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Comparative *ab initio* Investigation of Some Nitrogen Containing Heterocyclic Compounds Using DFT Calculation

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Quantum chemical calculations of energies, geometrical structure, harmonic vibrational frequencies and bonding features in the heterocyclic compounds of 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine have been carried out by density functional theory (DFT/B3LYP) method with 6-311++G(d,p) as basis set. The theoretical spectrogram for IR and Raman spectra of these compounds have been constructed. The vibrational frequencies are calculated and scaled values are compared with FT-IR experimental values (NIST) of these three compounds. The study is extended to compare and analyze the differences in some of the physical and chemical properties like bond parameters, atomic charges, thermodynamic properties, HOMO-LUMO analysis *etc*., in the heterocyclic compounds of 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine using quantum computational methods.

Keywords: 2-Amino-4-methylpyridine, 2-Amino-4-methylpyrimidine, 2-Amino-4-methyltriazine, DFT, HOMO-LUMO energy.

INTRODUCTION

Nitrogen containing heterocycles play vital role in pharmacological, agricultural and in analytical chemical laboratories [1] and thus it kindled the study of heterocyclic compounds with one nitrogen atom in the ring (pyridine derivative), two nitrogen atoms in the ring (pyrimidine derivative) and three nitrogen atoms in the ring (triazine derivative) as these compounds found to exhibit following applications. 2-Amino-4-methylpyridine (AMP) is reported to be inhibitors of inducible NO synthase [2] both *in vitro* and *in vivo* and it is found to be morphine like analgesic and as antinociceptive agents and the inhibition of nitric oxide synthase aggravates cisplatin-induced nephrotoxicity. Pyrimidines are considered to be important heterocyclic compounds not only because they are on integral part of genetic materials *viz*., DNA and RNA as nucleotides and nucleosides also they have important numerous biodynamic properties and biological activities such as bactericides, fungicides, vermicides and medicines [3]. Pyrimidine derivatives are ubiquitination inhibitors that inhibit the ubiquitin ligase activity, particularly of POSH polypeptides, are useful for the treatment of viral infections and neurological disorders and also used as PI-3-kinase inhibitors [4,5]. S-Triazine derivatives represent an important class of compounds due to their potential to be biologically active. They are known to be antiprotozoals, anticancer agents, estrogen receptor modulators, antimalarials, cyclin-dependent kinase modulators and antimicrobials [6]. They also have found widespread applications in the textile, plastic and rubber industries and are used as pesticides, herbicides, dyestuffs, optical bleaches, explosives and surface active agents [7].

Because of the realization of the chemical and biochemical importance of these derivatives, has occasioned a great revival of interest to select nitrogen containing heterocyclic compounds for the study. The selected heterocyclic compounds are 2-amino-4-methylpyridine (AMP), 2-amino-4-methylpyrimidine (AMPM) and 2-amino-4-methyltriazine (AMT). The compounds for comparison are selected in such a way that each compound increases by one hetero atom nitrogen in the aromatic ring by fixing the substituents amino and methyl groups in C2 and C4, respectively in all the three compounds. These molecules exhibit imine-enamine tautomerism due to the presence of ring nitrogen in the first position and amino group in the second carbon. The present investigation is to understand and analyze the differences in the structure and harmonic frequencies of the present compounds at DFT level employing the basis set 6-311+G(d,p). The optimized geometry and their molecular properties such as equilibrium energy, frontier orbital energy gap, dipole moment, polarizability, first static hyperpolarizability, thermodynamical properties, HOMO-LUMO analysis, some of the physical and chemical properties like bond parameters, atomic charges, *etc.*, in the title compounds have been studied using quantum computational methods to compare the properties and activity of the compounds which have been done for the first time.

The literature survey reveals that infrared and Raman spectra of pyridine and its mono and di substituted derivatives like halogenated pyridines have been studied by several investigators [8-10]. An harmonic vibrational analysis of 3,4-diaminopyridine and 3-aminopyridine by density functional theory calculations had been presented by Karpagam *et al.* [11]. Sundaraganesan *et al.* [12] had reported vibrational studies of 2-amino-5-methyl pyridine and 2-amino-6-methyl pyridine. Akyuz and Akyuz [13] reported the FTIR spectra of 2-amino-pyrimidine. Vibrational spectra, UV and NMR first order hyperpolarizability and HOMO-LUMO analysis of 2-amino-4-chloro-6-methyl pyrimidine have been reported by Jayavathanan *et al.* [14]. By literature survey it is come to know that neither quantum chemical calculation, nor the vibrational spectra of 2-amino-4-methyl-pyrimidine have been reported. The experimental and theoretical study on molecular structure, vibrational spectra, NBO analysis of amino and halo derivatives of 1,3,5-triazine have been reported by several authors [15-17]. From our extensive study of the literature it was clear that even though good amount of work was done on the derivatives of triazine, no details of FTIR and FTR and *ab initio* studies were available for the molecule 2-amino-4-methyltriazine. Hence an attempt is made in the present work to analyze the FTIR (NIST) spectrum and to carry out normal coordinate analysis using *ab initio* DFT methods with the help of Gaussian-09 program.

COMPUTATIONAL METHODS

The primary task for the computational work was to determine the optimized geometry of the investigated compounds. The molecular structures of the present compounds were optimized and corresponding vibrational harmonic frequencies were calculated using *ab initio* DFT with B3LYP methods with 6-311++G(d,p) basis sets without any constraint on the geometry. The stability of the optimized geometries was confirmed by wave number calculations, which gave positive values for all the obtained wave numbers.

The density functional theoretical calculation (DFT) of the present compounds were carried out with the version 8 of Gaussian 09W (revision B.01) program [18] on Intel Core2Duo/2.20 GHz processor. For the simulated IR and Raman spectra pure lorentzian band shapes with the band width of 10 cm^{-1} was employed using the Gabedit Version 2.32 [19]. Furthermore, true rotational constants, infrared and Raman intensity, Raman activity, atomic charges (Mulliken), dipole moment, translation energy (HOMO-LUMO), non-linear optical parameters (static electronic polarizability, anisotropy, first order and second order hyper polarizabilities) and other thermodynamical parameters were calculated. By combining the results of Gabedit [19] program with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy and the vibrations match quite well with the motions observed using the GAUSS VIEW [20] program.

RESULTS AND DISCUSSION

Molecular geometry: The DFT computational analysis shows that the three title molecules 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine under study fall under Cs point group symmetry and their structures are shown in Figs. 1-3. The parameters are calculated for the optimized structures. The calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and molecular properties. The assignments of the normal modes of the vibration of the investigated molecules along with the observed frequencies, unscaled frequencies and scaled frequencies obtained by DFT computation using the B3LYP/6-311++G(d,p) basis set are reported in Tables 1-3.

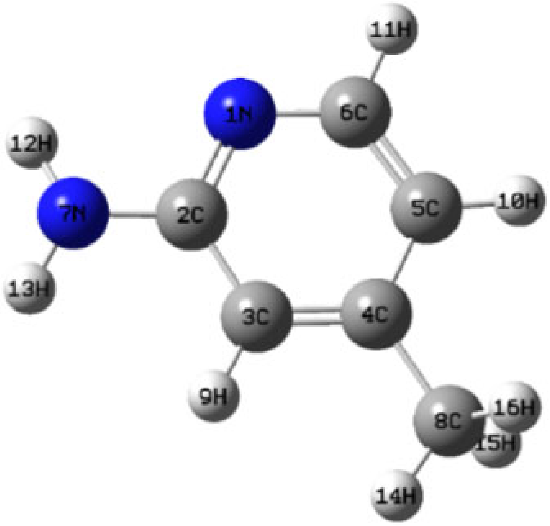

Fig. 1. Structure of 2-amino-4-methylpyridine

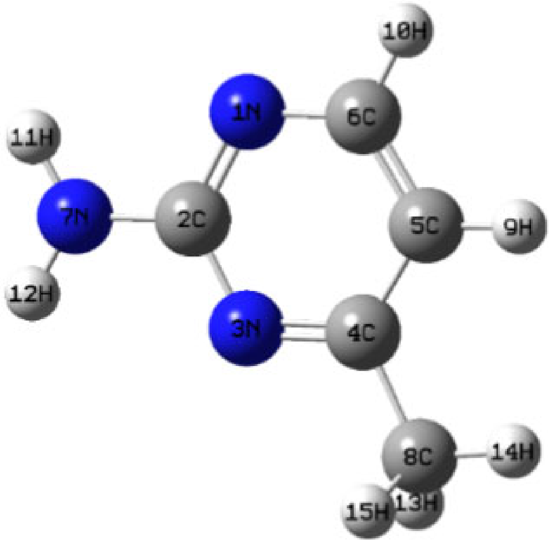

Fig. 2. Structure of 2-amino-4-methylpyrimidine

TABLE-1
EXPERIMENTAL AND CALCULATED FREQUENCIES, IR AND RAMAN INTENSITIES AND ASSIGNMENTS FOR 2-AMINO-4-METHYLPYRIDINE

Mode of vibration	Symmetric species	Observed[a] IR frequency (cm^{-1})		Calculated frequency (cm^{-1}): B3LYP/6-311++G			Vibrational assignment[b]
		Frequency	Intensity	Unscaled	IR intensity	Raman activity	
1	A'	3541vs	99.249	3692	28.947	54.926	ν_{asy} NH_2
2	A'	3391vs	81.231	3579	38.358	205.821	ν_{sy} NH_2
3	A'	3178vs	91.742	3180	14.058	150.051	νC-H
4	A'	3072s	71.972	3160	14.490	98.234	νC-H
5	A'	2909s	64.965	3145	21.929	98.271	νC-H
6	A'	2822m	44.695	3106	18.018	55.985	ν_{asy} C-H of CH_3
7	A'	2740m	36.687	3078	13.065	86.138	ν_{asy} C-H of CH_3
8	A'	2659m	33.684	3027	22.092	228.833	ν_{sy} C-H of CH_3
9	A'	1671vw	14.164	1651	357.332	25.368	δNH_2 + νC-C
10	A'	1634vw	3.654	1635	34.147	1.701	νC-C
11	A'			1601	57.841	10.395	νC-C + ν_{ring}C=N
12	A'			1519	17.255	7.334	δ_{asy}C-H of CH_3
13	A'			1496	76.439	2.686	νC-C + δ_{asy}C-H of CH_3
14	A'			1484	7.609	8.808	ν_{ring}C=N
15	A'	1465vw	6.156	1454	72.962	6.667	δ_{sy}C-H of CH_3
16	A'			1412	3.617	9.655	νC-N
17	A'	1340vs	97.247	1351	5.858	9.715	βC-H
18	A'	1302vs	97.498	1331	30.017	10.745	νC-CH_3
19	A'	1227vs	84.985	1302	6.224	1.551	βC-H
20	A'	1152s	71.972	1196	14.398	4.764	βC-H
21	A'	1127vs	83.484	1150	2.576	5.915	ρNH_2
22	A'			1071	0.627	0.523	ρCH_3
23	A"	1096vs	85.235	1058	3.746	0.063	Ring breathing
24	A"	1002m	41.441	1026	11.153	2.840	Triogonal bend + ρCH_3
25	A"			998	5.913	23.563	γC-H
26	A"	952m	32.933	978	0.437	0.254	γC-H
27	A"	927s	69.470	959	6.809	2.843	γC-H
28	A'	877s	53.203	863	10.434	0.083	βC-C-C
29	A'	846w	19.670	813	36.413	0.684	βC-C-C
30	A'	764s	52.453	777	0.997	18.613	βC-N-C
31	A'	714vs	13.664	759	1.160	0.280	βC-C-C
32	A'	658w	17.668	607	26.591	1.711	βC-N-C
33	A'	602w	22.422	581	2.290	8.488	βC-N
34	A"	570w	20.420	523	4.084	5.151	γC-C-C
35	A"	545m	49.199	509	207.643	1.280	γC-N
36	A"	477m	39.690	454	55.989	0.583	ωNH_2 + γC-N-C
37	A'	395s	56.206	439	6.033	1.191	βC-NH_2 + βC-CH_3
38	A"	308vs	95.496	377	55.734	0.503	γC-NH_2
39	A"	251m	32.182	294	2.757	0.783	tNH_2
40	A"	208m	41.191	210	2.069	0.859	tCH_3
41	A"			197	5.243	0.911	γC-C-C
42	A"			47	0.312	0.370	τCH_3

[a]vs-very strong; s-strong; m-medium; w-weak; [b]ν_{as}-asymmetric stretching; ν_s-symmetric stretching; δ-scissoring; ρ-rocking; τ-torsion; t-twisting; ω-wagging; β-in-plane bending; γ-out-of-plane bending

The simulated infrared and Raman spectra were drawn for unscaled frequencies for 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine and given in Figs. 4-6, respectively. These compounds show normal modes of vibration of which 2n-3 of all vibration lie in-plane (A′ species) and n-3 lie in the out-of-plane (A″ species) and all the normal modes are found to be active both in IR and Raman.

Vibrational assignment: The assignments of the normal modes of the vibration of the investigated molecules along with the observed IR frequencies (NIST) and unscaled frequencies, obtained by B3LYP/6-311++G(d,p) calculation are presented in Tables 1-3 for 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine, respectively. The experimental IR which is obtained from NIST is presented in Figs. 4(a) and 5(a). The simulated IR and Raman spectra of 2-amino-4-methyl-pyridine, 2-amino-4-methyl-pyrimidine and 2-amino-4-methyl-triazine are given in Figs. 4-6, respectively and the simulated IR and Raman spectra are drawn for unscaled frequencies.

In 2-amino-4-methylpyridine, 29 of all the 42 normal modes of fundamental vibrations are in-plane and 13 are out-

TABLE-2
EXPERIMENTAL AND CALCULATED FREQUENCIES, IR AND RAMAN INTENSITIES AND ASSIGNMENTS FOR 2-AMINO-4-METHYLPYRIMIDINE

Mode of vibration	Symmetric species	Observed[a] frequency (cm^{-1})		Calculated frequency (cm^{-1}): B3LYP/6-311++G (d,p)			Vibrational assignment[b]
		IR	Intensity	Unscaled	IR intensity	Raman activity	
1	A'	3724vw	1.06	3737	51.88	47.40	$\nu_{asy}NH_2$
2	A'	3636vw	5.90	3609	73.32	176.02	$\nu_{sy}NH_2$
3	A'	3496vw	8.85	3201	7.01	125.04	νC-H
4	A'	3180vw	1.06	3145	22.37	127.11	νC-H
5	A'	3148vw	0.85	3119	16.95	58.73	ν_{asy}C-H of CH_3
6	A'	3029vw	3.80	3094	8.64	80.90	ν_{asy}C-H of CH_3
7	A'			3037	12.14	220.89	ν_{sy}C-H of CH_3
8	A'			1636	577.60	21.38	δNH_2 + νC-C
9	A'			1616	98.43	10.77	νC-C + ν_{ring}C=N
10	A'			1601	127.87	3.18	νC-C + ν_{ring}C=N
11	A'	1407vw	1.06	1490	7.96	4.42	δ_{asy}C-H of CH_{3+}
12	A'			1484	168.07	5.33	νC-C + δ_{asy}C-H ofCH_3
13	A'			1477	8.04	8.04	ν_{ring} C=N
14	A'			1463	95.96	1.81	δ_{sy}C-H of CH_3
15	A'			1407	15.17	10.07	νC-N
16	A'			1367	7.92	6.66	βC-H
17	A'	1283vs	99.97	1281	18.96	6.79	$\nu C\text{-}CH_3$
18	A'			1259	8.40	4.52	βC-H
19	A'			1147	1.48	5.84	ρNH_2
20	A'	1086m	48.83	1091	1.40	1.04	ρCH_3
21	A"			1057	5.45	0.08	Ring breathing
22	A"	1024vw	4.43	1020	1.55	4.15	Trigonal bend + ρCH_3
23	A'			1009	5.17	15.43	νC-N + ρCH_3
24	A"	972vw	1.91	995	0.27	0.41	γC-H
25	A"	946vw	1.70	954	3.54	4.40	γC-H
26	A"			817	29.29	0.33	Ring asym deformation
27	A'	806vw	4.22	809	9.44	0.63	βC-C-C
28	A'	780vw	2.12	773	3.04	18.80	βC-N-C
29	A'	645vw	1.27	630	1.17	0.70	βN-C-N-C
30	A'			606	1.11	7.55	βC-N-C
31	A'	562vw	1.70	547	4.01	5.33	βC-N-N-C
32	A"			515	2.55	0.45	γC-C-C
33	A"	469vw	2.12	453	4.09	0.62	γC-N
34	A"			448	8.09	0.34	ωNH_2 + γC-N-C
35	A'	319vw	13.90	307	268.80	1.20	$\beta C\text{-}NH_2 + \beta C\text{-}CH_3$
36	A"			304	12.72	1.62	$\gamma C\text{-}NH_2$
37	A"	209vw	5.65	206	6.61	0.52	tNH_2
38	A"	185vw	2.89	176	3.94	0.59	tCH_3
39	A"	53vw	2.12	59	0.22	0.35	τCH_3

[a]vs-very strong; s-strong; m-medium; w-weak; [b]ν_{as}-asymmetric stretching; ν_s-symmetric stretching; δ-scissoring; ρ-rocking; τ-torsion; t-twisting; ω-wagging; β-in-plane bending; γ-out-of-plane bending

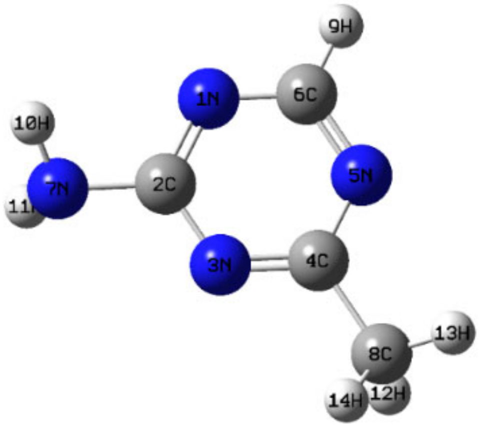

Fig. 3. Structure of 2-amino-4-methyltriazine

of-plane. In 2-amino-4-methylpyrimidine, 15 atoms provide 39 normal modes of vibrations, out of which, 27 are found to be in-plane and 12 are out of plane. Further, 2-amino-4-methyltriazine shows 36 normal modes of fundamental vibrations of which 25 lie in-plane and remaining in the out of plane. The vibrational analysis is performed for these three compounds on the basis of the characteristic vibrations of the amino-, methyl-, aromatic ring carbons-H strecthing, bending, rocking, wagging, *etc.* The vibrational assignments are presented in the Tables 1-3. These assignments agree well with the earlier work and also in line with the literature values.

Comparison of fundamental vibrations: The comparison is carried out for discussion only for those vibrational frequencies where the variations arise among the present compounds.

TABLE-3
CALCULATED FREQUENCIES, IR AND RAMAN INTENSITIES AND ASSIGNMENTS FOR 2-AMINO-4-METHYLTRIAZINE

Mode of vibration	Symmetric species	Calculated frequency (cm^{-1}): B3LYP/6-311++G (d,p)			Vibrational assignment[b]
		Unscaled	IR intensity	Raman activity	
1	A'	3751	69.20	48.08	$\nu_{asy}NH_2$
2	A'	3616	100.43	167.49	$\nu_{sy}NH_2$
3	A'	3154	21.95	138.87	νC-H
4	A'	3146	10.43	47.39	ν_{asy}C-H of CH_3
5	A'	3097	6.80	82.42	ν_{asy}C-H of CH_3
6	A'	3043	4.48	221.69	ν_{sy}C-H of CH_3
7	A'	1642	647.04	5.69	$\delta NH_2 + \nu C{=}N$
8	A'	1609	284.94	6.54	$\nu_{ring}C{=}N$
9	A'	1576	247.73	1.16	$\nu_{ring}C{=}N + \beta C\text{-}NH_2$
10	A'	1493	89.08	6.11	δ_{asy}C-H of $CH_3 + \gamma C\text{-}NH_2$
11	A'	1476	8.52	7.53	δ_{asy}C-H of CH_3
12	A'	1472	76.85	1.73	$\nu_{ring}C{=}N$
13	A'	1447	107.08	14.15	δ_{sy}C-H of CH_3
14	A'	1400	0.60	4.24	νC-N
15	A'	1360	5.26	0.49	βC-H
16	A'	1299	7.12	6.62	$\nu C\text{-}CH_3$
17	A'	1231	18.16	2.38	ωNH_2
18	A'	1095	8.06	0.63	$\rho NH_2 + \beta$C-N-C
19	A'	1067	6.53	0.21	$\rho CH_3 + \beta$C-N-C
20	A"	1017	9.58	0.89	Ring breathing
21	A"	1008	0.22	0.17	Triogonal bend + ρCH_3
22	A'	998	12.33	15.51	νC-N + $CH_3 + \rho CH_3$
23	A"	974	3.63	2.07	γC-H
24	A'	832	21.97	0.01	βC-N-C+ N-C-N
25	A'	814	6.01	17.50	βC-N-C
26	A'	652	0.14	0.58	βN-C-N
27	A"	607	3.04	8.82	$\gamma C\text{-}N\text{-}C{+}C\text{-}NH_2$
28	A'	576	6.07	4.67	βC-N
29	A"	568	0.02	0.12	$\gamma C\text{-}N\text{-}C{+}C\text{-}NH_2$
30	A"	455	4.83	0.66	γC-N
31	A"	444	3.01	0.92	$\omega NH_2 + \gamma$C-N-C
32	A'	312	6.41	0.89	$\beta C\text{-}NH_2 + \beta C\text{-}CH_3$
33	A"	193	14.77	0.37	$\gamma C\text{-}NH_2 + C\text{-}CH_3$
34	A"	176	45.98	0.09	tNH_2 + Ring asym deform
35	A"	138	165.11	0.01	tCH_3
36	A"	24	0.49	0.48	τCH_3

ν_{as}-asymmetric stretching; ν_s-symmetric stretching; δ-scissoring; ρ-rocking; τ-torsion; t-twisting; ω-wagging; β-in-plane bending; γ-out-of-plane bending

The substituents $-NH_2$ and $-CH_3$ groups are fixed in the same position C2 and C4 in all the three compounds whereas the 3C and 5C in 2-amino-4-methylpyridine are replaced by nitrogen in 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine, respectively. The fundamental vibrations of the substituent groups which are electron donating type, $-NH_2$ and $-CH_3$ in the present compounds are mainly taken for comparison and analyzed to understand the changes in the normal modes of fundamental vibrations of these groups which are listed in the Table-4.

It is quite interesting to note that the calculated frequency values for asymmetric and symmetric stretching vibrations of amino group in 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine (3692, 3737 and 3751 cm^{-1}, respectively) are gradually increased as the increase in the number of nitrogen atoms and due to the greater electronegativity and the repulsion of the lone pair of electrons of nitrogen atoms. Similar trend is observed even in the case of methyl group too. The $-NH_2$ group of all the compounds have scissoring (δNH_2), wagging (ωNH_2) and rocking (ρNH_2) modes of vibrations. The scissoring along with the stretching C-C vibration shows a lesser value (1651, 1636 and 1642 cm^{-1}) in the case of 2-amino-4-methylpyrimidine than other two molecules on comparison because the scissoring vibration is much sensitive to the atoms adjacent to the amino group. The charge transfer from the ring N to amino group is the reason for the lesser value which is also detailed under the thermodynamic properties in the present work. The other two modes *i.e.*, wagging and rocking frequency values of amino group have the gradual increase of frequency values with the more number of nitrogen atoms. In the case of vibration of rocking mode and trigonal bend of $-CH_3$, the frequency value of 2-amino-4-methyltriazine is found to be less (1026, 1020 and 1008 cm^{-1}) due to the presence of ring N on both the sides of the $-CH_3$ group, which alters the distribution of charges. The ring breathing frequency values 1058, 1057 and 1017 cm^{-1} of

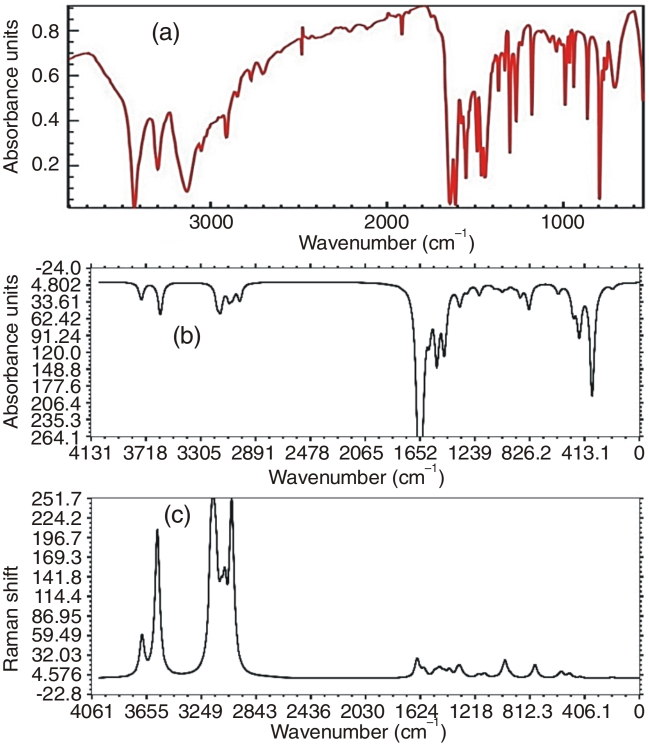

Fig. 4. (a) Experimental FTIR and (b) simulated IR and (c) Raman spectra of 2-amino-4-methylpyridine

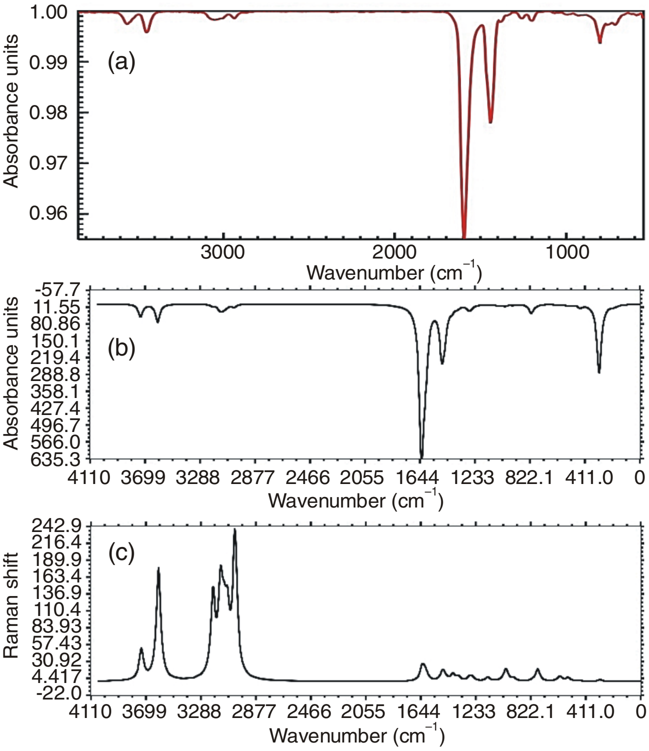

Fig. 5. (a) Experimental FTIR and (b) simulated IR and (c) Raman spectra of 2-amino-4-methylpyrimidine

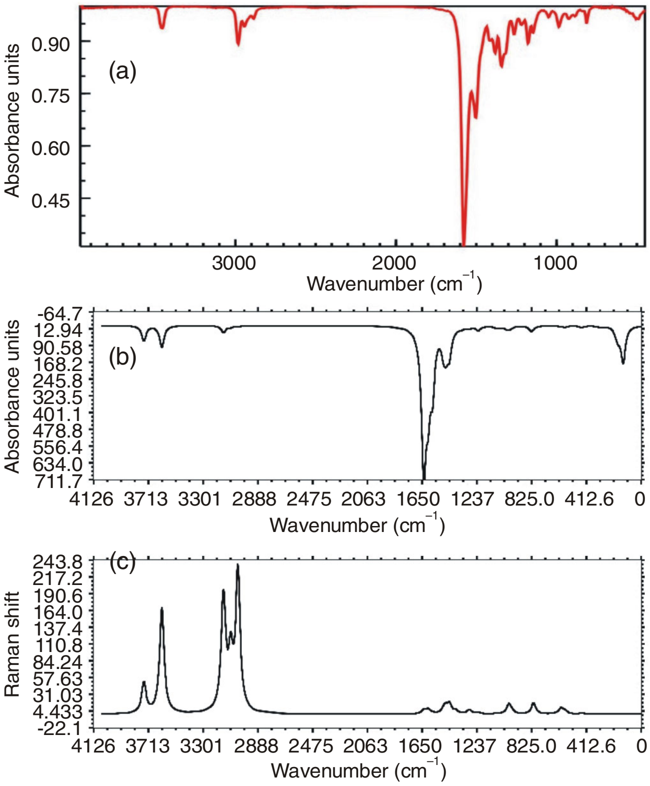

Fig. 6. (a) Experimental FTIR and (b) simulated IR and (c) Raman spectra of 2-amino-4-methyltriazine

2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine, respectively also noticeably decreased in 2-amino-4-methyltriazine because of the presence of more number nitrogen atoms which makes the ring more strain.

Comparison of bond length: In these three compounds, amino group is substituted at C2 and methyl group at C4 position. Hence the changes in the nature of bond length C2-N7 (N7-amino group nitrogen atom) and C4-C8 (C8-methyl group carbon atom) are mainly taken for comparison (Table-5). Some of the bond length values are listed (Table-6) for comparison. It is observed that with increase in number of nitrogen atoms in the heterocyclic ring the bond length C2-N7 (exo-bond) is decreasing. This may be due to more number of nitrogen atoms present in the triazine ring which are electro negative in character and there by extended conjugation is found to be there. It is found that the bond length values of C4-C8 (exo-bond) are not much affected as C2-N7. This implies that amino group is much affected by the presence of more nitrogen atoms in the ring than the methyl group. If the values of N1-C2 and N1-C6 are subjected to comparison it is noted that substitution of more number of nitrogen atoms does not alter the bond length of atoms present in the ring.

Comparison of bond angles: The breakdown of hexagonal symmetry of heterocyclic ring is obvious since there is negative deviation of C2-N1-C6 (117°) for 2-amino-4-methylpyridine, 115° for 2-amino-4-methylpyrimidine, 113° for 2-amino-4-methyltriazine (Table-5). The negative deviation is more in case of triazine as there are more number of nitrogen atoms and there is greater repulsion among them. These differences between the CNC angles in the ring correlating with the steric effect of the lone pair electrons are fully consistent with the valence shell electron pair repulsion theory [21]. The similar studies are seen in the literature [22,23] and as a result, it can be said that the ring of the triazine is significantly distorted from the ideal hexagonal form. Due to the same reason the exo-angles, C2-N7-H10 and C2-N7-H11 are found to be highest, particularly in the case of 2-amino-4-methyl-

TABLE-4
COMPARISON OF SOME VIBRATIONAL FREQUENCIES OF 2-AMINO-4-METHYLPYRIDINE, 2-AMINO-4-METHYLPYRIMIDINE AND 2-AMINO-4-METHYLTRIAZINE

Calculated frequency (cm^{-1})									Vibrational assignment
2-Amino-4-methylpyridine			2-Amino-4-methylpyrimidine			2-Amino-4-methyltriazine			
Unscaled	IR intensity	Raman activity	Unscaled	IR intensity	Raman activity	Unscaled	IR intensity	Raman activity	
3692	28.947	54.926	3737	51.88	47.40	3751	69.20	48.08	$\nu_{asy}NH_2$
3579	38.358	205.821	3609	73.32	176.02	3616	100.43	167.49	$\nu_{sy}NH_2$
3106	18.018	55.985	3119	16.95	58.73	3146	10.43	47.39	ν_{asy}C-H of CH_3
3078	13.065	86.138	3094	8.64	80.90	3097	6.80	82.42	ν_{asy}C-H of CH_3
3027	22.092	228.833	3037	12.14	220.89	3043	4.48	221.69	ν_{sy}C-H of CH_3
1651	357.332	25.368	1636	577.60	21.38	1642	647.04	5.69	$\delta NH_2 + \nu$ C-C
1484	7.609	8.808	1477	8.04	8.04	1472	76.85	1.73	ν_{ring}C=N
1150	2.576	5.915	1147	1.48	5.84	1095	8.06	0.63	ρNH_2
1058	3.746	0.063	1057	5.45	0.08	1017	9.58	0.89	Ring breathing
1026	11.153	2.840	1020	1.55	4.15	1008	0.22	0.17	Triogonal bend + ρCH_3

TABLE-5
COMPARISON OF GEOMETRICAL PARAMETERS (BOND LENGTH AND BOND ANGLE) OF 2-AMINO-4-METHYLPYRIDINE, 2-AMINO-4-METHYLPYRIMIDINE AND 2-AMINO-4-METHYLTRIAZINE

2-Amino-4-methylpyridine		2-Amino-4-methylpyrimidine		2-Amino-4-methyltriazine	
Parameter	Bond length (Å)	Parameter	Bond length (Å)	Parameter	Bond length (Å)
C2-C3	1.4092	N1-C2	1.3460	C2-N1	1.3462
C2- N1	1.3365	N1-C6	1.3304	C2-N3	1.3472
C2-N7	1.3838	C2-N3	1.3427	C2-N7	1.3506
C3-C4	1.3872	C2-N7	1.3651	C4-N3	1.3314
C3-H9	1.0852	N3-C4	1.3365	C4-N5	1.3460
C4-C5	1.4046	C4-C5	1.3978	C4-C8	1.4994
C4-C8	1.5072	C4-C8	1.5037	C6-N1	1.3279
C5-C6	1.3865	C5-C6	1.3912	C6-N5	1.3324
C5-H10	1.0839	C5-H10	1.0818	C6-H9	1.0872
C6-N1	1.3383	C6-H9	1.0871	N7-H10	1.0056
C6-11H	1.0868	N7-H11	1.0062	N7-H11	1.0055
C8-H14	1.0916	N7-H12	1.0062	C8-H12	1.0932
C8-H15	1.0942	C8-H14	1.0932	C8-H13	1.0932
C8-H16	1.0941	C8-H13	1.091	C8-H14	1.0886
N7-H12	1.0094	C8-H15	1.0932	–	–
N7-H13)	1.0077	–	–	–	–
Parameter	Bond angle (°)	Parameter	Bond angle (°)	Parameter	Bond angle (°)
C3-C2-N1	122.6572	C2-N1-C6	115.4252	N1-C2-N3	125.0648
C3-C2-N7	120.9814	N1-C2-N3	126.4338	N1-C2-N7	117.5718
N1-C2-N7	116.3237	N1-C2-N7	116.7013	N3-C2-N7	117.3634
C2-C3-C4	119.4615	N3-C2-N7	116.8533	N3-C4-N5	124.743
C2-C3-H9	119.9915	C2-N3-C4	117.0369	N3-C4-C8	118.0893
C4-C3-H9	120.5449	N3-C4-C5	121.1685	N5-C4-C8	117.1677
C3-C4-C5	117.6963	N3-C4-C8	116.6103	N1-C6-N5	126.7368
C3-C4-C8	121.3971	C5-C4-C8	122.2211	N1-C6-H9	116.4559
C5-C4-C8	120.9064	C4-C5-C6	116.7412	N5-C6-H9	116.8073
C4-C5-C6	118.5719	C4-C5-H10	121.7868	C2-N1-C6	113.8338
C4-C5-H10	121.0781	C6-C5-H10	121.4709	C2-N3-C4	115.1654
C6-C5-H10	120.3501	N1-C6-C5	123.1887	C4-N5-C6	114.4561
C5-C6-N1	124.2271	N1-C6-H9	116.0403	C2-N7-H10	119.5039
C5-C6-11H	120.2339	C5-C6-H9	120.7709	C2-N7-H11	119.5307
N1-C6-11H	115.5384	C2-N7-H11	117.8381	H10-N7-H11	120.9654
C2-N1-C6	118.1421	C2-N7-H12	117.7515	C4-C8-H12	109.7218
C2-C5-C6	117.3843	H11-N7-H12	119.0675	C4-C8-H13	109.7159
C4-C8-H15	111.6017	C4-C8-H14	109.9751	C4-C8-H14	110.7369
C4-C8-H14	110.8559	C4-C8-H13	111.7685	H12-C8-H13	106.9146
C4-C8-H16	110.8281	C4-C8-H15	109.9538	H12-C8-H14	109.8433
H14-C8-H15	108.1145	H14-C8-H13	108.9749	H13-C8-H14	109.8307
H14-C8-H16	108.0964	H14-C8-H15	107.0883	–	–
H15-C8-H16	107.1781	H13-C8-H15	108.9572	–	–
C2-N7-H12	114.4836	–	–	–	–
C2-N7-H13	117.7444	–	–	–	–
H12-N7-H13	115.1245	–	–	–	–

TABLE-6
COMPARISON OF BOND PARAMETERS IN 2-AMINO-4-METHYLPYRIDINE (AMP), 2-AMINO-4-METHYLPYRIMIDINE (AMPM) AND 2-AMINO-4-METHYLTRIAZINE (AMT)

Bond length	AMP	AMPM	AMT
C2-N7	1.3838	1.3651	1.3506
C4-C8	1.5072	1.5037	1.4994
N1-C2	1.3365	1.3461	1.3462
N1-C6	1.3383	1.3304	1.3279

triazine. In 2-amino-4-methylpyridine, the exo-angles C2-N7-H12 (114°) and C2-N7-H13 (117°) are observed. Although both the H12 and H13 are attached to the same N7, the H12 is in the proximity of ring C4, whereas H13 is in the proximity of ring N1 and hence due to the repulsion between lone pair – bond pair [24] which increases the bond angle in C2-N7-H13 (117°). But in 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine, both the hydrogens are in the same situation and hence the variation in exo-angles are not seen in these two cases (Table-5).

Comparison of Mulliken charges: The calculation of effective atomic charges of a molecular system plays an important role in *ab initio* computation and past studies show that Mulliken populations yield one of the simplest pictures of charge distribution in the molecule [25]. The electron distribution in the chosen molecules are studied and the calculated Mulliken charges are given in Table-7. It is found that the negative charge of N1 is more in the case of pyridine moiety as the lone pair of electrons are not under the influence of repulsion as seen in the cases of 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine. In case of 2-amino-4-methyltriazine though there are three nitrogen atoms, they are symmetrical and so the repulsion is reduced considerably in comparison with pyrimidine which is not symmetrical and hence there is less negative charge of N1 in pyrimidine. Using a similar line of thought the nature of charge distribution among all atoms in the chosen molecules can be understood.

TABLE-7
COMPARISON OF MULLIKEN ATOMIC CHARGES

Atom No.	AMP	Atom No.	AMPM	Atom No.	AMT
C2	-0.578616	C2	-0.022653	C2	-0.017245
C3	0.366808	N3	-0.1330992	C4	-0.114243
C4	0.226397	C4	0.108405	C6	0.064461
C5	-0.174617	C5	-0.052956	N3	-0.086547
C6	-0.291434	C6	-0.188824	N5	-0.089890
N1	-0.139136	N1	-0.198753	N1	-0.162104
N7	-0.275371	N7	-0.274388	N7	-0.278205
C8	-0.588422	C8	-0.618396	H10	0.256084
H9	0.148255	H9	0.187052	H11	0.267106
H10	0.168672	H10	0.161909	C8	-0.559095
H11	0.174535	H14	0.148538	H12	0.179033
H14	0.147003	H11	0.275333	H13	0.160212
H15	0.157331	H12	0.269983	H14	0.163957
H16	0.157770	H13	0.167299	H9	0.216476
H12	0.266408	H15	0.168442	–	–
H13	0.234419	–	–	–	–

AMP = 2-Amino-4-methylpyridine; AMPM = 2-Amino-4-methylpyrimidine; AMT = 2-Amino-4-methyltriazine

Comparison of thermodynamical properties: The total energy in these molecules (Table-8) are found to decrease from pyridine to triazine and hence the value is found to be less in the case of triazine and so this molecule is more stable. The same trend is seen in zero point energy values and molar capacity values too. Entropy is the measure of disorder and the value is found to be less in the case of 2-amino-4-methyltriazine proving its symmetrical structure and more in the case of 2-amino-4-methylpyrimidine proving its unsymmetrical nature. The dipole moment of aromatic compounds are influenced by the position and nature of the substituents on the benzene ring. The factors like atomic radius, type of hybridization, the polarizability of the non-bonding electrons and the mobile electrons also influence the dipole moment [26]. 2-Amino-4-methylpyrimidine which is the most asymmetry in nature has the least dipole moment value (0.9413 D) due to the lone pair

TABLE-8
COMPARISON OF THERMO-CHEMICAL PROPERTIES

Parameters	2-Amino-4-methylpyridine	2-Amino-4-methylpyrimidine	2-Amino-4-methyltriazine
Dipole moment (Debye)	2.3322	0.9413	2.1266
Total energy (au)	-343.06754963	-359.12223527	-375.17587996
Zero point energy (kcal mol^{-1})	83.04394	75.69089	68.28301
Entropy (cal mol^{-1} k^{-1})			
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	22.291	21.434	20.496
Rotational temperature (K)			
	0.19445	0.18291	0.19445
	0.09475	0.09401	0.09475
	0.06423	0.06262	0.06423
Rotational constants (GHz)			
	3.87932	3.81122	4.05171
	1.80278	1.95882	1.97435
	1.24122	1.30469	1.33842
Thermal energy (Kcal/mol)			
Translational	39.949	39.977	40.004
Rotational	28.006	27.892	27.798
Vibrational	17.048	16.687	19.485
Molar capacity at constant volume (cal/mol K)			
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	85.947	78.553	71.245

moment (orbital moment) and the vector nature of the dipoles. The other two molecules 2-amino-4-methylpyridine and 2-amino-4-methyltriazine has nearby values (2.3322 D and 2.1266 D). As the dipole moment is more in these two molecules, the inter-molecular interactions are stronger due to the dipole-dipole interactions which occur inside the molecule. Thermal energy is found to increase from 2-amino-4-methylpyridine to 2-amino-4-methyltriazine as the molecular weight of these molecules increases.

Comparison of HOMO-LUMO values: The HOMO, LUMO and HOMO-LUMO energy gap have been calculated for these molecules and given in Table-9. The conjugated molecules are characterized by a highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of intermolecular charge transfer (ICT) from the electron-donor to the efficient electron acceptor group through π-conjugated path. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gap between the HOMO and the LUMO molecular orbitals is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. Associated within the framework of SCF MO theory the ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as $I = -E_{HOMO}$ and $A = -E_{LUMO}$. The hardness corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO energy gap the harder the molecule. The global hardness, $\eta = 1/2(E_{LUMO}–E_{HOMO})$. The hardness has been associated with the stability of chemical system. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $\mu = 1/2(E_{HOMO} + E_{LUMO})$. The global electrophilicity index, $\omega = \mu^2/2\eta$ is also calculated and listed in Table-9. Chemical hardness is associated with the stability and reactivity of a chemical system and it measures the resistance to change in the electron distribution or charge transfer [27]. One can also relate the stability of the molecule to hardness, which means that the molecule with least HOMO. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intramolecular charge transfer and bioactivity of the molecule. Since the energy gap is found to be more for 2-amino-4-methyltriazine molecule than 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine (Fig. 7) and hence 2-amino-4-methyltriazine is more stable among the three molecules.

TABLE-9
COMPARISON OF HOMO, LUMO ENERGY GAPS
AND RELATED MOLECULAR PROPERTIES

Molecular properties	AMP	AMPM	AMT
E_{HOMO}	-0.02476	-0.04241	-0.04675
E_{LUMO}	-0.22198	-0.23662	-0.26536
HOMO-LUMO energy gap	0.19722	0.19421	0.21861
Global hardness (η)	-0.09861	-0.09711	-0.10931
Electronic chemical potential (μ)	-0.12337	-0.13952	-0.15606
Global electrophilicity (ω)	-0.07717	-0.10022	-0.1114

AMP = 2-Amino-4-methylpyridine; AMPM = 2-Amino-4-methylpyrimidine; AMT = 2-Amino-4-methyltriazine

Comparison of molecular polarizability: Many organic molecules, containing conjugated π electrons are characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum were weak in the IR spectrum and *vice versa*. But the intermolecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. One of the objectives of the present investigation is to study the effect of polarizability and these values are given in Table-10. Mean polarizability <α> is found to be more for 2-amino-4-methylpyridine molecule. Using the x, y and z components, the magnitude of the dynamic first hyperpolarizability β can be calculated and these values are given in Table-11. To study

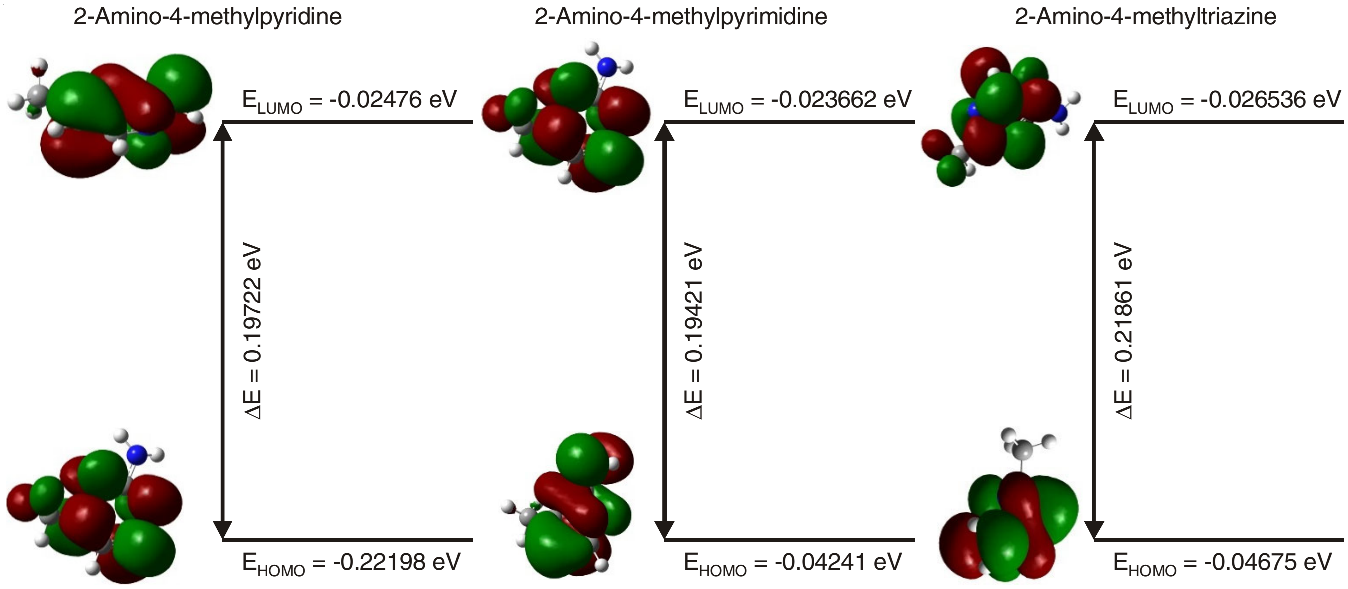

Fig. 7. Frontier molecular orbitals of 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine

TABLE-10
COMPARISON OF POLARIZABILITY VALUES

Polarizability	AMP	AMPM	AMT
α_{XX}	112.673531	105.035365	99.6622269
α_{XY}	-5.13296211	-3.86098761	4.50579862
α_{YY}	95.3198964	90.7964271	81.3361737
α_{XZ}	-0.305809658	-0.162964338	0.00272302305
α_{YZ}	0.175571217	0.159325355	-0.000968204826
α_{ZZ}	53.8872923	50.6533149	46.7709231
$\langle\alpha\rangle$	87.29357323	82.161702333	75.92311

AMP = 2-Amino-4-methylpyridine; AMPM = 2-Amino-4-methylpyrimidine; AMT = 2-Amino-4-methyltriazine

TABLE-11
COMPARISON OF HYPER POLARIZABILITY VALUES

Hyper polarizability	AMP	AMPM	AMT
β_{XXX}	-132.015869	-128.548972	60.5810789
β_{XXY}	203.364731	185.539625	178.899950
β_{XYY}	-91.0438495	-97.5524995	47.5777091
β_{YYY}	-34.7872162	-38.1232051	-59.4788697
β_{XXZ}	13.4356273	7.77071290	0.00112360563
β_{XYZ}	-2.81955173	-3.63526349	-0.0219290528
β_{YYZ}	2.53482293	3.29544573	-0.0468116743
β_{XZZ}	-16.8757859	-11.3703985	-4.43074731
β_{YZZ}	16.9655691	-5.14233943	-10.8723624
β_{ZZZ}	9.91675079	2.54458668	0.0725222424
β_{TOTAL} (e.s.u)	2.5477×10^{-30}	2.3197×10^{-30}	2.0285×10^{-30}

AMP = 2-Amino-4-methylpyridine; AMPM = 2-Amino-4-methylpyrimidine; AMT = 2-Amino-4-methyltriazine

the NLO properties of a molecule, the value of urea molecule which is a prototypical molecule is taken as threshold value for the purpose of comparison. The first polarizability value of all the present molecules (2.5477×10^{-30}, 2.3197×10^{-30} and 2.0285×10^{-30} e.s.u) are found to be greater than urea (β for urea is 0.3728×10^{-30} e.s.u) [28] and hence the compounds under investigation are assumed to be good NLO materials. The hyper polarizability value is found to be more for 2-amino-4-methylpyridine and 2-amino-4-methyl-pyrimidine molecules inferring their non-linear prosperity. The high hyperpolarizability value of 2-amino-4-methylpyridine and 2-amino-4-methylpyrimidine make them for the use of NLO devices in optical computing, telecommunications and optical signal processing. The theoretical calculation of β components is very useful as this clearly indicates the direction of charge delocalization. The largest β_{zzz} value of 2-amino-4-methylpyridine indicates charge delocalization is perpendicular to the bond axis and the involvement of π orbitals in intra-molecular charge transfer process.

Conclusion

Thus, *ab initio* computation (DFT/B3LYP) is proved to be a powerful tool for the Quantum chemical calculations of energies, geometrical structure, harmonic vibrational frequencies and bonding features in the heterocyclic compounds of 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine. For the first time, some of the physical and chemical properties like bond parameters, atomic charges, electronic properties, dipole moment, Mulliken charge, thermodynamic properties, HOMO-LUMO analysis, *etc.* have been compared and analyzed the difference in these properties due to the structural difference in the heterocyclic compounds of 2-amino-4-methylpyridine, 2-amino-4-methylpyrimidine and 2-amino-4-methyltriazine using quantum computational methods. In this present *ab initio* calculation, it is found that among the present compounds, comparatively 2-amino-4-methyl-pyrimidine possesses more asymmetry. 2-Amino-4-methylpyridine and 2-amino-4-methylpyrimidine are almost equally soft molecules, more reactive and can offer electrons easily to the acceptors. 2-Amino-4-methyltriazine is symmetrical, chemically hard, more stable and less reactive. In conclusion, these theoretical calculations and simulations not only provide a lot of useful information to the chemists but also aid the researchers in the field of biology and pharmaceuticals to build a good relationship between structures and properties of these compounds through theoretical analysis.

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