	1.070		C2-C3-C4	120.01	120.01		C2-C3-C4-H14	180	180
C4-C5	1.405	1.362	1.391	C2-C3-H13	120.00	119.99		H13-C3-C4-C5	180	180
C4-H14	1.070	1.070		C4-C3-H13	120.00	119.99		C3-C4-C5-F6	180	180
C5-F6	1.350	1.350	1.35	C3-C4-C5	120.44	120.87		H14-C4-C5-C7	180	180
C5-C7	1.357	1.359		C3-C4-H14	119.78	119.56		C4-C5-C7-H15	180	180
C7-C8	1.400	1.398	1.387	C5-C4-H14	119.78	119.56		F6-C5-C7-C8	180	180
C7-H15	1.070	1.070	1.081	C4-C5-F6	119.78	119.56		C5-C7-C8-C9	180	180
C8-C9	1.401	1.401	1.45	C4-C5-C7	120.44	120.87		H15-C7-C8-C2	180	180
C9-N10	1.147	1.147	1.158	C6-C5-C7	119.78	119.56				
				C5-C7-C8	120.01	120.01	119.3			
				C5-C7-H15	120.00	119.99				
				C8-C7-H15	120.00	119.99	120.64			
				C2-C8-C7	119.56	119.12	120.3			
				C2-C8-C9	120.22	120.44				
				C7-C8-C9	120.22	120.44	121.81			

A-Microwave data (benzonitrile), Taken from references [3,39,40]

Table 2: IR intensities, Raman intensities, reduced masses, force constants, depolarization ratios and vibrational assignments are obtained for 2A5FBN calculated by HF/6-311++G (2d,p) basis set

Symmetric species Cs	Mode No	Observed wavenumber (cm)		HF/6-311++G (2d,p)				a	b	c	Vibrational assignments
		IR	FTR	Un scaled	Scaled	IR intensity	Raman intensity				
A"	1	3923		3971	3951	59.686	26.6398	0.6376	1.1059	10.275	νNH (100)
A"	2	3842		3842	3823	88.799	101.3765	0.1099	1.0462	9.0997	νNH (100)
A'	3			3363	3346	0.7626	113.3061	0.2898	1.0945	7.2916	νCH (99)
A"	4	3352		3355	3338	2.9374	212.3969	0.2054	1.096	7.268	νCH (99)
A'	5			3331	3314	8.7354	101.5200	0.5319	1.0902	7.1251	νCH (100)
A"	6	2211	2324	2551	2538	92.700	1183.663	0.2444	12.697	48.682	νNC (91)
A"	7	1835		1818	1809	28.629	240.3761	0.7445	3.6802	7.1676	νCC (39)+βHNH (14)
A"	8			1795	1786	123.152	84.6138	0.3125	1.3548	2.5729	βHNH (76)
A'	9	1721		1759	1750	16.5305	246.0242	0.4017	6.0903	12	νCC(54)
A'	10	1639	1636	1654	1646	283.576	37.3526	0.5392	2.8099	4.5304	βHCC (42)
A"	11	1546		1569	1561	50.1451	13.1138	0.7442	4.6782	6.7812	νCC (44)
A'	12	1421		1424	1417	34.112	790.6069	0.1273	2.8288	3.3814	νNC (40)+βHCC (14)
A"	13			1418	1410	49.5354	623.9064	0.1128	2.2446	2.6574	βHCC (31)+νFC (19)+νCC (16)
A'	14	1331	1334	1354	1347	64.5379	133.5722	0.2794	2.5844	2.7925	βCCC (37)+νFC (18)

A'	15	1294	1284	1296	1290	18.5299	93.1383	0.5943	1.7203	1.7031	βHCC (47)+νCC (24)
A"	16	1245	1172	1219	1213	24.4703	110.6074	0.2904	1.9592	1.715	βHCC (24)+νCC (23)+βHNC (20)
A'	17			1192	1186	94.5335	432.0893	0.7106	2.3512	1.9692	νCC (60)+βHCC (20)
A"	18	1137		1117	1111	20.8594	100.9687	0.2721	1.8681	1.3731	βHNC (32)+βHCC (29)+νCC (10)
A"	19			1068	1063	0.0084	4.7304	0.75	1.3415	0.9023	δCCCH (66)+τHCCN (25)
A"	20			1020	1015	20.9705	2.2558	0.75	1.4955	0.9171	νCC (50)+νFC (12)+βCCC (12)
A'	21			1020	1015	26.0222	731.7705	0.0675	4.6471	2.8478	δCCCH (89)
A'	22	935	948	916	912	37.9014	5.6913	0.75	1.5713	0.7774	τHCCN (65)+δCCCH (18)
A'	23	870		859	854	37.8215	769.1921	0.0682	4.9094	2.1325	βCCC (30)+νNC (20)
A'	24	819	798	804	800	0.951	81.6011	0.75	3.8143	1.4525	δNCCC (42)+τCCCC (19)+δCCCC (17)
A'	25	787	710	768	765	11.4551	817.5094	0.1208	7.7499	2.6958	βCCC (36)+νCC (21)
A'	26	696		667	663	0.6415	336.8139	0.75	4.8101	1.2599	τCCCC (40)+τCCCN (26) +δCCCC (20)
A'	27			659	656	6.183	251.1804	0.4845	5.5583	1.4229	βCCN (31)+βCCC (31)
A'	28	569	590	554	551	27.4796	48.1694	0.75	3.1528	0.5699	δNCCC (32)+τCCCC (28)+τCCCN (27)
A'	29	521		537	534	4.4107	1262.265	0.1804	8.1555	1.3837	νCC (36)+βCCC (23)
A'	30		492	495	492	0.524	1290.412	0.6688	6.6819	0.964	βCCN (37)+βCCC (31)
A'	31			456	454	1.395	88.7062	0.3088	5.9739	0.7334	βCCF (43)+βCCC (21)
A'	32		446	448	446	1.2048	280.7654	0.75	3.5638	0.4214	τCCCC (73)+τCCCN (17)
A'	33			391	389	1.3533	604.4660	0.75	6.7128	0.604	τCCCF (53)+τCCCC (12)+δNCCC (11)
A'	34		354	382	380	0.6381	101.5521	0.75	1.0702	0.0922	τHNCC (84)
A'	35		318	345	343	0.9123	188.0701	0.3575	5.1685	1.0702	βCCN (36)+βCCF (33)+βCCC (16)
A'	36			173	172	0.4898	1209.850	0.75	7.6787	0.1357	τCCCF (32)+δCCCC (28)+τCCCC (23)
A'	37			156	155	8.9177	6656.069	0.745	9.3773	0.1348	βCCC (52)+βCCN (41)
A'	38			143	142	4.1657	1346.611	0.75	4.5598	0.0548	τCCCC (53)+δCCCC (28)+τCCCN (10)

υ stretching; υ_s-symmetric stretching; υ_{as}-asymmetric stretching; β in-plane-bending; δ-out-of-plane; τ torsion; a-Depolarition Ratio; b-Reduced mass; c-Force constants

C-C and C-C-C vibrations

Benzonitriles are the substituents cyanogens groups and the benzene ring has almost the same length of the all carbons bond and minimum deviation. The eleven stretching (mode no. 7, 9, 11, 13, 15, 16, 17, 18, 20, 25, 29) carbon vibrations slouch in the region 500-1850 cm^{-1} and ten bending of vibrations slouch above the region 1300 cm^{-1}. From the research, the six similar carbon bonding can produce benzene the same time that ring vibrating the six C-C stretching modes are scanned through FTIR in the region at 1835, 1721, 1639, 1546, 1421 cm^{-1} (mode no. 7-12) and the theoretical values at 1818, 1759, 1654, 1569, 1424, 1418 cm^{-1} (mode no. 7-13) coincides each other. The recorded spectral values of C-C-C bending modes at 1331, 870, 787 and 521 cm^{-1} values are equal with predicted numerical.

Amino group vibrations

The region about 3500-3300 cm^{-1} is allotted for the stretching vibrations of the N-H in amines. The range 3500-3420 cm^{-1} for the asymmetric stretching, 500-300 cm^{-1} for the torsion, 1850-900 cm^{-1} for in-plane bending for the –NH vibrations [23]. From the above results, the theoretical calculations of NH are in the range at 3923, 3842 cm^{-1} (mode no. 1, 2) and 1835, 1245, 1137 cm^{-1} (mode no. 7, 16, 18) for the stretching and bending vibrations, respectively. And these data compared with the IR data gives the good agreement results. In the present research molecule occur the medium range at 1639 and 1636 cm^{-1} in the computerized and observed methods, correspondingly. At the same time the rocking and wagging of the –NH2 vibrations also taken from anticipated frequencies. Therefore, the region at 1636, 569, 391 and 345 cm^{-1} are point out the amino rocking, wagging, torsion and twisting modes in that order. While compare the earlier reports like 2-amino-4-methylbenzothiazole [24], 2-amino-5-ethyl-1,3,4-thiadiazole [25] and 2-amino-5-chlorobenzoxazole [26] it gives the fruitful agreements.

C-F vibrations

The vibrations of ring and halogen atoms bonds are having the heavy metal ions on the side-line of molecules and corresponding vibrations because of the lowering molecular symmetry [14,27]. The strong region of C-F stretching vibrations correspondingly at 1331 and 1354 cm^{-1} exists in the calculated and experimental assignments. These results are compared with the some results like 2-amino-6-fluorobenzothiazole [23], 2-fluoro-5-methylbenzonitrile [14] and p-fluorobenzonitrile [28] gives the good agreement. The regions 1418, 1354 and 1020 cm^{-1} had the stretching, 456 and 345 cm^{-1} had in-plane and 391 cm^{-1} had torsion for the title molecule. These are identified using computational methods and compared with experimental data.

C-N and C≡N vibrations

Benzonitrile molecule vibrational frequency of the cyano group (C-N) is unchanged even which are affected inconsequentially by the new substitution on the phenyl ring. C≡N added with the compound which becomes the aromatic ring, a region absorbed at 2240-2221 cm^{-1} [26,29] and which is the feature to stretching vibrations. In the present research of 2-amino-5-fluorobenzonitrile the strong IR and FTR bands at 2211, 2324 cm^{-1} was assigned in stretching vibrations. The C-C≡N stretching, in plane vibrations are examined in the regions at 1219, 1117, 659, 495, 348, 156 cm^{-1} (mode no. 16, 18, 27, 30, 35, 37) theoretically and which compared with practical values at 1245, 1137 (IR) and 1172, 492, 318 (FTR) gives well coincides.

Atomic charge analysis

Mulliken population and NPA are the best analytical methods to find the atomic charges. In the recent study predicted the atomic charges using the highest basis set in B3LYP. The atomic charges of 2A5FBN is tabulated and plotted of the comparative results in Table 3 and Figure 4 by the above mentioned methods. From the results, concluded the C3 and C7 are electro negativity by the both methods. C2, C5, C9 showed the electro positivity through the NPA and electro negativity through the Mulliken charge analysis and other carbons C4, C8 showed both signs for both methods. This is due to the fact that attachment of the new substituent molecules. For that reason the new substituent molecules like N1, N10 and F6 are showing the electro negativity. The hydrogen atoms have an electro positivity of two methods because of the H11, H12 are join together the electro negative atom N1 and H13, H14, H15 are bonding with the electro negative charged atoms C3, C4, C7 respectively. In the carbons, C8 be able to network by the negatively signed part of the receptor easily because of it is the most positively charged part.

Table 3: Comparison of Mulliken population analysis, natural population analysis of 2A5FBN

Atoms	Mulliken	NPA
N1	-0.474	-0.76336
C2	-0.592	0.2177
C3	-0.227	-0.23761
C4	0.090	-0.20402
C5	-0.123	0.37094
F6	-0.337	-0.3522
C7	-0.310	-0.1889
C8	1.549	-0.23834
C9	-0.304	0.2771
N10	-0.231	-0.32421
H11	0.245	0.38865
H12	0.277	0.40219
H13	0.120	0.20494
H14	0.155	0.21861
H15	0.161	0.2285

In the contrast, N1 is able to interact with the donor atom because of its most negatively charged part. Nitrogen can form a bond with a proton and other electrophilic atoms while sharing its free electron pair. Nitrogen is able to share its free electron pair to form a bond with a proton and other electrophilic atoms [7].

Electronic properties

Frontier Molecular Orbitals (FMO)

The FMO are bounded with two orbitals of HOMO and LUMO which stands for the highest occupied molecular orbital and lowest unoccupied molecular orbital. The reactivity and properties of the molecules depends on the difference between the energy of the both orbitals. Table 4 shows that there is a difference in energy gap of different basis sets as shown in Figure 5. The plots occupied and unoccupied orbitals are computed by B3LYP/6-311++G (2d, p) level for 2A5FBN (in gas phase).

From the plotted diagram the regions of the both orbitals bounded in the molecules are notified. The calculated energy of occupied orbital is -6.23 eV and -8.56 eV as well as the unoccupied orbital value are -1.74 eV and -0.8 eV in B3LYP and HF respectively. The energy gap between the orbitals is 4.49 eV. The values have to be compared with the benzene ring for convenience. The pure benzene ring occupied orbital value 6.6221 eV is taken into consideration since the earlier reports and chemical potential (ρ), chemical hardness (η), Global softness (s), Electro negativity (χ), Electrophilicity index (ω), Dipole moment (μ) like a chemical relativities properties are calculated using the Koopman's theorem and is reported by Parr and Pearson [21]. The FMO energy parameters as well as equivalent Density of State (DOS) of 2A5FBN are shown in Figure 6 [30].

The molecule has highest flow of electrons between donors and acceptors, the total energy should be low, which is calculated by the electrophilicity. The value of benzene ring is 2.182 eV and for the present studies it is 4.473 eV, this may be due to adding of the substituent element with benzonitrile.

The benzene ring has 3.80205 eV and the title compound has corresponding values for two methods at 3.985 and 3.880 eV electro negativity, which denote the covalent bond attraction of the electrons from the atoms. The benzene value of Global hardness is 3.3110 eV, from the DFT get the lower global hardness value of 2.245 eV and highest value 4.680 eV by HF method.

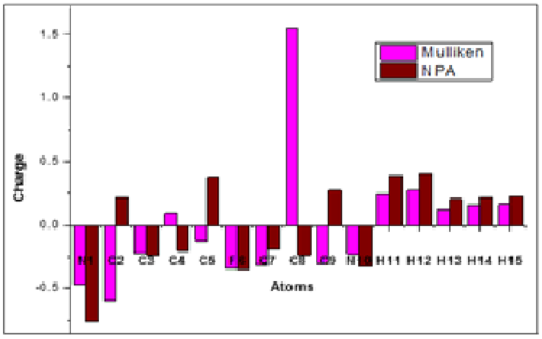

Figure 4: Mulliken and natural population's charges of 2A5FBN

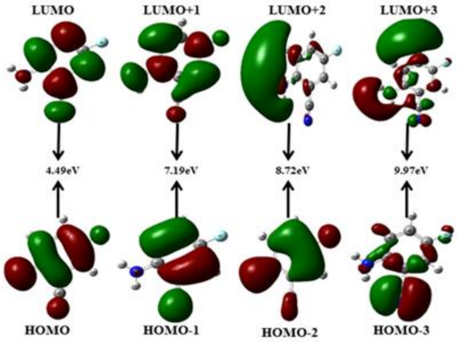

Figure 5: The selected frontier molecular orbitals of 2A5FBN with the energy gaps

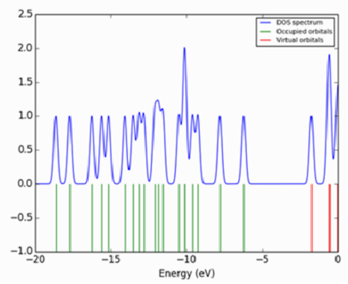

Figure 6: The frontier molecular orbital energies and corresponding density of state spectrum of 2A5FBN

This result shows the 2A5FBN compound is less stable in the DFT and more stable in HF methods while compared with the benzene. It is also dominated that the result of Global softness of the compound is less for both methods to compare with benzene. Finally, the intermolecular interactions of the benzene ring are not very strong because of the zero dipole moment. This research molecule has the strong intermolecular interactions for the reason that the value of dipole moment are 1.827 and 1.871 Debye in DFT and HF methods, which gives the good charge flow, beginning from negative to positive.

Natural bond analysis

NBO analysis is the welcome method for determining the intra and inter-molecular interactions of the 2A5FBN. Electron density percentage was very high from all orbital details, for the reason that the NBO analysis provide the almost perfect 'natural Lewis structure' picture and gives the sequences in two filled and virtual orbital spaces [31]. From the Gaussian NBO results the parameters of donor type (i), acceptor type (j), occupancy, the stabilization energy E (2), ICT, Electron Density Transfer (EDT) and cooperative effect associated with electron delocalization between the donor and acceptor is estimated by the B3LYP highest basis set and tabulated the Table 5. They provided the largest E (2), close enough interactions and occupancy of the each of the donor and acceptor electrons resulting from the second-order micro disturbance theory reported [32].

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

Where, $\langle\sigma|F|\sigma\rangle^2$ or F_{ij}^2 is the Fock matrix element i and j orbitals, ε_σ^* and ε_σ are the energies of σ*and σ and n_σ is the population of the donor σ orbital.

The title molecule has σ to σ* transition occur, σ (C4-C5), σ (N1-H11), σ (C9-N10), σ (C8-C9) with antibonding σ*(C5-C7), σ*(C2-C8), σ* (C8-C9), σ* (C9-N10) and stabilization energies of 4.49, 4.29, 8.14, 9.03 Kcal/mol respectively. This recent molecules highest transition is identified in π to π* with probable transitions of carbon bonding taking place π (C2-C8) to π* (C3-C4), π (C2-C8) to π* (C5-C7), π (C3-C4) to π* (C5-C7), π (C3-C4) to π* (C2-C8), π (C5-C7) to π* (C2-C8), π (C5-C7) to π* (C3-C4) and the stabilization energies of 13.68, 23.02, 14.96, 21.51, 13.97, 20.34 Kcal/mol correspondingly. π (C2-C8) shows comparable stabilization energy of 13.68 Kcal/mol and 23.02 Kcal/mol with π* (C3-C4) and π* (C5-C7) respectively. (C5-C7) shows a comparable stabilization energy of 13.97 and 20.34 Kcal/mol with π*(C2-C8) and π*(C3-C4) respectively. This reveals that C5-C7 prefers to be an acceptor than to be a donor with C2-C8. In opposition, π (C3-C4) shows a comparable stabilization of 14.96 Kcal/mol and 21.51 Kcal/mol with π* (C5-C7) and π*(C2-C8) respectively. This gives the explanation that C5-C7 prefers to be an acceptor than to be a donor with C3-C4. σ to σ* and π* occurs between F6, N10 and N1, F6 to C4-C5, C8-H9 and C2-C8, C5-C7 with energies of 6.64, 10.97 and 49.39, 17.75 Kcal/mol, in that order. The four loan pairs of the molecule divided into two fluorine and nitrile is observed. The whole result is concluded that the largest stabilization energy is loan pair N1 to π* (C2-C8) and the lowest is σ (N1-C2) to σ* (N1-H12).

Table 4: HOMO and LUMO energy gaps and related molecular properties of 2A5FBN

Basic set	B3LYP/6-311++G (2d,p)	HF/6-311++G (2d,p)
SCF energy (a.u)	-479.231	-476.450
Dipole moment (Debye) (μ)	1.827	1.871
LUMO (eV)	-1.740	0.800
HOMO (eV)	-6.230	-8.560
ENERGY GAP (eV)	-4.490	-9.360
Electro negativity (χ)	-3.985	-3.880
Chemical potential (ρ)	3.985	3.880
Global hardness (η)	2.245	4.680
Global softness (s)	0.445	0.214
Electrophilicity index (ω)	4.473	9.079
EHOMO-1 (eV)	-7.800	-10.170
ELUMO+1 (eV)	-0.610	1.230
EHOMO-1-ELUMO+1 (eV)	-7.190	-11.400

UV-Visible analysis

The molecules absorbed the radiation in the region of ultraviolet or visible and excite the electrons like π electrons or non-bonding electrons (n-electrons) to higher anti-bonding orbitals. The electronic transitions of the novel compound 2A5FBN plotted using TD-DFT with the highest basis set according to the Franck-Condon principle [33] shown in the Figure 7 From the calculation, the computed absorption bands are presented at 299.13, 257.39 and 229.42 nm is corresponding with the oscillator strength at 0.1346, 0.0029 and 0.0768 in gas phase. Table 6 contains the theoretical electronic excitation energies, absorption wavelength, oscillator strengths and major contribution of the electron transitions between the HOMO to LUMO. From the Gauss sum results, the major contrition of the three wavelengths had 89, 99 and 72% for the H-L, H-L+1 and H-L+2 transitions with excitation energy 4.49 eV, 7.19 eV and 7.49 eV respectively. The peak at 257.39 nm with H-L+1 transition coincide with the pure benzene ring the transition is at 260 nm, 200 nm [7,34]. So this shows the 99% of the major contributions. The energy wills increase despite the fact of change the transition levels, so the absorption bands are shifted to longer wavelength, which is called the bathochromic shift.

Optical property

The investigation of structural, bonding application and vibrational analysis of FTIR and FTR spectroscopy modes are augmentation by predicting the hyperpolarizability for the potential application of the title compound in the field of NLO [35]. The Prediction of molecular lies in the Second-order polarizability or First-order hyperpolarizability (β), Linear polarizability (α), Anisotropic tensor (Δα) and Dipole moment (μ) using the x, y, z components from the Gaussian 09W output have stated in the B3LYP method on the basis of the finite-field approach as follows:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}} \qquad (2)$$

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

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2\right]^{1/2} \qquad (4)$$

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{zzy} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2} \qquad (5)$$

From the results the molecule has higher values of dipole moment, linear polarizability and hyperpolarizability is important for more active NLO properties. The calculated value of dipole moment (μ) was found to be 1.8274 Debye. The highest value of dipole moment is observed at -1.7338 Debye for component μ_x. The polarizability, anisotropy of the polarizability and hyperpolarizability of 2A5FBN is calculated 129.415 × 10^{-33} esu, 209.318 × 0^{-33} esu and 596.933 × 10^{-33} esu respectively (Table 7). In the NLO system, the hyperpolarizability β value is the major part. The dipole moment and first hyperpolarizability of title molecule is approximately 1.19 and 1.73 times than those of urea (μ and β of urea are 1.5285 Debye and 343.272 × 10^{-33} esu) [35].

Table 5: Second order perturbation theory analysis of Fock matrix in NBO basis for 2A5FBN

Donor (i)	Type	Ed (i) (e)	Acceptor (j)	Type	Ed (j) (e)	E(2)[a] (kJ/mol)	E(i)- E(j)[b] (kJ/mol)	f(i,j)[c] (a.u)
N 1-C 2	σ	1.9897	C 2-C 8	σ*	0.0340	2.25	1.42	0.051
N 1-C 2	σ	1.9897	N 1-H 12	σ*	0.0089	0.6	1.29	0.025
N 1-H 11	σ	1.9897	N 1-C 2	σ*	0.0176	0.55	1.17	0.023
N 1-H 11	σ	1.9897	C 2-C 8	σ*	0.0340	4.49	1.24	0.067
N 1-H 12	σ	1.9886	C 2-C 3	σ*	0.0231	4.41	1.23	0.066
N 1-H 12	σ	1.9886	C 9-N 10	π*	0.0172	0.51	0.79	0.018
C 2-C 3	σ	1.9694	C 2-C 8	σ*	0.0340	4.1	1.27	0.064
C 2-C 8	σ	1.9582	C 9-N 10	σ*	0.0117	4.66	1.68	0.079
C 2-C 8	π	1.6362	C 3-C 4	π*	0.3041	13.68	0.29	0.057
C 2-C 8	π	1.6362	C 5-C 7	π*	0.3291	23.02	0.29	0.074
C 2-C 8	π	1.6362	C 9-N 10	δ*	0.0994	22.1	0.38	0.088
C 3-C 4	σ	1.9725	N 1-C 2	σ*	0.0176	3.75	1.23	0.061
C 3-C 4	σ	1.9725	C 5-F 6	σ*	0.0298	3.72	1	0.055
C 3-C 4	π	1.7486	C 5-C 7	π*	0.3291	14.96	0.3	0.061
C 3-C 4	π	1.7486	C 2-C 8	π*	0.4646	21.51	0.29	0.075
C 3-H 13	σ	1.9775	C 2-C 8	σ*	0.0340	4.13	1.1	0.06
C 4-C 5	σ	1.9787	C 5-C 7	σ*	0.0245	4.29	1.3	0.067
C 4-H 14	σ	1.9766	C 2-C 3	σ*	0.0231	4.22	1.08	0.06
C 5-F 6	σ	1.9952	C 7-C 8	σ*	0.0221	1.32	1.56	0.041
C 5-C 7	π	1.7179	C 2-C 8	π*	0.4646	13.97	0.29	0.06
C 5-C 7	π	1.7179	C 3-C 4	π*	0.3041	20.34	0.3	0.071
C 7-C 8	σ	1.9585	C 9-N 10	π*	0.0172	4.73	1.67	0.08
C 7-H 15	σ	1.9747	C 4-C 5	σ*	0.0296	4.23	1.06	0.06
C 8-C 9	σ	1.9772	C 9-N 10	σ*	0.0117	9.03	1.7	0.111
C 9-N 10	σ	1.9933	C 8-C 9	σ*	0.0298	8.14	1.6	0.103
C 9-N 10	δ	1.9646	C 2-C 8	π*	0.4646	7.06	0.35	0.05
LP								
N 1		1.7767	C 2-C 8	π*	0.4646	49.39	0.28	0.113
F 6		1.9708	C 4-C 5	σ*	0.0296	6.64	0.94	0.071
F 6		1.9346	C 5-C 7	π*	0.3291	17.75	0.44	0.084
N 10		1.9719	C 8-C 9	σ*	0.0298	10.97	1.05	0.096

[a]E(2) means energy of hyper conjugative interaction (stabilization energy); [b]Energy difference between donor and acceptor i and j NBO orbitals; [c]F(i, j) is the Fork matrix element between i and j NBO orbitals

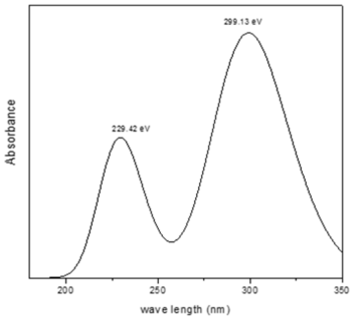

Figure 7: Calculated UV-Visible spectrum of 2A5FBN

Table 6: Energy excitations, wavelength and oscillator strength of the 2A5FBN

Wavelength (nm)	Energy gap	Oscillatory strength	Symmetry	Major contributions	Percentage	Transition
299.13	4.49	0.1346	Singlet -A'	HOMO- > LUMO	89%	$\pi \rightarrow \pi^*$
257.39	7.19	0.0029	Singlet -A"	HOMO- > L+1	99%	$\pi \rightarrow \pi^*$
229.42	7.27	0.0768	Singlet -A'	HOMO- > L+2	72%	$\pi \rightarrow \pi^*$

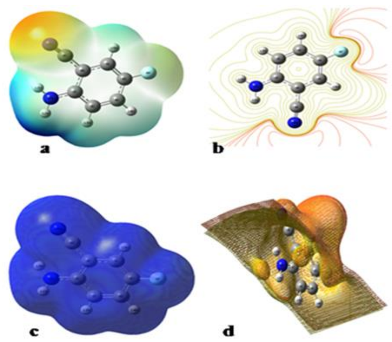

Figure 8: (a) The electrostatic potential, (b) Total electron density, (c) Contour map and (d) MEP of 2A5FBN

Table 7: First order hyperpolarizability of the 2A5FBN

Parameters	B3LYP/6-311++G (2d,p)
μ_x	1.7338281
μ_y	0
μ_z	-0.5775176
μ=	1.8274Debye
α_{xx}	119.336824
α_{xy}	0
α_{yy}	52.0441553
α_{xz}	13.0112942
α_{yz}	0
α_{zz}	113.8133249
α	129.415 × 10-33 esu
$\Delta\alpha$=	209.318 × 10-33 esu
β_{xxx}	-102.7814997
β_{xxy}	0
β_{xyy}	35.1111412
β_{yyy}	0
β_{xxz}	-33.0404581
β_{xyz}	0
β_{yyz}	-21.6894758
β_{xzz}	-1.2575992
β_{yzz}	0
β_{zzz}	49.927353
β_0	596.933 × 10-33 esu

Molecular electrostatic potential

The electronic density consideration is one of the finest methods to determinant of atomic and molecular properties, which is closely related with MEP. This is very passionate about the electrophilic and nucleophilic approaching. The two approaches had different colors plotting on the molecules. If the reaction takes place in red color, the region is electrophilic and will be attracted to negative; here electron distribution is high and the blue color represents a nucleophilic.

The molecular size, shape, positive negative and neutral electrostatic potential regions are illustrated by using this method for which parameters are decided for the molecular structure, physicochemical properties [36]. In this research paper, the Electrostatic Potential (ESP), TED, counter map and MEP of 2A5FBN are drawn in Figure 8. From the visual results, the color represents different regions. The deepest red and blue colors are indicating the strong repulsion (negative) and strong attraction (positive) of regions respectively. The Green color indicates the zero electrostatic potential or neutral charge. The title molecule nitrogen and carbons have higher electron density because of the higher electro negativity value [37]. So, these atoms are surrounding a red portion on it. The counter map and the total electron density surface had good agreement with the negative and positive sites of the molecules [26].

Thermodynamic properties

The theoretical harmonic frequencies and the quantities are tabulated in Table 8 on the basis of the HF/B3LYP by 6-311G++ (2d,p) level the standard statistical thermodynamic functions: Self consistent field energy, zero point vibrational energy, rotational constants, rotational temperatures, standard heat capacities, entropies, enthalpy and Gibbs free energy for the title compounds [38].

From these results, it can be concluded the thermodynamical functions of the DFT method is less than HF *Ab initio* method. These results are accommodating to analyze the further applications of the molecules and promote the scope future researchers.

Table 8: Thermodynamics parameters of 2A5FBN

Thermodynamic parameters of 2A5FN	**B3LYP/6-311++G (2d,p)**	**HF/6-311++G (2d,p)**
Self-consistent field energy (a.u)	-479.231	-476.450
Zero point vibrational energy (kcal/mol)	66.603	71.321
Rotational constant (GHz)	2.368	2.376
	1.045	1.066
	0.725	0.736
Rotational temperature (K)	0.114	0.114
	0.050	0.051
	0.035	0.035
Thermal energy (kcal/mol)		
Total	71.686	76.095
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	69.908	74.317
Specific heat capacity at constant volume (cal/mol K)		
Total	30.979	29.031
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	25.017	23.069
Dipole moment (Debye)	1.827	1.871
LUMO (eV)	-1.740	0.800
HOMO (eV)	-6.230	-8.560
Energy gap (eV)	-4.490	-9.360
Entropy(S) (cal/mol K)		
Total	88.386	86.437
Translational	40.636	40.636
Rotational	29.572	29.534
Vibrational	18.178	16.267
Gibbs Free Energy	0.073	0.081
Enthalpy	-479.120	-476.332

CONCLUSION

From the HF/DFT methods by 6-311++G (2d,p) basis sets, computed the geometrical parameters and optimized structure. FTIR and FTR vibrational frequencies are analyzed and explained vibrations assignments, reduced mass, force constant and ratio using the HF method. The novel molecule has good electronic property which is found since the frontier molecular orbital, UV-Visible and NBO analysis. From the predictions, the energy gap, excitations energies and intra-interactions charge transformation of the molecules had enhance values.

The molecule is higher and in well agreement with urea dipole moment and hyperpolarizability values. The visual representation from MEP, MPA and NPA shows the charge distributions of the molecules and regions. Thus the thermal parameters are tabulated for helping the future researchers and innovative thinkers.

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