

Theoretical Investigations and Second Harmonic Generations Studies of 2-Amino-5-Nitrobenzophenone

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ABSTRACT

The experimental and theoretical studies of 2-Amino-5-nitrobenzophenone (2A5NBP) were inspected for electronic structure and other properties by Density Functional Theory (DFT). The molecular geometry of 2A5NBP in the ground state has been calculated by using the theoretical methods (B3LYP) invoking a basis set. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were estimated by time-dependent DFT (TD-DFT) approach. In addition, nonlinear optics (NLO) properties, Natural Bond Orbital (NBO) analysis and Molecular Electrostatic Potential (MEP) and atomic charges of carbon, nitrogen and oxygen were calculated.

KEY WORDS: 2A5NBP, MEP, B3LYP

1. INTRODUCTION

Benzophenone is the child molecule to the parent molecule ammonia to toluene, which had the enormous changing with the consequence of the particular ratio (Frank Klinitas, 1951). Benzonitrile has the nick names like phenyl cyanide or cyanobenzene; 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 cholecystographic tests, urology media, miticides and medicine productions (Adel El-Azab, 2016).

In this compound produce medical, pharmaceuticals, antiseptics, bioactive sensors react with ammonia. This ammonia benzophenone derivative had widespread applications that exist in the commercial and scientific world (Sudha, 2011). These ammonia benzophenone 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 (Tyagi, 1990). Vasoconstriction is fabricated of using ammonia benzonitrile as well as it has an activity of cardiovascular (Songyuan Dai, 2008). 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 (Govindharaju, 2014).

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 (Arockiasamy Ajaypraveenkumar, 2017). 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.

The present letter 2-Amino-5-nitrobenzophenone (2A5NBP) have inspected both observed and calculations method. The literature review concluded that, there are no publications of the title compound 2A5NBP using the theoretical methods. From the equilibrium molecular structure, parameters 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 DFT methods using the hybrid basis sets (Al-Sehemi, 2013).

2. METHODS AND METATERIALS

The molecule 2-Amino-5-nitrobenzophenone (2A5NBP) of spectral grade was purchased from sigma Aldrich Chemical Co. U.S.A in powder form and was used as such without further purification.

Computational details: The GAUSSIAN 09W program is used for predicted the quantum computational calculations of 2A5NBP (Shajikumar, 2016) with the original version with three parameter functional by way of applying ab-initio Becke-Lee-Yang-Parr hybrid method in correlations B3LYP (Parr, 1989) level with different basis sets on Intel Core i3 3.3 GHz processor personal computer to derive the complete geometry optimization (Sundaraganasan, 2009). 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 (Saravanan, 2015). 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. 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 HOMO and LUMO energy distribution Thermo dynamical parameters are resolute by the TD-DFT calculations (Anbarasan, 2011). The energy absorption spectra and energy gap plot drawn from Gauss view 5.0 programs (Lin-Vien, 1991).

3. RESULTS AND DISCUSSION

Molecular Geometry: Cs point group symmetry molecule equilibrium structure of 2A5NBP has been constructed and displayed in the Figure.1. The research compound has optimized by two dissimilar basis sets by DFT method. From the results, B3LYP methods with 6-311+G (d, p) and 6-311++G (d, p) predicted a good and minimum energy of 2A5NBP as -837.126600473 and -837.131694126 a.u, respectively. The length, angle and dihedral angel for bonding of each atoms of the compound has computed and tabulated in Table.1. 2A5NBP has benzonitrile group, phenone group and amino group substituent and so this is called as 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 (Murugan, 2012). The ammonia and phenone group occupy the hydrogen atoms placed in the ring. This changing of atoms, modify the angles in faultless structure of hexagonal (Arockiasamy Ajaypraveenkumar, 2016). The molecule has fifteen carbons bonds, ten C–H, two N–O & N–C and one N–H & C–O bonds. From that result, it is found that the benzene and phenone group have almost the same length of the all carbons bond and deviation should be around 0.005 Å it only corresponds with the earlier reports. There is no crystal structure for the 2A5NBP, the carbons bonding decreased in phenone group from benzonitrile. The length of the C≡N bond had 1.47Å is computed by both basic sets. 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 1.54Å.

Table.1. Equilibrium parameters of 2A5NBP

Bond Length	A	B	Bond Angle	A	B	Dihedral Angle	A	B
N1-C3	1.47	1.47	C3-N1-O27	120	120	O27-N1-C3-C2	180	180
N1-O27	1.24	1.36	C3-N1-O28	120	120	O27-N1-C3-C4	0	0
N1-O28	1.24	1.20	O27-N1-O28	120	120	O28-N1-C3-C2	0	0
C2-C3	1.40	1.54	C3-C2-C7	120	120	O28-N1-C3-C4	180	180
C2-C7	1.40	1.36	C3-C2-H17	120	120	C7-C2-C3-N1	180	-150
C2-H17	1.07	1.07	C7-C2-H17	120	120	C7-C2-C3-C4	0	30
C3-C4	1.40	1.36	N1-C3-C2	120	120	H17-C2-C3-N1	0	180
C4-C5	1.40	1.54	N1-C3-C4	120	120	H17-C2-C3-C4	180	0
C4-H18	1.07	1.07	C2-C3-C4	120	120	C3-C2-C7-C6	0	0
C5-C6	1.40	1.36	C3-C4-C5	120	120	C3-C2-C7-C8	-180	180
C5-H19	1.07	1.07	C3-C4-H18	120	120	H17-C2-C7-C6	-180	0
C6-C7	1.40	1.54	C5-C4-H18	120	120	H17-C2-C7-C8	0	180
C6-N16	1.47	1.47	C4-C5-C6	120	120	C3-C2-H17-H20	180	180
C7-C8	1.54	1.54	C4-C5-H19	120	120	C7-C2-H17-H20	0	0
C8-O9	1.43	1.26	C6-C5-H19	120	120	N1-C3-C4-C5	180	180
C8-C10	1.40	1.54	C5-C6-C7	120	120	N1-C3-C4-H18	0	0
N9-H25	0.96	1.54	C5-C6-N16	120	120	C2-C3-C4-C5	0	180
C10-C11	1.40	1.36	C7-C6-N16	120	120	C2-C3-C4-H18	180	0
C10-C15	1.40	1.36	C2-C7-C6	120	120	C3-C4-C5-C6	0	0
C11-C12	1.40	1.07	C2-C7-C8	120	120	C3-C4-C5-H19	180	180
C11-H20	1.07	1.54	C6-C7-C8	120	120	H18-C4-C5-C6	180	0
C12-C13	1.40	1.07	C7-C8-O9	120	120	H18-C4-C5-H19	0	180
C12-H21	1.07	1.36	C7-C8-C10	120	120	C4-C5-C6-C7	0	180
C13-C14	1.40	1.07	O9-C8-C10	120	120	C4-C5-C6-N16	180	0
C13-H22	1.07	1.54	C8-O9-H25	109	120	H19-C5-C6-C7	-180	0
C14-C15	1.40	1.07	C8-C10-C11	120	120	H19-C5-C6-N16	0	180
C14-H23	1.07	1.07	C8-C10-C15	120	120	C5-C6-C7-C2	0	180
C15-H24	1.07	1.00	C11-C10-C15	120	120	C5-C6-C7-C8	180	0
C16-H26	1.00	1.00	C10-C11-C12	120	120	N16-C6-C7-C2	180	0

C16-H29	1.00	0.81	C10-C11-H20	120	120	N16-C6-C7-C8	0	180
C17-H20	0.70	0.96	C12-C11-H20	120	120	C5-C6-N16-H26	90	180
			C11-C12-C13	120	120	C5-C6-N16-H29	-30	0
			C11-C12-H21	120	120	C7-C6-N16-H26	-90	-90
			C13-C12-H21	120	120	C7-C6-N16-H29	150	150
			C12-C13-C14	120	120	C2-C7-C8-O9	180	90
			C12-C13-H22	120	120	C2-C7-C8-C10	0	-30
			C14-C13-H22	120	120	C6-C7-C8-O9	0	180
			C13-C14-C15	120	120	C6-C7-C8-C10	180	0
			C13-C14-H23	120	120	C7-C8-O9-H25	30	0
			C15-C14-H23	120	120	C10-C8-O9-H25	-150	180
			C10-C15-C14	120	120	C7-C8-O9-C11	0	180
			C10-C15-H24	120	120	C7-C8-O9-C15	180	0
			C14-C15-H24	120	109	O9-C8-C10-C11	180	0
			C6-C16-H26	109	109	O9-C8-C10-C15	0	180
			C6-N16-H29	109	109	C8-C10-C11-C12	180	180
			H26-N16-H29	109	150	C8-C10-C11-H20	0	0
			C2-H17-H20	144	150	C15-C10-C11-C12	0	0
			C11-H20-H17	156	109	C15-C10-C11-H20	-180	180
						C8-C10-C15-C14	180	180
						C8-C10-C15-H24	0	0
						C11-C10-C15-C14	0	0
						C11-C10-C15-H24	180	180
						C10-C11-C12-C13	0	0
						C10-C11-C12-H21	180	180
						H20-C11-C12-C13	180	180
						H20-C11-C12-H21	0	0
						C10-C11-H20-C17	0	0
						C12-C11-H20-C17	180	180
						C11-C12-C13-C14	0	180
						C11-C12-C13-H22	180	0
						H21-C12-C13-C14	180	0
						H21-C12-C13-H22	0	180
						C12-C13-C14-C15	0	180
						C12-C13-C14-H23	180	0
						H22-C13-C14-C15	180	0
						H22-C13-C14-H23	0	180
						C13-C14-C15-C10	0	180
						C13-C14-C15-H24	-180	0
						H23-C14-C15-C10	180	0
						H23-C14-C15-H24	0	180
						C2-H17-H20-C11	0	0

A-B3LYP/6-311+g(d,p); B-B3LYP/6-311++g(d,p)

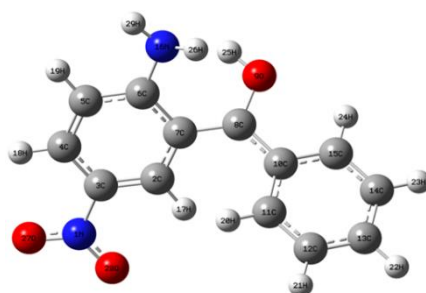


Figure.1. Optimized structure of 2A5NBP

Atomic charge Analysis: Mulliken population analysis is 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 2A5NBP is tabulated and plotted of the comparative results in Table.2 and Figure.2 by the above mentioned methods. From the results, concluded the C2, C3, C5, C6, C9, C11, C12, C13 and C14 are electro negativity by the both methods. C4, C7, C8, C10 and C15 showed the electro positivity through the Mulliken charge analysis 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, N16 are showing the electro negativity. The hydrogen and oxygen atoms have an electro positivity of two methods because of the H25, H26 are joining together the electro negative atom N16 and O27, O29 are bonding with the electro negative atom N16 atom. In the carbons, C7 be able to network by the negatively signed part of the receptor easily because of it is the most positively charged part. In the contrast, N16 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 (Guntram Rauhut, 1995).

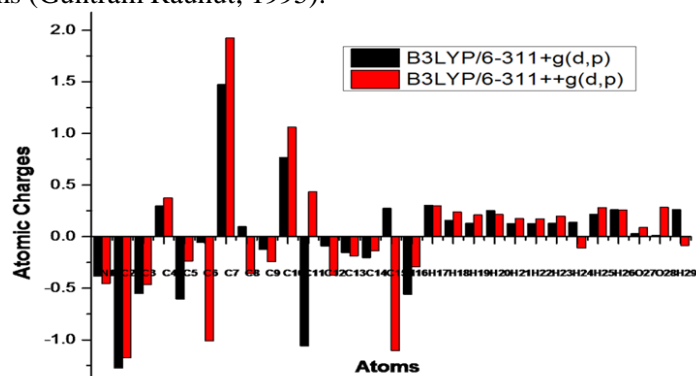


Figure.2. Mulliken charges of 2A5NBP

Table.2. Mulliken Population Analysis of 2A5NBP.

Atoms	6-311+g(d,p)	6-311++g(d,p)	Atoms	6-311+g(d,p)	6-311++g(d,p)
N1	-0.3841	-0.4537	N16	-0.56	-0.2913
C2	-1.2755	-1.1756	H17	0.30542	0.30162
C3	-0.552	-0.4648	H18	0.15929	0.23847
C4	0.29702	0.37424	H19	0.13032	0.21051
C5	-0.6046	-0.2375	H20	0.25401	0.21619
C6	-0.0552	-1.0102	H21	0.12621	0.17706
C7	1.47392	1.92548	H22	0.1274	0.17307
C8	0.09582	-0.3539	H23	0.12815	0.19815
C9	-0.1243	-0.2445	H24	0.14088	-0.1121
C10	0.76631	1.06254	H25	0.21803	0.28018
C11	-1.0593	0.43614	H26	0.26117	0.25853
C12	-0.091	-0.3715	O27	0.03117	0.09129
C13	-0.1553	-0.1858	O28	0.01177	0.28414
C14	-0.2036	-0.1368	H29	0.2621	-0.0864
C15	0.27579	-1.1035			

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.3 shows that there is a difference in energy gap of different basis sets as shown in Figure.3. From the plotted diagram the regions of the both orbitals bounded in the molecules are notified. The calculated energy of occupied orbital is -4.646 as well as the unoccupied orbital value are -4.187eV in B3LYP. The energy gap between the orbitals is 0.459eV. The pure benzene ring occupied orbital value 6.6221eV is taken into consideration since the earlier reports and chemical potential (ρ), chemical hardness (η), Global softness (s), Electronegativity (χ), Electrophilicity index (ω), Dipole moment (μ) like a chemical relativities properties are calculated using the Koopman's theorem and is reported by R.G.Parr et al (R G Parr, 1983; V Arjunan, 2011). 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 2.182eV and for the present studies it is 0.5067eV, this may be due to adding of the substituent element with benzophenone. The benzene ring has 3.80205eV and the title compound has corresponding value at 4.4165eV electro negativity, which denotes the covalent bond attraction of the electrons from the atoms. The benzene value of Global hardness is 3.3110eV, from the DFT get the lower global hardness value of 0.295eV. This result shows the 2A5NBP compound is more stable in the DFT.

It is also dominated that the result of Global softness of the compound is more 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 0.753 Debye, which gives the good charge flow, beginning from negative to positive.

Table.3. HOMO and LUMO energy gaps and related molecular properties of 2A5NBP

Energy Parameters	B3LYP
SCF energy(a.u)	-837.313
Dipole moment(Debye)(μ)	0.75343Debye
LUMO	-4.187
HOMO	-4.646
Energy Gap	-0.459
Electronegativity (χ)	-4.4165
Chemical Potential (μ)	4.4165
Global Hardness (η)	0.2295
Global softness (s)	4.357298475
Electrophilicity Index (ω)	0.506793375
EHOMO-1(eV)	-7.82
ELUMO+1(eV)	-1.36
EHOMO-1 - ELUMO+1(eV)	-6.46

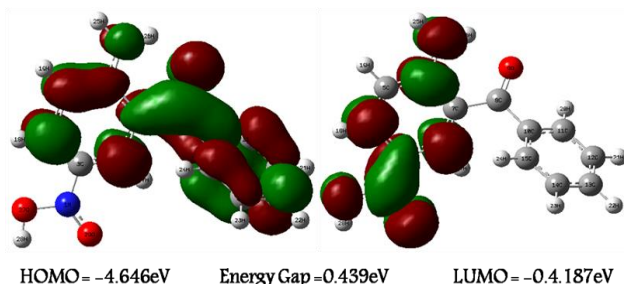


Figure.3. The selected frontier molecular orbitals of 2A5NBP with the energy gaps

Natural Bond Analysis: NBO analysis is the welcome method for determining the intra and inter-molecular interactions of the 2A5NBP. 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 (S Muthu, 2011). From the Gaussian NBO results the parameters of donor type (i), acceptor type (j), occupancy, the stabilization energy $E(2)$, Intermolecular Charge Transfer (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.4. 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 (C James, 2006).

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

Where $(\sigma|F|\sigma)^2$ 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 (C8-O9), σ (C5-H19), σ (C4-C5) with antibonding σ^* (C14-H23) and stabilization energies of 82.81, 32.99, 17.53 Kcal/mol respectively. This recent molecules highest transition is identified in π to π^* with probable transitions of carbon bonding taking place π (C12-C13) to π^* (C10-C11), π (C6-C7) to π^* (C2-C3), π (C4-C5) to π^* (C6-C7), π (C2-C3) to π^* (C4-C5) and the stabilization energies of 10.87, 10.43, 9.35, 9.06 Kcal/mol correspondingly. σ to σ^* and π^* occurs between O9, O27, O29 and N1, N16 to C7-C8, N1-O29, N1-C3 and C2-C3, C6-C7 with energies of 1.3, 0.96, 2.44 and 10.52, 24.26 Kcal/mol, in that order. The five loan

pairs of the molecule divided into three oxygen and two nitrile is observed. The whole result is concluded that the largest stabilization energy is σ (C8-O9) to σ^* (C14-H23) and the lowest is σ (N1-O29) to σ^* (C12-H21).

Table.4. Second order perturbation theory analysis of Fock matrix in NBO basis for 2A5NBP

Donor (i)	Type	Ed/e	Acceptor (j)	Type	Ed/e	E(2)	E(i)- E(j)	f(i,j)
N1 - C3	σ	0.99393	C14 - H23	σ^*	0.00679	0.3	5.05	0.049
N1 - C3	σ	0.99393	O27 - H28	σ^*	0.00711	0.73	4.33	0.071
N1 - O27	σ	0.99694	C14 - H23	σ^*	0.00679	0.42	5.19	0.059
N1 - O29	σ	0.99739	C12 - H21	σ^*	0.00641	0.26	1.54	0.026
N1 - O29	σ	0.99739	C14 - H23	σ^*	0.00679	7.47	5.28	0.251
C2 - C3	σ	0.98343	N16 - H26	σ^*	0.01703	2.99	4.33	0.144
C2 - C3	π	0.85778	C 4 - C 5	π^*	0.14591	9.06	0.3	0.066
C2 - C7	σ	0.98381	N 1 - C 3	σ^*	0.03281	2.06	1.01	0.058
C2 - H17	σ	0.96105	C15 - H24	σ^*	0.03119	5.01	4.03	0.18
C3 - C4	σ	0.98571	C 2 - C 3	σ^*	0.01042	2.35	1.26	0.069
C4 - C5	σ	0.98675	C14 - H23	σ^*	0.00679	17.53	4.92	0.372
C4 - C5	π	0.87804	C 6 - C 7	π^*	0.22987	9.35	0.3	0.07
C4 - H18	σ	0.98766	C 5 - C 6	σ^*	0.01215	2	1.07	0.059
C5 - C6	σ	0.98507	C 6 - C 7	σ^*	0.0148	2.36	1.25	0.068
C5 - H19	σ	0.98903	C14 - H23	σ^*	0.00679	32.99	4.7	0.498
C6 - C7	σ	0.98332	C 5 - C 6	σ^*	0.01215	2.19	1.25	0.066
C6 - C7	π	0.80552	C 2 - C 3	π^*	0.21172	10.43	0.28	0.068
C6 - N16	σ	0.99386	C 6 - C 7	σ^*	0.0148	1.34	1.4	0.055
C7 - C8	σ	0.98839	C 2 - C 3	σ^*	0.01042	1.27	1.18	0.049
C8 - O9	σ	0.99733	C14 - H23	σ^*	0.00679	82.81	5.05	0.818
C8 - C10	σ	0.98959	C 8 - O 9	σ^*	0.00346	0.26	1.11	0.021
C8 - C10	σ	0.98959	C15 - H24	σ^*	0.03119	8.69	4.1	0.241
C10 - C11	σ	0.98823	N16 - H26	σ^*	0.01703	11.96	4.29	0.287
C10 - C11	π	0.81164	C14 - H23	σ^*	0.00679	20.98	4.43	0.425
C10 - C15	σ	0.98722	C10 - C11	σ^*	0.01064	1.92	1.26	0.062
C11 - C12	σ	0.98949	C 8 - C10	σ^*	0.0294	1.82	1.08	0.057
C11 - H20	σ	0.9893	C10 - C15	σ^*	0.01096	2.24	1.1	0.063
C12 - C13	σ	0.99046	C11 - C12	σ^*	0.00716	1.17	1.29	0.049
C12 - C13	π	0.81952	C10 - C11	π^*	0.18427	10.87	0.28	0.07
C12 - H21	σ	0.99067	C13 - C14	σ^*	0.00805	1.81	1.09	0.056
C13 - C14	σ	0.9902	C12 - H21	σ^*	0.00641	1.49	1.19	0.053
C13 - H22	σ	0.99079	C11 - C12	σ^*	0.00716	1.74	1.12	0.056
C14 - C15	σ	0.98862	C 8 - C10	σ^*	0.0294	1.75	1.08	0.055
C14 - C15	π	0.82502	C12 - C13	π^*	0.16421	9.99	0.29	0.068
C14 - H23	σ	0.99036	C10 - C15	σ^*	0.01096	2.19	1.11	0.062
C15 - H24	σ	0.96167	C 2 - H17	σ^*	0.03306	18.03	1.15	0.182
N16 - H25	σ	0.9948	C 6 - C 7	σ^*	0.0148	2.21	1.21	0.066
N16 - H26	σ	0.99441	C 5 - C 6	σ^*	0.01215	2.25	1.21	0.066
O27 - H28	σ	0.99482	N 1 - C 3	σ^*	0.03281	1.62	1.09	0.054
N1 - O27	σ	0.99694	N 1 - C 3	σ^*	0.03281	1.01	0.11	0.045
LP								
N1	σ	0.92513	C 2 - C 3	π^*	0.21172	10.52	0.36	0.083
O9	σ	0.98597	C 7 - C 8	σ^*	0.0286	1.3	1.09	0.048
N16	σ	0.87322	C 6 - C 7	π^*	0.22987	24.26	0.28	0.11
O27	σ	0.99259	N 1 - O29	σ^*	0.01192	0.96	1.03	0.04
O29	σ	0.99144	N 1 - C 3	σ^*	0.03281	2.44	1.11	0.066
E(2) means energy of hyper conjugative interaction (stabilization energy).								
Energy difference between donor and acceptor i and j NBO orbitals.								
F(i, j) is the Fock matrix element between i and j NBO orbitals.								

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 non-linear optics (NLO) (Gladis Anitha, 2015). The Prediction of molecular lies in the second-order polarizability or first-order hyperpolarizability (β_0), linear polarizability (α), anisotropic tensor ($\Delta\alpha$) 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,

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

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

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

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

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 0.75343 Debye. The highest value of dipole moment is observed at 0.64069 Debye for component μ_x . The polarizability, anisotropy polarizability and hyperpolarizability of 2A5NBP is calculated 3757.7358x10⁻³³esu, 434.9583x10⁻³³esu and 16501.6503x10⁻³³esu respectively (Table.5). In the NLO system, the hyperpolarizability β_0 value is the major part. The first hyperpolarizability of title molecule is approximately 48.07 times than those of urea (β_0 of urea is 343.272 x10⁻³³esu) (M Govindarajan, 2012).

Table.5. First order hyperpolarizability of the 2A5NBP

Parameters	B3LYP	Parameters	B3LYP
μ_x	0.64069	β_{xxx}	-169.5929883
μ_y	-0.3037912	β_{xxy}	-3.8281393
μ_z	-0.2719708	β_{xyy}	-32.2624677
μ	0.75343Debye	β_{yyy}	-15.360326
α_{xx}	259.0812777	β_{xxz}	624.1324525
α_{xy}	0.0743868	β_{xyz}	-7.9272673
α_{yy}	91.8836905	β_{yyz}	-1.3768551
α_{xz}	-17.3271338	β_{xzz}	-1371.667606
α_{yz}	1.7910498	β_{yzz}	-75.1883501
α_{zz}	251.9801953	β_{zzz}	455.89073
α_0	434.9583x10 ⁻³³ esu	β_0	16501.6503x10 ⁻³³ esu
α	3757.7358x10 ⁻³³ esu	β_0	1910.0679a.u

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 Molecular electrostatic potential (MEP). This is very passionate about the electrophilic and nucleophilic 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 (E Gladis Anitha, 2015). In this research paper, the electrostatic potential (ESP), total electron density (ED), counter map and MEP of 2A5NBP are drawn in Fig.3.4. 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 (V K Rastogi, 2007). 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 (V Arjunan, 2011).

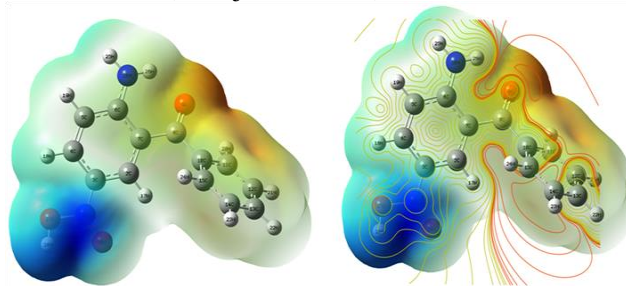


Figure.4. Electrostatic Potential map and Counter map of 2A5NBP

4. CONCLUSION

From the B3LYP methods by two basis sets, computed the geometrical parameters and optimized structure. The novel molecule has good electronic property which is found since the frontier molecular orbital and NBO analysis. From the predictions, the energy gap and intra-interactions charge transformation of the molecules had enhance values. The first hyperpolarizability of 2A5NBP is approximately 48.07 times than those of urea (β_0 of urea is 343.272×10^{-33} esu). The visual representation from MEP, MPA shows the charge distributions of the molecules and β_0 are tabulated for helping the future optical material researchers and innovative thinkers.

REFERENCES

- Adel El-Azab S, Jalaja K, Alaa Abdel-Aziz A.M, Abdulrahman Al-Obaid M, Sheena Mary Y, Yohannan Panicker C, Van Alsenoy C, Spectroscopic analysis (FT-IR, FT-Raman and NMR) and molecular docking study of ethyl 2-(4-oxo-3-phenethyl-3,4-dihydroquinazolin-2-ylthio)-acetate, *Journal of Molecular Structure*, 1119, 2016, 451-461.
- Al-Sehemi AG, Irfan A, Fouda AM, Synthesis, characterization and density functional theory investigations of the electronic, photophysical and charge transfer properties of donor-bridge-acceptor triaminopyrazolo [1, 5-a] pyrimidine dyes, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 111, 2013, 223-229.
- Anbarasan P M, Subramanian M K, Manimegala S, Suguna K, Ilangovan V, Sundaraganesan N, 4-Chlorotoluene: Spectral studies and quantum chemical calculations, *Journal of Chemical and Pharmaceutical Research*, 3 (3), 2011, 123-136.
- Arjunan V, Balamourougane P.S, Mythili C.V, Mohan S, Experimental spectroscopic (FTIR, FT-Raman, FT-NMR, UV-Visible) and DFT studies of 2-amino-5-chlorobenzoxazole, *Journal of Molecular Structure*, 1003, 2011, 92-102.
- Arjunan V, Balamourougane PS, Mythili C.V, Mohan S, Experimental spectroscopic (FTIR, FT-Raman, FT-NMR, UV-Visible) and DFT studies of 2-amino-5-chlorobenzoxazole, *Journal of Molecular Structure*, 1003, 2011, 92-102.
- Arockiasamy Ajaypraveenkumar R, Ganapathi Raman, Vibrational Frequencies, NBO Analysis, NLO Properties, UV-Visible and Homo-Lumo Analysis of 2-Chloro-3-Methoxybenzoxazole with Experimental (FT-IR and FT-Raman) Techniques and Quantum Mechanical Calculations, *Journal of Chemical and Pharmaceutical Sciences*, 1, 2017, 27-41.
- Arockiasamy Ajaypraveenkumar, Ganapathi Raman R, Sebastian S, Geometrical Structure, Vibrational Spectra, NLO, NBO, Electronic Transitions and Thermo dynamical Analysis of 5-Fluoro-2-Methylbenzoxazole by DFT Computational Method, *Recent Trends in Materials Science and Applications, SPPHY*, 189, 2017, 629-654.
- Frank Klinitas A, Pltman, Herbert mussen E R, Woodbury N L, Process For The Production of Benzoxazole, Application, Patented, 119, 1951, 571.
- Gladis Anitha E, Joseph Vedhagiri S, Parimala K, Conformational stability, vibrational spectra, NLO properties, NBO and thermodynamic analysis of 2-amino-5-bromo-6-methyl-4-pyrimidinol for dye sensitized solar cells by DFT methods, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 140, 2015, 544-562.
- Gladis Anitha E, Joseph Vedhagiri S, Parimala K, Spectroscopic (FT-IR, FT-Raman and UV-Visible) investigations, NMR chemical shielding anisotropy (CSA) parameters of 2,6-Diamino-4-chloropyrimidine for dye sensitized solar cells using density functional theory, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 136, 2015, 1557-1568.
- Govindarajan M, Karabacak M, Periandy S, Tanuja D, Spectroscopic (FT-IR, FT-Raman, UV and NMR) investigation and NLO, HOMO-LUMO, NBO analysis of organic 2,4,5-trichloroaniline, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 97, 2012, 231-245.
- Govindharaju R, Balasubramanian S, Rajasekar K, Ramachandramoorthy T, Preparation, Spectroscopic Characterization and Biological Activities of Co (II) and Ni (II) Complexes with 2-Aminobenzoxazole and Octanoate Ligands, *International Journal of Pharma Research & Review*, 3 (10), 2014, 8-13.
- Guntram Rauhut, Peter Pulay, Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields, *The Journal of Physical Chemistry*, 1995, 99, 3093-3100.
- James C, AmalRaj A, Reghunathan R, Hubert Joe I, JayaKumar V.S, Structural conformation and vibrational spectroscopic studies of 2, 6-bis (p-N, N-dimethyl benzylidene) cyclohexanone using density functional theory, *Journal of Raman Spectroscopy*, 37 (12), 2006, 1381-1392.

Lin-Vien D, Colthup N B, Fateley W G, Grasselli J G, The Handbook of Infrared and Raman Characteristics, Academic Press, New York, 1991.

Murugan M, Balachandran V, 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.

Muthu S, Isac Paulraj E, Spectroscopic investigation and molecular modeling studies on some pharmaceutical materials, Journal Chemical Pharmacy Research, 3 (5), 2011, 323-339.

Parr R R, Yang R G, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, USA, 1989.

Parr R G, Pearson R G, Absolute hardness, companion parameter to absolute electronegativity, The Journal of American Chemical Society, 105, 1983, 7512-7516.

Rastogi V.K, Palafox M.A, Singhal S, Ojha S.P, Kiefer W, Geometrical parameters, vibrational wavenumbers, and relationships established with six difluorobenzonitriles, International Journal of Quantum Chemistry, 107 (5), 2007, 1099.

Rauhut G, Pulay P, Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields, The Journal of Physical Chemistry, 99, 1995, 3093-3100.

Saleem H, Subashchandrabose S, Ramesh Babu N, Syed Ali Padusha M, Spectrochim. Acta Part A, Mol. Biomol. Spectrosc, (15) 00168-7, 2015, 1386-1425.

Saravanan R R, Seshadri S, Gunasekaran S, Mendoza-Merono R, Garcia-Granda S, Conformational analysis, X-ray crystallographic, FT-IR, FT-Raman, DFT, MEP and molecular docking studies on 1-(1-(3-methoxyphenyl)ethylidene) thiosemicarbazide, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 139, 2015, 321-328.

Shajikumar, Arockiasamy Ajaypraveenkumar and Ganapathi Raman R, Molecular Optimized Structure, NLO Applications Like Frequency Doubling and SHG, Fock Matrix of NBO Analysis, HOMO and LUMO Frontier Orbital Energies Analysis, Different Thermochemistry Properties of 4-Fluoro-3-Methylbenzonitrile Based on Quantum Chemical Calculations, Journal of Chemical and Pharmaceutical Sciences, 9 (4), 2016, 2063-2072.

Songyuan Dai, Jian Weng, Yifeng Sui, Shuanghong Chen, Shangfeng Xiao, Yang Huang, Fantai Kong, Xu Pan, Linhua Hu, Changneng Zhang, Kongjia Wang, The design and outdoor application of dye-sensitized solar cells, Inorganica Chimica Acta, 361, 2008, 786-791.

Sudha S, Sundaraganesan N, Kurt M, Cinar M, Karabacak M, FT-IR and FT-Raman spectra, vibrational assignments, NBO analysis and DFT calculations of 2-amino-4-chlorobenzonitrile, Journal of Molecular Structure, 985, 2011, 148-156.

Sundaraganesan N, Elango G, Sebastian S, Subramani P, Molecular structure, vibrational spectroscopic studies and analysis of 2-fluoro-5-methylbenzonitrile, Indian Journal of Pure and Applied Physics, 47, 2009, 481-490.

Tyagi O D, Yadav M, Textbook of Synthetic Drugs, fifth ed., Anmol Publications, New Delhi, 1990, 49.