Vibrational Spectroscopic Study and NBO Analysis On 2-Chloro-4, 6-Diamino-1,3,5-Triazine Using DFT Method

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Abstract

In this work, we report a combined experimental and theoretical study on molecular structure, vibrational spectra, NBO analysis of 2-chloro-4,6-diamino-1,3,5-triazine(CDAT). The FT-Raman and FT-IR spectra of CDAT were recorded in the solidphase. The molecular geometry, harmonic vibrational frequencies and bonding features of CDAT in the ground state have been calculated by using density functional method (B3LYP) with standard 6-311++G** basis set. Stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. All the normal modes of vibrations are assigned and calculations of total energy distribution (TED) are also performed.

Keywords: 2-chloro-4,6-diamino-1,3,5-triazine, FT-IR and FT-Raman spectroscopy, NBO, DFT calculations, Thermodynamic functions, Total energy distribution

Introduction

Triazine and its derivatives are known for their biological and pharmaceutical importance. Triazines are also useful as chromophore groups in colorants and Chlorine attached in Triazine compounds undergo nucleophilic substitution reactions well with with hydroxyl groups in cellulose fibres. Some triazine family compounds are used in pharmaceutical industry as coupling agent for the synthesis of peptide in solid phase as well as solution and as side chain of antibiotics. Triazine compounds are used in formulating bactericide and fungicide. They are used as preservatives in oil field applications. They are used as disinfectant, industrial deodorant and biocide in water treatment. They are used as bleaching agents[1] .

Literature survey reveals that to the best of our knowledge, the results based on quantum chemical calculations and FT-IR,FT-Raman spectral studies and NBO analysis on 2-chloro-4,6-diamino-1,3,5-triazine (CDAT) have no reports. Herein, we reported detailed interpretations of the infrared and Raman spectra based on the experimental and theoretical results, which are acceptable and supportable to each other.

In the present work, we have attempted to study the thermo dynamical functions and bonding nature of CDAT by using B3LYP level of theory throughout with the 6-311++G** basis set implemented in the Gaussian 09 program suite[2]. Geometries obtained from DFT calculation were then used to perform NBO analysis.

Methodology

Experimental and Theoretical Methods

The compound CDAT was obtained from Sigma-Aldrich chemical company USA, with a stated purity of 99% and it was used as such without further purification. The FT-Raman spectrum of CDAT was recorded using 1064nm line of Nd:YAG laser as excitation wavelength in the region 3500-100cm^{-1} on thermo electron corporation model Nexus 670 spectrometer equipped with FT-Raman module accessory. The FT-IR spectrum of the titled compound was recorded in the region 400-4000cm^{-1} on Perkin Elmer Spectrophotometer in KBr pellet. The spectrum was recorded at room temperature with a scanning speed of 30cm^{-1}min^{-1} and the spectral width of 2.0cm^{-1}.

Computational Method

Quantum chemical calculations were used for CDAT to carry out the optimized geometry and vibrational wavenumbers with the 2009 version of the Gaussian suite of program [2] using the Becke-3-Lee-Yang-Parr(B3LYP) functional [3,4] supplemented with standard 6-311++G** basis set. The vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program[5]. The analysis for the vibrational modes of CDAT is presented in some detail in order to better describe the basis for the assignments. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the lack of imaginary values with

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wavenumber calculations. The Cartesian representation of the theoretical force constant has been computed at the fully optimized geometry by assuming the molecule belongs to C_s point group symmetry. The transformation force field from Cartesian to internal local symmetry coordinates, the scaling the subsequent normal coordinate analysis (NCA), calculation of total energy distribution (TED) were done on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius [6,7].

A detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 42 standard internal coordinates containing 9 redundancies were defined as given in Table 1. From these, a non-redundant set of local symmetry coordinates was construed by suitable linear combinations of internal coordinates following the recommendation of Pulay *et al* [8] and they are presented in Table 2. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

Table 1. Internal coordinates of 2-chloro-4, 6-diamino-1, 3, 5-triazine.

No(i)	Symbol	Type	Definition
Stretching			
1-6	r_i	C-N(Aromatic)	C2-N1, C2-N3, C4-N3, C4-N5, C6-N5, C6-N1
7-8	r_i	C-N(Amino)	C4-N8, C6-N11
9-12	P_i	N-H	N8-H9, N8-H10, N11-H12, N11-H13
13	Q_i	C-Cl	C2-Cl7
In-plane bending			
14-19	α_i	Ring	N1-C2-N3, C2-N3-C4, N3-C4-N5, C4-N5-C6, N5-C6-N1, C6-N1-C2
20-21	δ_i	NCCl	N1-C2-Cl7, N3-C2-Cl7
22-25	β_i	NCN	N3-C4-N8, N5-C4-N8, N5-C6-N11, N1-C6-N11
26-29	π_i	CNH	C4-N8-H9, C4-N8-H10, C6-N11-H12, C6-N11-H13
30-31	π_i	HNH	H9-N8-H10, H12-N11-H13
Out-plane bending			
32	ω_i	NCl	Cl7-C2-N1-N3
33-34	ω_i	NC	N8-C4-N3-N5, N11-C6-N5-N1
35-36	ω_i	NH	C4-N8-H9-H10, C6-N11-H12-H13
Torsion			
37-42	τ_i	τRing	N1-C2-N3-C4, C2-N3-C4-N5, N3-C4-N5-C6, C4-N5-C6-N1, N5-C6-N1-C2, C6-N1-C2-N3

Table 2. Symmetry coordinates of 2-chloro-4, 6-diamino-1, 3, 5-triazine.

No	Symbol[a]	Definition[b]
1-6	C-N(Aromatic)	r1, r2, r3, r4, r5, r6
7-8	C-N(Amino)	r7, r8
9-10	$(NH_2)_{SS}$	$(P9+P10)/\sqrt{2}$, $P11+P12)/\sqrt{2}$
11-12	$(NH_2)_{asym}$	$(P9-P10)/\sqrt{2}$, $(P11-P12)/\sqrt{2}$
13	C-Cl	Q13
14	R1trigd	$(\alpha14-\alpha15+\alpha16-\alpha17+\alpha18-\alpha19)/\sqrt{6}$
15	R1sym	$(-\alpha14-\alpha15+2\alpha16-\alpha17-\alpha18+2\alpha19)/\sqrt{12}$
16	R1asym	$(\alpha14-\alpha15+\alpha17-\alpha18)/\sqrt{2}$
17	NCCl	$(\delta20-\delta21)/\sqrt{2}$
18-19	NCN	$(\beta22-\beta23)/\sqrt{2}$, $(\beta24-\beta25)/\sqrt{2}$
20-21	$NH_{2\ rock}$	$(\pi26-\pi27)/\sqrt{2}$, $(\pi28-\pi29)/\sqrt{2}$
22-23	$NH_{2\ twist}$	$(\pi26+\pi27)/\sqrt{2}$, $(\pi28+\pi29)/\sqrt{2}$
24-25	$NH_{2\ scissor}$	$(2\pi30-\pi26-\pi27)/\sqrt{6}$, $(2\pi31-\pi28-\pi29)/\sqrt{6}$
26	NCl	$\omega32$
27-28	NCN	$\omega33$, $\omega34$
29-30	$NH_{2\ Wagg}$	$\omega35$, $\omega36$
31-33	τRing	$(\tau37-\tau38-\tau39-\tau40-\tau41-\tau42)/\sqrt{6}$, $(\tau37-\tau39-\tau40-\tau41)/\sqrt{12}$, $(-\tau37+2\tau38-\tau39-\tau40+2\tau41-\tau42)/2$

[a]These symbols are used for description of the normal modes by TED in Table 4, [b]The internal coordinates used here are defined in Table 1

Natural bond orbital analysis was also performed by the Gaussian suite of program at the B3LYP level of theory analysis transforms the canonical delocalized Hartee Fock (HF) *MOs* into localized orbital's that are closely tied to chemical bonding concepts. This process involves sequential transformation of non orthogonal atomic orbital's (*AOs*) to the sets of natural atomic orbital's (*NAOs*), natural hybrid orbital's (*NHOs*) and NBOs. Natural bond orbital analysis gives the accurate possible natural Lewis structure picture of orbital because all orbital are mathematically chosen to include the highest possible percentage of the electron density. Interaction between both filled and virtual orbital spaces information correctly explained by the NBO analysis, it could enhance the analysis of intra- and inter-molecular interactions. The interaction between filled and antibonding orbital's represent the deviation of the molecule from the Lewis structure and can be used as the measure of delocalization. This noncovalent bonding–antibonding interaction can be quantitatively described in terms of the second order perturbation interaction energy ($E^{(2)}$)[9-12]. This energy represents the estimate of the off-diagonal NBO Fock Matrix elements. It can be deduced from the second – order perturbation approach [13];

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{(i,j)}^2}{\varepsilon_j - \varepsilon_i} \text{-------------- (2)}$$

Where q_i is the ith donor orbital occupancy, $\varepsilon_j, \varepsilon_i$ the diagonal elements (orbital energies) and F (j,i) the off diagonal NBO Fock Matrix element.

Result and Discussion
Geometric structure

The molecular structure of CDAT having C_S point group symmetry. The most optimized geometry is performed at B3LYP/6-311++G** basis set of CDAT molecule with atoms numbering are shown in Fig1. The optimized bond lengths and bond angles of the title compound which are calculated using DFT (B3LYP) method with 6-311++G** basis set is shown in Table 3. From Table 3 it is found that C2-Cl7 bond length is very high and its corresponding value is 1.7547A°. This is clearly indicates that C2-Cl7 occupy the low energy value. The next higher bond length value is 1.3529A°. This value is found at N1–C6, N3–C4, respectively. For the title compound the C–N group bond length is found at the range 1.31-1.33 A° (i.e.N1–C2, C2–N3, C4–N5, N5–C6 are 1.3175, 1.3175, 1.3379, 1.3378A°, respectively). It shows that the C–N bond occupies higher energy level as compare to C–Cl bond. The

least bond length value is 1.0053A° and it is found at amino group (i.e. N8–H10, N11–H13). These bond length values clearly indicate that this amino group occupies the higher energy level as compare to C–Cl and C–N groups.

For the title compound, the higher bond angles are found at N1–C2–N3, N3–C4–N5, N1–C6–N11, H9-N8-H10, H12-N11-H13 and their corresponding values are 128.49°, 125.50°, 125.50°, 121.01 ° and 121.01 °, respectively. The N3–C2–Cl7 and N1–C2–Cl7 bond angles are found at 115.76° .The least bond angle value is 113.10° and it is found at C2–N1–C6, C2–N3–C4, group. These are listed in Table 3.

Vibrational assignments

The vibrational assignments in the present work are carried out based on the calculated frequencies, infrared intensities, Raman activities as well as characteristic group frequencies. The 33 normal modes of CDAT are distributed among the symmetry species as √3N– 6 =23A'(in-plane) + 10A" (out-of-plane). The detailed vibrational assignments of fundamental modes of CDAT along with observed and calculated frequencies, IR intensity and Raman scattering activities and normal mode descriptions have been reported in Table 4. The observed experimental FT-IR and FT-Raman spectra and theoretically predicted IR and Raman spectra at DFT and B3LYP levels are shown in Figs 2 and 3, respectively. It is convenient to discuss the vibrational spectra of CDAT in terms of characteristic spectral region as describe below.

The NH_2 group gives rise to the six internal modes of vibrations such as; the symmetric stretching, the anti-symmetric stretching, the symmetric deformation or the scissoring, the rocking, the wagging and torsional mode. The frequency of asymmetric stretching vibration is higher than that of symmetric one. If the two N–H bonds of the NH_2 group symmetric, these modes satisfy an empirical relation as suggested by Bellamy and Williams[14] as,

ν_{sy} =345.5+0.876 ν_{asy}

Where ν_{sy} and ν_{asy} represents as symmetric and asymmetric wavenumbers.

In our title molecule CDAT the –NH_2 symmetric and asymmetric stretching modes are observed in the range at 3505-3205cm^{-1} (modes no's 1 - 4) in FT-IR spectra. The computed values are found in the range at 3754-3617cm^{-1}.The computed an harmonic frequencies for CDAT are shows very good agreement with recorded spectral-data.

Table 3. Optimized geometrical parameters of 2-chloro-4,6-diamino-1, 3, 5-triazine obtained by B3LYP/6-311G** density functional calculations

Parameters	Bond length(Å)	Parameters	Bond	angle(°)
N1-C2	1.3175	C2-N1-C6	113.10	
N1-C6	1.3529	N1-C2-N3	128.49	
C2-N3	1.3175	N1-C2-Cl7	115.76	
C2-Cl7	1.7547	N3-C2-Cl7	115.76	
N3-C4	1.3529	C2-N3-C4	113.11	
C4-N5	1.3379	N3-C4-N5	125.50	
C4-N8	1.3495	N3-C4-N8	116.61	
N5-C6	1.3378	N5-C4-N8	117.89	
C6-N11	1.3495	N1-C6-N5	114.31	
N8-H9	1.0056	N1-C6-N11	125.50	
N8-H10	1.0053	N5-C6-N11	116.61	
N11-H12	1.0056	C4-N5-C6	117.89	
N11-H13	1.0053	C4-N8-H9	119.29	
		C4-N8-H10	119.70	
		H9-N8-H10	121.01	
		C6-N11-H12	119.29	
		C6-N11-H13	119.70	
		H12-N11-H13	121.01	

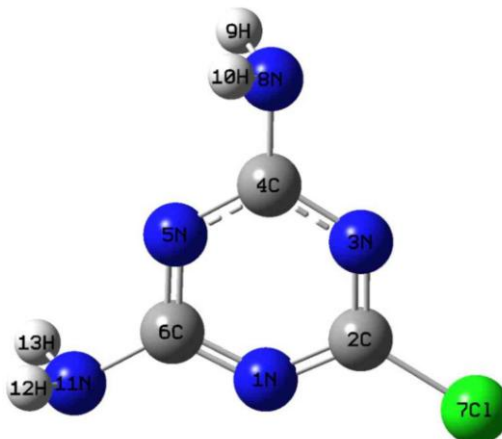Fig.1 Molecular structure of 2-chloro-4,6-diamino-1,3,5-triazine

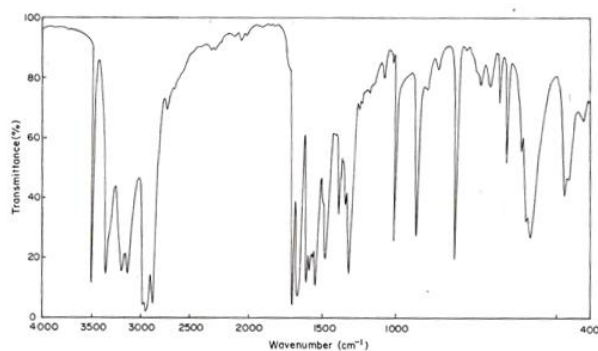Fig. 2. Observed FT-Raman spectrum of 2-chloro-4,6-diamino-1,3,5-triazine

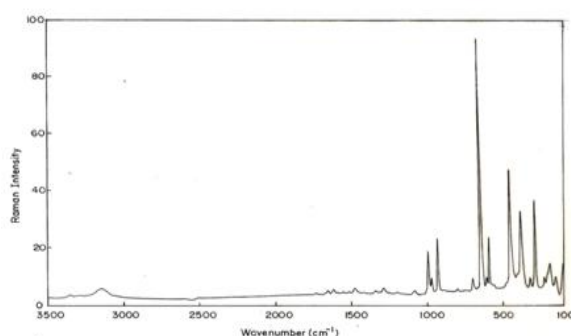Fig. 2. Observed FT-Raman spectrum of 2-chloro-4,6-diamino-1,3,5-triazine

Table 4. Vibrational Assignments of 2-chloro-4,6-diamino-1, 3, 5-triazine obtained by B3LYP/6-311G** density functional calculations

No.	Symmetry Species	Observed Frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Vibrational Assignement/TED(%)
		Infrared	Raman		
1	A′	3505		3754	NH$_2$ asymmtric stretching (99)
2	A′	3410	3405	3753	NH$_2$ asymmetric stretching (99)
3	A′	3250		3619	NH$_2$ symmetric stretching (98)
4	A′	3205		3617	NH$_2$ symmetric stretching (98)
5	A′	1600		1658	NH$_2$ scissoring (80)
6	A′	1580		1631	NH$_2$ scissoring (81)
7	A′		1560	1606	C=N stretching (86)
8	A′	1530		1565	C=N stretching (86)
9	A′	1485	1490	1510	C=N stretching (86)
10	A′	1400		1462	C-N stretching (84)
11	A′	1300	1310	1333	C-N stretching (85)
12	A′	1260		1286	C-N stretching (83)
13	A′	1230	1230	1165	NH$_2$ rocking (65)
14	A′	1055		1040	NH$_2$ rocking (65)
15	A′	1020		1036	Ring in-plane-bending (52)
16	A′	980	980	990	Ring in-plane-bending (53)
17	A′	910		923	Ring in-plane-bending (52)
18	A″		820	824	Ring out-of-plane bending (38)
19	A″		710	742	Ring out-of-plane bending (38)
20	A″	670		682	Ring out-of-plane bending (40)
21	A′	620		636	C-N stretching (71)
22	A′	570	570	583	C-N stretching (70)
23	A″	550		565	NH$_2$ twisting (52)
24	A″	530		564	NH$_2$ twisting (53)
25	A′	520	520	525	C-N in-plane bending (71)
26	A′		415	430	C-Cl stretching (82)
27	A″		310	328	C-N out-of-plane bending (62)
28	A′		240	252	C-Cl in-plane bending (60)
29	A′		180	195	C-N in-plane bending (54)
30	A″		165	182	C-N out-of-plane bending (48)
31	A″		155	167	C-Cl out-of-plane bending (50)
32	A″		135	145	NH$_2$ wagging (61)
33	A″		106	118	NH$_2$ wagging (60)

In addition, NH_2 group has scissoring, rocking, wagging and torsion modes. The internal deformation vibrations known as NH_2 scissoring frequency and they are found at 1600(mode no 5) and $1580cm^{-1}$ (mode no 6) in FT-IR spectra. The scissoring modes predicted at 1658 and 1631 cm^{-1} by B3LYP / 6-311++G** method shows good agreement with experimental data. The computed values have been assigned at 145 (mode no 32) and $118cm^{-1}$ (mode no 33) in CDAT molecule by B3LYP/6-311++G** method have been assigned to NH_2wagging modes. The NH_2wagging modes are observed at 135 and $106cm^{-1}$ in FT-Raman spectra. The computed value have been found at 1165 (mode no 13) and $1040cm^{-1}$(mode no14) in CDAT molecule by B3LYP/6-311++G** method and the observed values are found at 1230 and $1055m^{-1}$ in FT-IR spectra have been assigned to NH_2 rocking mode respectively. The NH_2 twisting modes are observed at 550(mode no 23) and $530cm^{-1}$ (mode no 24) in FT-IR spectra. The computed NH_2 twisting modes are found at 565 and $564cm^{-1}$.These fundamental modes shows very good agreement with computed harmonic frequency as well as recorded spectral data.

C-Cl vibration

The vibrations belonging to the bond between the ring and halogen atoms are worth to the ring to discuss here, since mixing of the vibrations is possible due to the lowering vibration of the molecular symmetry and the presence of heavy atom on the periphery of the molecule [15]. Rastogi *et al.*[16]assigned vibrations of C-X group(X=F, Cl and Br) in the frequency range $1292-485cm^{-1}$.Based on the above literature value the band observed at $415cm^{-1}$ (mode no 26) in FT-Raman spectra are assigned to C-Cl stretching vibration. The theoretically computed C–Cl stretching vibration observed at $430cm^{-1}$ by B3LYP/6-311++G** method shows good agreement with recorded spectral data.

The C–Cl in-plane bending mode has strong to medium intensity generally in the region 550- $250cm^{-1}$. The theoretical wavenumber has been found at $252cm^{-1}$ (mode no 28) of CDAT molecule by B3LYP/6-311++G** method has been assigned to C–Cl in-plane bending mode. This value is in good agreement with the observed spectral value at $240cm^{-1}$ in FT-Raman.

The band observed at $155cm^{-1}$(mode no 31) in FT-Raman spectra is assigned to the C–Cl out-of-plane bending mode of CDAT.

C-N, C=N vibration

The identification of C–N and C=N vibrations are a very difficult task, since the mixing of several modes are possible in the region. Silverstein *et al.*[17]assigned C–N stretching absorption in the region 1266–$1382cm^{-1}$ for hetero aromatic amines. Hence in the present investigation, the theoretically computed C=N, C-N stretching vibration observed at 1606, 1565, 1510, 1462, 1333, $1286cm^{-1}$(mode no's 7, 8, 9, 10, 11, 12) and $636,583cm^{-1}$ (mode no's 20, 21) by B3LYP/6-311++G** method. The bands observed at 1560, 1530, 1485, 1400, 1300 $1260cm^{-1}$ and 620, $570cm^{-1}$ in both FT-IR and FT-Raman spectra have been assigned to C=N and C–N stretching vibrations, respectively. The C–N in-plane bending modes are observed at 520 cm^{-1}(mode no 25) in both IR and Raman spectra and 180 cm^{-1}(mode no 29) in FT-Raman spectrum. The computed values to be at $525cm^{-1}$ and 195 cm^{-1} in CDAT molecule by B3LYP/6-311++G** method have been assigned to C–N in-plane bending vibrations. The band observed at $310cm^{-1}$(mode no 27) and $165cm^{-1}$ (mode no 30) in FT-Raman spectra are assigned to the C–N out-of-plane bending mode of CDAT. These vibrations show very good agreement with computed harmonic frequency as well as recorded spectral data.

Mulliken atomic charge

Mulliken atomic charge calculation [18] has an important role in the application of quantum chemical calculation to molecular system. Because of atomic charges affect dipole moment, polarizability, electronic structure and more a lot of properties of molecular systems. The calculated Mulliken charge values are listed in Table 5. The charge changes with 6-311++G**basis set due to polarization. The charge of Cl7 atom is 0.4376 electrons for CDAT molecule. In amino group, the H9 and H13 atom accommodate less positive charge and becomes less acidic. These lead to C4 and C6 become high positive and become high acidic as compare to C2.

Table 5– Mulliken atomic charges of 2-chloro-4,6-diamino-1, 3, 5-triazine

Atom	charge	Atom	charge
N1	-0.08418	Cl7	0.437654
C2	-0.6741	N8	-0.3522
N3	-0.08418	H9	0.304317
C4	0.086805	H10	0.298784
N5	-0.27062	N11	-0.35219
C6	0.086796	H12	0.30432
		H13	0.29879

HOMO-LUMO energy

The HOMO represents the highly occupied molecular orbital and LUMO represent the low unoccupied molecular orbital. The HOMO-LUMO energy gap of CDAT was calculated at the B3LYP /6-311++G** level. The LUMO as electron acceptor represents the ability to obtain an electron, The HOMO represents the ability to donate an electron [19]

HOMO energy = –0.26631a.u
LUMO energy = –0.03795a.u
HOMO-LUMO energy gap =-0.22836a.u.

Thermodynamical parameters

In addition to the vibrational assignments, several thermodynamic parameters [20] are also calculated on the basis of vibrational analysis at B3LYP/6-311++G** level. The calculated thermodynamic properties are presented in Table 6. The self consistent field (SCF) energy, zero point vibrational energies (ZPVE), rotational constants, dipole moment and entropy $S_{vib}(T)$ are calculated to the extent of accuracy and variations in the ZPVEs seem to be insignificant.

Table 7. Thermo dynamical parameters 2-chloro-4,6-diamino-1, 3, 5-triazine

Thermo dynamical parameter	Values
Zero-point vibrational energy (Joules/Mol)	232555.3
(Kcal/Mol)	55.58205
Zero-point correction (Hatred/Particle)	0.088576
Thermal correction to Energy	0.097088
Thermal correction to Enthalpy	0.098032
Thermal correction to Gibbs Free Energy	0.054765

NBO analysis

The Table 7 shows that the first two columns give the type of orbital and occupancy between 0 and 2.000 electrons. The type can be bonding, lone pair and anti bonding .A normal Lewis structure would not have any anti-bonding orbital, so the presence of anti bonding orbital's shows deviation from normal Lewis structure. Anti-bonding localized orbital's are called non-Lewis NBO's. If the occupancy is not 2.000, then there is deviation from an ideal Lewis structure. The CDAT molecule shows some deviations, otherwise is well approximated using Lewis structure.

In this Table, BD (N1–C2) orbital with 1.98768 electrons has 59.32% N1 character in a $sp^{1.6}$ hybrid and has 40.68% C2 character in a $sp^{1.6}$ hybrid. The $sp^{1.73}$ hybrid on N has 63.25% p-character. The $sp^{1.73}$ hybrid on C has 62.04% p-character. An idealized sp^2 hybrid has 75% p-character. The BD (N1–C2) bond then corresponds roughly to the quantitative concept of interacting sp^3 hybrids. The two coefficients, 0.7727 and 0.6348 are called polarization coefficients. The sizes of these coefficients show the importance of the two hybrids in the formation of the bond. The nitrogen has larger percentage of this NBO, at 59.32% and gives the larger polarization coefficient of 0.7702 because it has the higher electronegativity. Similarly BD(N1–C6), BD(C2–N3), BD(C2–Cl7), BD(N3–C4), BD(C4–N5), C4-N8, BD(N5–C6), BD(C6–N11), BD(N8–H9), BD(N8–H10), BD(N11–H12)and BD(N11–H13) bonding orbital's are also shows nitrogen and chlorine have the lesser percentage of NBO'S and gives the lesser polarization coefficients as compare to BD(N1-C2) bond. This shows that nitrogen and chlorine in above bonding orbital have less

electronegative as compare to BD(N1-C2). At the end of the table nitrogen and chlorine lone pair NBO's are expected to be Lewis structure.

Table 8. NBO results showing the formation of Lewis and non Lewis orbital's-----the valence hybrids corresponding to the intramolecular N-H …...Cl Hydrogen bonds in CDAT

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BOND(A-B)	ED/ ENERGY (a.u)	ED_A(%)	ED_B(%)	NBO	S(%)	P(%)
BD(1)N1-C2	1.98768	59.32	40.68	$0.7702(sp^{1.64})_{N}+$	36.55	63.25
				$0.6378(sp^{1.73})_{C}$	37.91	62.04
BD(1)N1-C6	1.97334	41.57	58.43	$0.6447(sp^{2.04})_{N}+$	32.27	67.53
				$0.7644(sp^{1.94})_{C}$	34.06	65.90
BD(1)C2-N3	1.98768	59.32	40.68	$0.6447(sp^{1.64})_{C}+$	37.91	62.04
				$0.6663(sp^{1.73})_{N}$	36.55	63.25
BD(1)C2-Cl7	1.98284	54.19	45.81	$0.7362(sp^{3.14})_{C}+$	24.11	62.04
				$0.6418(sp^{5.12})_{Cl}$	16.27	63.25
BD(1)N3-C4	1.97334	41.57	58.43	$0.6447(sp^{2.04})_{N}+$	32.27	67.53
				$0.7644(sp^{1.94})_{C}$	34.06	65.90
BD(1)C4-N5	1.98291	58.49	41.51	$0.7648(sp^{1.88}))_{C}+$		
				$0.5992(sp^{1.90})_{N}$	34.71	65.20
					34.45	65.45
BD(1)C4-N8	1.99079	59.96	40.09	$0.7744(sp^{2.22})_{C}+$	30.99	68.93
				$0.5992(sp^{1.53})_{N}$	39.45	60.49
BD(1)N5-C6	1.98291	41.57	58.43	$0.6447(sp^{2.04})_{N}+$	32.27	67.53
				$0.7644(sp^{1.94})_{C}$	34.06	65.90
BD(1)C6-N11	1.99079	59.96	40.09	$0.7744(sp^{2.22})_{C}+$	30.99	68.93
				$0.5992(sp^{1.53})_{N}$	39.45	60.49
BD(1)N8-H9	1.98940	29.58	70.42	$0.5439(sp^{2.30})_{C}+$	30.26	69.70
				$0.5992(sp^{0.0})_{N}$	99.94	0.06
BD(1)N8-H10	1.98951	29.74	70.26	$0.5453(sp^{2.31})_{N}+$	30.23	69.73
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
BD(1)N11-H12	1.98940	29.58	70.42	$0.5439(sp^{2.30})_{N}+$	30.26	69.70
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
BD(1)N11-H13	1.98951	29.74	70.26	$0.5453(sp^{2.31})_{N}+$	30.23	69.73
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
BD*(1)N1-C2	0.04121	59.32	40.68	$0.7702(sp^{1.64})_{N}+$	36.55	63.25
				$0.6378(sp^{1.73})_{C}$	37.91	62.04
BD*(1)N1-C6	0.04144	41.57	58.43	$0.6447(sp^{2.04})_{N}+$	32.27	67.53
				$0.7644(sp^{1.94})_{C}$	34.06	65.90
BD*(1)C2-N3	0.04121	59.32	40.68	$0.6447(sp^{1.64})_{C}+$	37.91	62.04
				$0.6663(sp^{1.73})_{N}$	36.55	63.25
BD*(1)C2-Cl7	0.07475	54.19	45.81	$0.7362(sp^{3.14})_{C}+$	24.11	62.04
				$0.6418(sp^{5.12})_{Cl}$	16.27	63.25
BD*(1)N3-C4	0.04144	41.57	58.43	$0.6447(sp^{2.04})_{N}+$	32.27	67.53
				$0.7644(sp^{1.94})_{C}$	34.06	65.90
BD*(1)C4-N5	0.03483	58.49	41.51	$0.7648(sp^{1.88}))_{C}+$	34.71	65.20
				$0.5992(sp^{1.90})_{N}$	34.45	65.45
BD*(1)C4-N8	0.03394	59.96	40.09	$0.7744(sp^{2.22})_{C}+$		
				$0.5992(sp^{1.53})_{N}$	30.99	68.93
					39.45	60.49
BD*(1)N5-C6	0.03483	41.57	58.43	$0.6447(sp^{2.04})_{N}+$	32.27	67.53
				$0.7644(sp^{1.94})_{C}$	34.06	65.90
BD*(1)C6-N11	0.03394	59.96	40.09	$0.7744(sp^{2.22})_{C}+$	30.99	68.93
				$0.5992(sp^{1.53})_{N}$	39.45	60.49
BD*(1)N8-H9	0.00625	29.58	70.42	$0.5439(sp^{2.30})_{N}+$	30.26	69.70
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
BD*(1)N8-H10	0.00646	29.74	70.26	$0.5453(sp^{2.31})_{N}+$	30.23	69.73
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
BD*(1)N11-H12	0.00625	29.58	70.42	$0.5439(sp^{2.30})_{N}+$	30.26	69.70
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
BD*(1)N11-H13	0.00646	29.74	70.26	$0.5453(sp^{2.31})_{N}+$	30.23	69.73
				$0.5992(sp^{0.0})_{H}$	99.94	0.06
LP(1)N1	1.89945	-----	-----	$sp^{2.21}$	31.13	69.71

LP(1)N3	1.89945	-----	-----	sp$^{2.21}$	31.13	68.71
LP(1)N5	1.90387	-----	-----	sp$^{2.21}$	31.14	68.78
LP(1)Cl7	1.99273	-----	-----	sp$^{0.19}$	83.82	16.17
LP(1)N8	1.74037	-----	-----	sp$^{1.00}$	0.00	99.99
LP(1)N11	1.74037	-----	-----	sp$^{1.00}$	0.00	99.99

Table 9. The second order perturbation energies E(2) (kcal/mol)corresponding to the most important charge transfer interactions (donor-acceptor) in the compounds studied by B3LYP/ 6-311++G**method

Donor NBO (i)	Acceptor NBO (j)	E$^{(2)}$(kcal/mol)	E(j)–E(i) (a.u)	F(i,j) (a.u)
BD(1)N1-C2	BD*(1)N1-C6	0.99	1.36	0.033
BD(1)N1-C2	BD*(1)C2-N3	1.74	1.41	0.045
BD(1)N1-C2	BD*(1)C-N11	3.8	1.35	0.064
BD(1)N1-C6	BD*(1)N1-C2	1.25	1.36	0.037
BD(1)N1-C6	BD*(1)C2-Cl7	6.04	0.96	0.069
BD(1)N1-C6	BD*(1)N5-C6	1.42	1.34	0.039
BD(1)C2-N3	BD*(1)N1-C2	1.74	1.41	0.045
BD(1)C2-Cl7	BD*(1)N1-C6	3.13	1.19	0.055
BD(1)C2-Cl7	BD*(1)N3-C4	3.13	1.19	0.055
BD(1)N3-C4	BD*(1)C2-N3	1.25	1.36	0.037
BD(1)N3-C4	BD*(1)C2-Cl7	6.05	0.96	0.069
BD(1)N3-C4	BD*(1)N8-H10	1.95	1.24	0.044
BD(1)C4-N5	BD*(1)N3-C4	1.37	1.33	0.038
BD(1)C4-N5	BD*(1)N8-H9	1.8	1.26	0.043
BD(1)C4-N8	BD*(1)C2-N3	1.94	1.4	0.047
BD(1)C4-N8	BD*(1)N5-C6	1.96	1.38	0.047
BD(1)N5-C6	BD*(1)N1-C6	1.37	1.33	0.038
BD(1)C6-N11	BD*(1)N1-C2	1.94	1.4	0.047
BD(1)N8-H9	BD*(1)C4-N5	4.56	1.2	0.066
BD(1)N8-H10	BD*(1)N3-C4	4.37	1.17	0.064
BD(1)N11-H12	BD*(1)N5-C6	4.56	1.2	0.066
BD(1)N11-H13	BD*(1)N1-C6	4.37	1.17	0.064
LP(1)N1	BD*(1)C2-N3	12.6	0.89	0.096
LP(1)N1	BD*(1)C2-Cl7	3.4	0.5	0.037
LP(1)N3	BD*(1)N1-C2	12.6	0.89	0.096
LP(1)N3	BD*(1)C2-Cl7	3.4	0.5	0.037
LP(1)N5	BD*(1)N1-C6	11.89	0.85	0.091
LP(1)Cl7	BD*(1)N1-C2	1.11	1.45	0.036
LP(1)Cl7	BD*(1)C2-N3	1.11	1.45	0.036
LP(1)N8	BD*(2)C4-N5	59.73	0.26	0.116
LP(1)N11	BD*(2)N1-C6	59.75	0.25	0.116

Perturbation theory energy analysis

Delocalization of the electron density between occupied Lewis type (bond (or) lone pair) NBO orbital's and formally unoccupied (antibond (or) Rydberg) non Lewis NBO orbital's corresponding to a stabilizing donor- acceptor interaction. The energy of this interaction can be estimated by the second order perturbation theory [13]. Table 8 lists the calculated second order interaction energies ($E^{(2)}$) between the donor –acceptor orbital's in CDAT.

The most important interaction energies, related to the resonance in the benzene ring are electron donating from the BD(N1–C6),BD(N3–C4),LPN1,LPN3,LPN5,LPN8, LPN11 to the antibonding acceptor BD*(C2–Cl7), BD*(C2–Cl7),BD*(C2–N3),BD*(N1–C2),BD*(N1–C6),BD*(C4–N5),BD*(N1–C6), orbital's and their corresponding energies are 6.04, 6.05, 16.06, 16.06, 11.89, 59.73, 59.75kcal/mol, respectively. These interactions clearly indicate the strongest stabilization energy increase of electron delocalization occurs due to substitution of the molecule.

Conclusion

The present investigation thoroughly analysed the vibrational spectra, both infrared and Raman of 2-chloro-4,6-diamino-1,3,5-triazine molecule. All the vibrational bands observed in the FT-IR and FT-Raman spectra of the compound are assigned to the various modes of vibration. The complete vibrational assignments of wave numbers are made on the basis of total energy distribution (TED). The influences of amino acid and chlorine atom to the vibrational frequencies of the title compound have been studied. Quantum chemical calculations help us to identify the structural and symmetry properties of the title compound. The good agreement of the calculated and observed vibrational spectra reveals the advantages of higher basis set for quantum chemical calculation. The calculated HOMO and LUMO energies also show that charge transfer occurs within the molecule. In addition, Mulliken atomic charge and thermodynamic functions of the title compound were also presented. NBO analysis has been shown improper weak N-H….Cl hydrogen bond from the electron density of the electron lone pair with the antibonding orbital. The stabilization energy has been calculated from second order perturbation theory.

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