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Electronic Structure, Optical Properties and Vibrational Analysis of Anilazine by First Principles

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ABSTRACT

Anilazine is a nonspecific fungicide, functioning as an alkylating agent. The triazine ring loses a chlorine atom, and then reacts rapidly with amino and thiol groups by nucleophilic substitution. The equilibrium geometry of Anilazine in the ground state have been determined and analyzed by Density functional theory (DFT) employing 6-311 G (d, p) as the basis set. The harmonic frequencies of Anilazine have also been calculated to understand its complete vibrational dynamics. The study of simulated spectra provides important information about the ability of the computational method to describe the vibrational modes. The molecular HOMO, LUMO composition, energy gap, and MESP contours have also been drawn to explain the activity of 5-amino-1, 3, 4-thiadiazol-2(3H)-one.

Keywords- Anilazine, Vibrational Analysis, Polarizability, Hyperpolarizability, Electronic properties

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INTRODUCTION

The triazines have planar six-membered benzene-like ring but with three carbons replaced by nitrogens. The three isomers of triazine are distinguished by the positions of their nitrogen atoms, and are referred to as 1, 2, 3-triazine, 1, 2, 4-triazine, and 1, 3, 5-triazine. Other aromatic nitrogen heterocycles are pyridines with one ring nitrogen atom, diazines with 2 nitrogen atoms in the ring and tetrazines with 4 ring nitrogen atoms. The best known triazines are derivatives of the 1,3,5-triazine derivatives melamine and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine). With three amino substituents melamine is a precursor to commercial resins. Another triazine extensively used in resins is benzoguanamine. Chlorine-substituted triazines are components of reactive dyes [1]. These compounds react through a chlorine group with hydroxyl groups present in cellulose fibres in nucleophilic substitution; the other triazine positions contain chromophores. Triazine compounds are often used as the basis for various herbicides. A series of 1, 2, 4-triazine derivatives known as bis-triazinyl bipyridines (BTPs) have been considered as possible extractants for use in the advanced nuclear reprocessing [2-4]. BTPs are molecules containing a pyridine ring bonded to two 1, 2, 4-triazin-3-yl groups. Triazine-based ligands have been used to bind three dinuclear arene ruthenium (or osmium) compounds to form metallaprisms [5]. 1, 3, 5-triazine, also called s-triazine, is an organic chemical compound with the formula $(HCN)_3$. It is a six-membered heterocyclicaromatic ring, one of several isomeric triazines. S-triazine and its derivatives are useful in a variety of applications. As a reagent in organic synthesis, s-triazine is used as the equivalent of hydrogen cyanide (HCN). Being a solid (vs a gas for HCN), triazine is sometimes easier to handle in the laboratory. One application is in the Gattermann reaction, used to attach the formyl group to aromatic substrates [6]. N- and C-substituted triazines are used industrially. The most common derivative of 1, 3, 5-triazine is 2,4,6-triamino-1,3,5-triazine, commonly known as melamine or cyanuramide. Another important derivative is 2,4, 6-trihydroxy-1,3,5-triazine better known ascyanuric acid. Trichloro-1,3,5-triazine (cyanuric chloride) is the starting point for the manufacture of many herbicides such

as Simazine and atrazine. Chlorinated triazines are the basis of an important family of reactive dyes, which are covalently attached to cellulosic materials [7]. Anilazine is a nonspecific fungicide, functioning as an alkylating agent. The triazine ring loses a chlorine atom, and then reacts rapidly with amino and thiol groups by nucleophilic substitution. The second chlorine atom on the triazine ring is equally reactive initially, but loses reactivity following the removal of the first chlorine. In this way it is conserved for a future reaction at a more specific site. High concentrations are required for fungicidal activity, presumably because the chemical must weaken the cell membrane of the fungus before it can have any critical effects on cell organelles. This compound was selected for testing because its use results in its distribution in the environment and in food products. It is structurally related to cyanuric acid, which was thought to be carcinogenic at the time anilazine was considered for testing. As an anilino compound, anilazine is related to the monocyclic aromatic amines, such as o-toluidine, which are also carcinogens [9, 10].

As a part of our ongoing research [11-18], the main objective of the present study is to investigate in detail the vibrational spectra of important biological molecule anilazine. To the best of our knowledge no detailed DFT calculations have been performed on anilazine so far in the literature.

MATERIALS AND METHODS

COMPUTATIONAL METHODS

Initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface. The gradient corrected Density Functional

Theory (DFT) with the three-parameter hybrid functional (B3) [19] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [20] has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, and energies of the optimized structures, using GAUSSIAN 09 and Spartan 14 software [21, 22]. The calculated vibrational frequencies have also been scaled by a factor of 0.963 [23]. By combining the results of the GAUSSVIEW'S program [24] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. We used this approach for the prediction of IR frequencies of title compound and found it to be very straightforward. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for anhormonicity. A number of studies [25, 26] have been carried out regarding calculations of vibrational spectra by using B3LYP methods with 6-311 G (d, p) basis set. The scaling factor (0.963) was applied successfully for B3LYP method and was found to be easily transferable in a number of molecules. Thus vibrational frequencies calculated by using the B3LYP functional with 6-311G (d, p) as basis set, can be utilized to eliminate the uncertainties in the fundamental assignment in the IR spectra.

RESULTS AND DISCUSSION

Optimization

Optimized parameters calculated by B3LYP method with 6-31G (d, p) as basis set are listed in Table 1 and are in accordance with the atom numbering scheme as shown in Figure 1. After geometry optimization local minimum energy obtained for structure optimization with 6-31G (d, p) basis set is approximately -1945.5906 a.u. The (C-C) bond length varies between 1.392Å-1.4107 Å, while (C-H) bond length is 1.054Å-1.0849 Å, whereas (C-N) bond length is 1.3148 Å -2.2385 Å. The (C-Cl) bond length is 1.7429-1.765 Å, while (N-H) bond length is 1.0136-2.2385. The (C-C-C) bond angle varies between 119.4156-121.6256, while (C-C-H) bond angle varies between118.824-121.1115 degree. The (C-C-N) bond angle varies from 112.2517 to 132.0903 degree, while (C-N-N) bond angle is 114.2794-127.9328 The (N-C-Cl) bond angle varies 115.7392-116.6136 degree, while (C-C-Cl) bond angle varies from 118.3806 to 119.9938 degree.

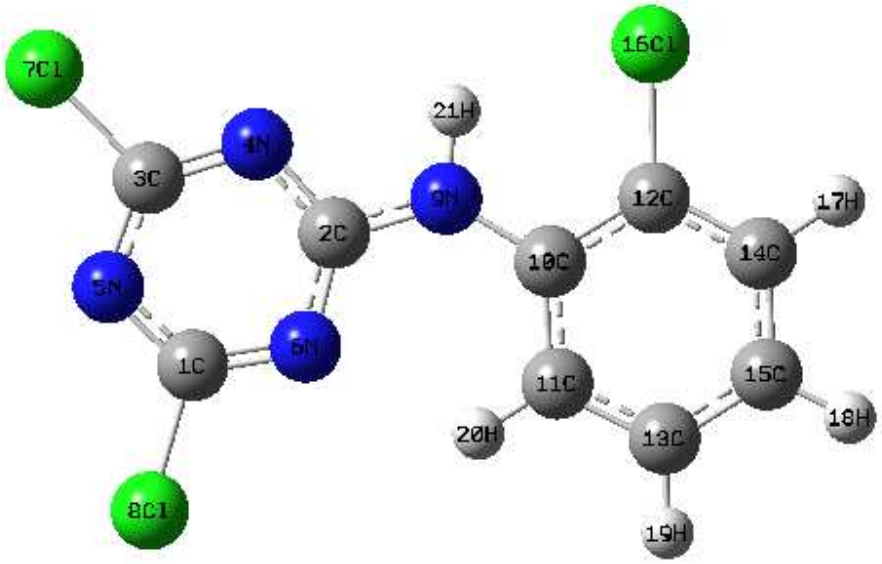

Fig.1-Model molecular of Anilazine

TABLE-1 Bond Length (Å) and Bond Angle of Crystal structure of anilazine

S.NO.	PARAMETER	EXPERIMENTAL VALUE	CALCULATED VALUE
		"Bond length"	
1	C_1-N_5	1.319	1.3278
2	C_1-N_6	1.320	1.3228
3	C_1-Cl_8	1.722	1.7442
4	C_2-N_4	1.348	1.3575
5	C_2-N_6	1.340	1.3469
6	C_2-N_9	1.351	1.3554
7	C_3-N_4	1.311	1.3148
8	C_3-N_5	1.332	1.337
9	C_3-Cl_7	1.724	1.7429
10	N_6-H_{20}	0.9500	2.2385
11	N_9-C_{10}	1.407	1.4048
12	N_9-H_{21}	0.8800	1.0136
13	C_{10}-C_{11}	1.389	1.4046
14	C_{10}-C_{12}	1.399	1.4107
15	C_{11}-C_{13}	1.394	1.3927
16	C_{11}-H_{20}	0.9500	1.0801
17	C_{12}-C_{14}	1.382	1.392
18	C_{12}-Cl_{16}	1.735	1.765
19	C_{13}-C_{15}	1.375	1.3938
20	C_{13}-H_{19}	0.9500	1.0854
21	C_{14}-C_{15}	1.383	1.3937
22	C_{14}-H_{17}	0.9500	1.0841
23	C_{15}-H_{18}	0.9500	1.0849
		Bond angle	
24	N_5-C_1-N_6	129.10	127.9328
25	N_5-C_1-Cl_8	115.58	116.0028
26	N_6-C_1-Cl_8	115.32	116.0645
27	N_4-C_2-N_6	125.21	124.4356
28	N_4-C_2-N_9	114.35	114.2794
29	N_6-C_2-N_9	120.43	121.285
30	N_4-C_3-N_5	128.42	127.6472
31	N_4-C_3-Cl_7	116.36	116.6136
32	N_5-C_3-Cl_7	115.21	115.7392

33	C_2-N_4-C_3	113.30	113.9482
34	C_1-N_5-C_3	111.18	112.2517
35	C_1-N_6-C_2	112.78	113.7846
36	C_2-N_9-C_{10}	131.55	132.0903
37	C_2-N_9-H_{21}	114.2	112.4044
38	C_{10}-N_9-H_{21}	114.2	115.5053
39	N_9-C_{10}-C_{11}	124.50	124.3078
40	C_{11}-C_{10}-C_{12}	117.95	117.8532
41	N_9-C_{10}-C_{12}	117.55	117.839
42	C_{10}-C_{11}-C_{13}	120.3	120.3639
43	C_{10}-C_{11}-H_{20}	119.8	118.845
44	C_{13}-C_{11}-H_{20}	119.7	120.7911
45	C_{10}-C_{12}-C_{14}	121.7	121.6256
46	C_{10}-C_{12}-Cl_{16}	119.51	119.9938
47	C_{14}-C_{12}-Cl_{16}	118.75	118.3806
48	C_{11}-C_{13}-C_{15}	120.6	121.0246
49	C_{11}-C_{13}-H_{19}	119.8	118.824
50	C_{15}-C_{13}-H_{19}	119.7	120.1514
51	C_{12}-C_{14}-C_{15}	119.3	119.7314
52	C_{12}-C_{14}-H_{17}	120.3	119.1571
53	C_{15}-C_{14}-H_{17}	120.3	121.1115
54	C_{13}-C_{15}-C_{14}	120.1	119.4156
55	C_{13}-C_{15}-H_{18}	120.0	120.789
56	C_{14}-C_{15}-H_{18}	120.0	119.7955

Atomic charge, Polarizability, Hyper polarizability and Thermodynamic Properties:
The Mullikan atomic charges for all atoms of the anilazine compound are calculated by B3LYP, methods with 6-31G (d, p) as basis set in gas phase and are presented in Table (2).

Dipole moment (μ), polarizability <α> and total first static hyper polarizability β [27, 28] are also calculated (In Table 2 and 3) by using density functional theory. They can be expressed in terms of *x*, *y*, *z* components and are given by following equations 1, 2 and 3-

$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1\backslash 2}$ ---------- (1)

$<\alpha> = 1\backslash 3\,[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$ ---------- (2)

$\beta_{Total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1\backslash 2} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1\backslash 2}$ --- (3)

The β components of Gaussian output are reported in atomic units.

Where (1 a.u. = $8.3693X10^{-33}$ e.s.u.). For Anilazine, the calculated dipole moment value is 4.2863Debye. Having higher dipole moment than water (2.16 Debye), Anilazine can be used as better solvent. As we see a greater contribution of α_{zz} in molecule which shows that molecule is elongated more towards Z direction and more contracted to Y direction. $\beta_{xxx,}$ β_{xzz} contribute larger part of hyper polarizibity in the molecule. This shows that X axis plane and XZ plane are more optical active in these directions.

Several calculated thermodynamic properties based on the vibration analysis at B3LYP, 6-31G (d, p) level, like internal thermal energy (E), constant volume heat capacity CV, and entropy S, have been calculated and listed in table (4). At the room temperature, conduction band is almost empty so electronic contribution in total energy is negligible. Thermodynamic parameters clearly indicate that vibration motion plays a crucial role in assessing thermo dynamical behavior of title compounds. The calculated dipole moments at B3LYP/6-31G (d, p) level for anilazine.

TABLE-2 Mulliken Atomic Charges of Crystal structure of anilazine

S.NO.	ATOMS	ATOMIC CHARGES
1	C	0.262313
2	C	0.679957
3	C	0.257375
4	N	-0.442115
5	N	-0.373972
6	N	-0.445673
7	Cl	0.063276
8	Cl	0.059938
9	N	-0.375479
10	C	0.347255
11	C	0.068437
12	C	-0.164582
13	C	0.001050
14	C	0.041764
15	C	0.023441
16	Cl	-0.002987
17	H	0.000000
18	H	0.000000
19	H	0.000000
20	H	0.000000
21	H	0.000000

TABLE-3 Polarizibility and Hyper Polarizibility of Crystal structure of anilazine

S.NO.	**PARAMETER**	**POLARIZIBILITY**
1.	α_{XX}	-109.1706
2.	α_{YY}	-108.9265
3.	α_{ZZ}	-111.3698
4.	α_{XY}	4.8454
5.	α_{XZ}	-0.0008
6.	α_{YZ}	0.0021
α		**109.8223**
S.NO.	**PARAMETER**	**HYPER POLARIZIBILITY**
1.	β_{XXX}	81.2062
2.	β_{YYY}	7.9008
3.	β_{ZZZ}	-0.0058
4.	β_{XYY}	4.0502
5.	β_{XXY}	12.0652
6.	β_{XXZ}	-0.0060
7.	β_{XZZ}	-18.1361
8.	β_{YZZ}	-5.2504
9.	β_{YYZ}	0.0033
10.	β_{XYZ}	0.0013
β		**57.9038**

TABLE-4 Thermodynamic Properties of Crystal structure of anilazine

PARAMETER	**E (Thermal) Kcal/Mol**	**CV Cal/Mol-Kelvin**	**S Cal/Mol-Kelvin**
Total	92.834	49.004	119.578
Translational	0.889	2.981	42.722
Rotational	0.889	2.981	34.058
Vibrational	91.057	43.043	42.798

Electronic properties

The interaction with other species in a chemical system is also determined by frontier orbital's, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gape helps to distinguish the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gape is more polarized having reactive part as far as reaction is concerted [29]. The frontier orbital gape in case of the given molecule is 3.83 eV for anilazine given in Table 5.

The contour plots of the HOMO, LUMO and MESP structures of the molecule are shown in Figure 2. The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive,

negative, and neutral electrostatic potential region in terms of grading and is very useful in the investigation of molecular structure with its physiochemical property relationship [30, 31].

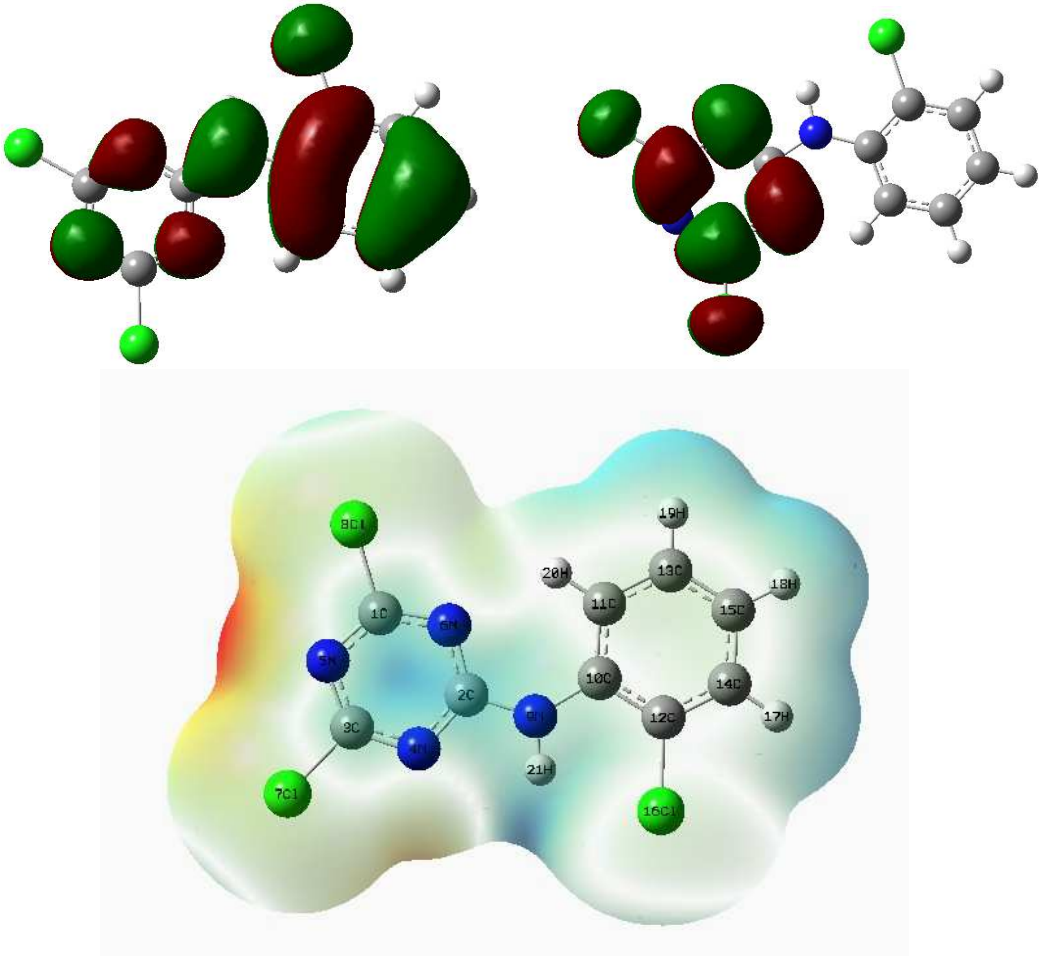

Figure 2. HOMO (Left) - LUMO (Right) and MESP (Below) pictures of anilazine

TABLE-5 Total energy, Dipole Moment, Homo, Lumo and Energy gap of anilazine

PARAMETERS	VALUE
Total Energy E (a.u.)	-1945.59061568
Dipole moment (Debye)	3.6698
Lumo	-0.07525
Homo	-0.21635
Frontier orbital Energy Gap (eV)	-0.1411 a.u (-3.83792 ev)

Assignment of fundamentals

Anilazine has 21 atoms 57 normal modes of vibration. We made a reliable one-to-one correspondence between the fundamentals and the frequencies calculated by DFT (B3LYP). The relative bands intensities are also very satisfactory along with their positions. Some important modes are discussed hereafter. The harmonic- vibration frequencies, calculated for the title molecule are listed in Table 6.

Vibrational modes description

Spectral region above 2800 cm^{-1}: C-H stretching vibrations are generally observed in the region 2800 cm^{-1} to 3200 cm^{-1}. Accordingly, in the present study for Anilazine, the C-H stretching vibrations are calculated at and 3070, 3083, 3095, 3136 and 3438 cm^{-1}, respectively having appropriate IR intensity.

Spectral region from 1000 cm^{-1} to 2300 cm^{-1}: In the present study, C-H and C-C wagging vibrations are observed at 1146, 1114, 1036 cm^{-1}. In plane bending Vibration (β) are observed in the region 1448,1430,1267,1012, 989 cm^{-1} and 388 cm^{-1}. Between the region 1000- 2300 cm^{-1} we have observed wave numbers 1533,1502,1305,1234, 1179 cm^{-1} and 944 cm^{-1} due to the whole ring deformation.

Spectral region below 1000 cm^{-1}: Ring Torsion is shown in the region 741 cm^{-1}, while Twisting in benzene ring is shown at 374 cm^{-1}. Ring Breathing vibrations are observed in the region 667 cm^{-1} and also out of plane banding (C-C-H) is observed at 958, 919 and 848 cm^{-1}.

TABLE-6 Calculated Wave Numbers and its respective I.R. Intensity Crystal structure of anilazine

S.NO.	FREQUENCY	I.R. INTENCITY	VIBRATIONAL ASSINGMENT
	19	0.4958	Whole molecule bend from middle
	45	0.0003	Whole molecule bend from middle
	78	0.5668	Whole molecule bend from middle
	131	0.0644	γ(C-C-C)
	148	0.0003	γ(N-C-N)
	154	0.4	Whole molecule bend from middle
	167	0.4644	γ(N-C-N)
	193	0.0064	Out of plane bending in whole ring
	196	2.4426	τ(C-N-C-Cl)
	245	1.4195	Whole molecule bend from middle
	285	0.5942	γ(C-C-C) in ring
	374	3.1314	Twist in benzene ring
	388	5.4323	β(C-C-C) in benzene ring
	415	3.8058	τ(C-N-C-Cl)
	433	3.1446	γ(C-C-C)
	448	2.4069	τ(C-N-C-Cl)
	468	4.1656	τ(C-N-C-Cl)
	527	0.7388	γ(C-C-C)
	594	25.3004	τ in benzene ring
	624	1.8899	γ(C-N-C)
	647	37.0743	$\omega(N_9\text{-}H_{21})$
	667	33.6217	Breathing in benzene ring
	682	17.9077	$\omega(N_9\text{-}H_{21})$
	693	2.1165	γ(C-C-C)
	708	0.0749	τ(C-C-C-C)+τ(C-N-C-N)
	741	48.0791	τ(C-C-H)
	780	41.0769	γ(C-N-C)
	803	68.4194	τ in whole molecule
	848	120.4787	τ in(C-N-C-N)
	848	16.0957	γ(C-C-H) in ring
	919	2.8617	γ(C-C-H) in ring
	944	5.0059	Ring deformation
	958	0.4663	γ(C-C-H) in ring
	989	62.7044	β(C-C-C) in Benzene ring
	1012	70.4665	β(C-C-C) in Benzene ring
	1036	23.533	$\omega(C_{15}\text{-}H_{18})+\omega(C_{14}\text{-}H_{17})+\omega(C_{13}\text{-}H_{19})+\omega(C_{11}\text{-}H_{20})$
	1114	0.9543	$\omega(C_{15}\text{-}H_{18})+\omega(C_{14}\text{-}H_{17})+\omega(C_{13}\text{-}H_{19})+\omega(C_{11}\text{-}H_{20})$
	1146	0.3555	$\omega(C_{15}\text{-}H_{18})+\omega(C_{14}\text{-}H_{17})+\omega(C_{13}\text{-}H_{19})+\omega(C_{11}\text{-}H_{20})$
	1179	52.1487	Ring deformation
	1208	262.971	$\beta(N_4\text{-}C_3\text{-}N_5)$
	1234	223.8301	Ring deformation
	1267	35.0567	β(C-C-H) in whole Benzene ring
	1277	7.1317	Ring deformation in Benzene ring
	1305	163.3011	Ring deformation
	1370	303.8021	$\beta(C_2\text{-}N_9\text{-}H_{21})$
	1430	90.7715	β(C-C-H) In Benzene ring
	1448	40.057	β(C-C-H) In Benzene ring
	1502	219.6283	Ring deformation
	1533	1472.065	Ring deformation
	1545	332.1038	ν(C-C) in Benzene ring
	1577	331.3886	ν(C-C) in Benzene ring
	1589	97.3424	ν(C-C) in Benzene ring
	3070	1.9517	$\nu(C_{13}\text{-}H_{19})+\nu(C_{15}\text{-}H_{18})$

	3083	9.976	$\nu(C_{14}\text{-}H_{17})+\nu(C_{15}\text{-}H_{18})+\nu(C_{13}\text{-}H_{19})$
	3095	6.149	$\nu(C_{14}\text{-}H_{17})+\nu(C_{15}\text{-}H_{18})$
	3136	12.5687	$\nu(C_{11}\text{-}H_{20})$
	3438	101.208	$\nu(N_9\text{-}H_{21})$

Abbreviations: ν: Stretching; β: -in plane bending; γ: out of plane bending, τ: torsion, Ꞷ: wagging, S: scissoring

CONCLUSION

Quantum chemical study, which involves full geometry optimization, entropy, total energy and vibration frequency calculation, for this molecule has been carried out. All these studies are based on certain assumptions and as such have their own limitations. The experimental data, which have been used, also have their dependability within certain limits. These are briefly discussed as follows. All frequencies are real in the molecule. Hence the compound is stable. The equilibrium geometry and harmonic frequencies of anilazine were determined and analyzed at DFT level of theory using 6-311G (d, p) as the basis set. The vibrational frequency calculation proved that both structures are stable (no imaginary frequency). Normal modes analysis provides detailed description of vibrational dynamics of the molecules in question. The detailed vibrational assignments have been done theoretically. So this study has an importance for experimental researchers who are interested in the FTIR spectra of this compound.

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REFERENCES

[1] Horst Tappe, Walter Helmling, Peter Mischke, Karl Rebsamen, Uwe Reiher, Werner Russ, Ludwig Schläfer and Petra Vermehren "Reactive Dyes"in Ullmann's Encyclopedia of Industrial Chemistry **2000**, Wiley-VCH, Weinheim.
[2]Geist, Andreas; Michael Weigl; Udo Müllich; Klaus Gompper (**2000**). "ACTINIDE (III) LANTHANIDE (III) PARTITIONING USING n-Pr-BTP AS EXTRACTANT: EXTRACTION KINETICS AND EXTRACTION TEST IN A HOLLOW FIBER MODULE". 6th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation: 641–647. Retrieved 30 April2013
[3]Hill, C.; D. Guillaneux, X. Hérès, N. Boubals and L. Ramain. "SANEX-BTP PROCESS DEVELOPMENT STUDIES". Retrieved 30 April **2013**.
[4]Development Of Electrochemical Separations Of Uranium And Re Elements From Fluoride Melts, https://www.oecd-nea.org/pt/docs/iem/jeju02/session2/SessionII-15.pdf.
[5] Hudson, Michael J.; Michael G. B. Drew; Mark R. StJ. Foreman; Clément Hill; Nathalie Huet; Charles Madic; Tristan G. A. Youngs (**2003**). *Dalton Transactions* (9): 1675–1685. doi :10.1039/B301178J. Retrieved 30 April **2013**.
[6] Roswitha M. Böhme, Qun Dang "1, 3, 5-Triazine" in Encyclopedia of Reagents for Organic Synthesis **2008** John Wiley & Sons. doi:10.1002/047084289X.rt158.pub2
[7] Horst Tappe, Walter Helmling, Peter Mischke, Karl Rebsamen, Uwe Reiher, Werner Russ, Ludwig Schläfer and Petra Vermehren "Reactive Dyes"in Ullmann's Encyclopedia of Industrial Chemistry **2000**, Wiley-VCH, Weinheim. doi:10.1002/14356007.a22_651
[9] Anilazine, http://en.wikipedia.org/wiki/Anilazine, **2015**.
[10] BIOASSAY OF ANILAZINE FOR POSSIBLE CARCINOGENICITY, National Cancer Institute carcinogenesis technical, u.s department of health, education and welfare public healt service national institutes of health report series no 104, **1978**.
[11] Vibrational spectra, HOMO, LUMO, MESO surfaces and reactivity descriptors of amylamine and its isomers, a DFT study, Apoorva Dwivedi, Ambrish Srivastava, Abhishek Bajpai, *spectrochimica acta part A: molecular and biomoleculat spectroscopy*, 149, (**2015**), 343-351.
[12] Comparative Study of Vibrational spectra of two well known natural products Lupeol and Lupenone Using Density Functional Theory, Apoorva Dwivedi, Anoop kumar pandey, Neeraj misra, *Spectroscopy: An International Journa*l Volume 27 (**2012**), Issue 3, Pages 155–166 doi:10.1155/2012/486304.
[13] Apoorva Dwivedi, Anoop Kumar Pandey, Neeraj Misra., *Spectroscopy: An International Journal* 26 (**2011**) 367–385.
[14] "Quantum chemical study of Etodolac (Lodine)" Apoorva Dwivedi and Neeraj Misra, *Der Pharma Chemica*, **2010**, 2(2): 58-65. [ISSN 0975-413X].

[15] Neeraj Misra, Apoorva Dwivedi, Anoop Kumar Pandey, Sanjeev Trivedi, *Der Pharma Chemica,* **2011**, 3(3):427-448.
[16] Anoop Kumar Pandey, Apoorva Dwivedi, Neeraj misra, *Spectroscopy*, Volume 2013 (**2013**), Article ID 937915, 11 pages.
[17] A Bajpai, AK Pandey, K Pandey, A Dwivedi, *Journal of Computational Methods in Molecular Design* 4 (1), 64-69.
[18] Saurabh Pandey, Apoorva Dwivedi, Ambrish K. Srivastava, Neeraj Misra, Balladka K. Sarojini , Billava J. Mohan and Badiadka Narayana, *Der Pharma Chemica*, **2014**, 6(5):70-79.
[19] A.D. Becke, *J. Chem. Phys*, **1993**, 98, 5648.
[20] C. Lee, W. Yang, R.G. Parr, *Phys. Rev*. **1988**, B 37, 785.
[21] Frisch, M. J. et al Gaussian 09; Gaussian, Inc., Pittsburgh, PA, **2009**.
[22] https://www.wavefun.com/products/windows/Spartan14/win_spartan.html, Spartan 14 software, **2014**.
[23] P.L.Fast, J.Corchado, M.L.Sanches, D.G.Truhlar, *J.Phys.Chem A.* **1999**, 103, 3139.s
[24] A.Frisch, A.B.Nelson, AJ.Holder, Gauss view, Inc.Pittsburgh PA, **2000**.
[25] Shamoon Ahmad Siddiqui, Apoorva Dwivedi, Neeraj Misra, N. Sundaraganesan, *Journal of Molecular Structure: THEOCHEM* 847 (**2007**) 101-102.
[26] Shamoon Ahmad Siddiqui, Apoorva Dwivedi, P. K. Singh, Tanveer Hasan, Sudha Jain, N. Sundaraganesan, H. Saleem, Neeraj Misra, *Journal of Theoretical and Computational Chemistry* Vol. 8, No. 3 (**2009**) 433–450.
[27] Parr R. G. and Yang W., Density-Functional Theory of Atom und Molecules, Oxford University Press, Oxford, (**1989**).
[28] Becke A. D., *J. Chem. Phys*., (**1993**), 98, 1372.
[29] I. Fleming, frontier Orbitals and Organic Chemical Reactions, John Wiley & Sons, New York, NY, USA, **1976**.
[30] J. S. Murray and K. Sen, Molecular Electrostatic Potential, Concepts and Applications, Elsevier, Amsterdam, The Netherlands, **1996**.
[31] J. Sponer and P. Hobza, *International Journal of Quantum Chemistry*, vol. 57, no. 5, pp. 959-970, **1996**.