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Archives of Physics Research, 2013, 4 (3):67-77
(http://scholarsresearchlibrary.com/archive.html)

ISSN : 0976-0970
CODEN (USA): APRRC7

The Vibrational Spectroscopic (FT-IR & FTR) study and HOMO & LUMO analysis of 6-Methyl Quinoline using DFT Studies

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ABSTRACT

Solid phase FTIR and FT-Raman spectra of 6-Methyl Quinoline (6MQ) have been recorded in the region 3400-50 cm^{-1}. The spectra were interpreted with aid of normal coordinate analysis based on DFT using standard B3LYP/6-311++G (d, p) basis set. After scaling there is good agreement between the observed and the calculated frequencies. The calculated first order hyperpolarizability shows that the molecule is an attractive molecule for future applications in non linear optics. The calculated Homo-Lumo energies show that charge transfer occurs within the molecule. Mullikan population analysis on atomic charges is also calculated. The study is extended to study the thermodynamic properties of 6MQ.

Keywords: 6-Methylquinoline, Vibrational analysis, FTIR, FTR, DFT calculation, Homo-Lumo analysis, thermodynamical properties, Gaussian 09.

INTRODUCTION

Quinolines are heterocyclic compounds having the combination of pyridine and benzene rings [1]. When a methyl group replaces hydrogen attached to the quinoline ring in sixth position then it is called as 6-methylquinoline [6MQ]. The derivatives of methyl quinolines have many applications [2-4], for e.g., 2-methylquinoline is used as an intermediate in the production of dyes and in food coloring. 7-methylquinoline is used to inhibit corrosion in steel.8-Methylquinoline has been used to treat human and animal skin disorders and also as intermediate for pharmaceutical manufactures .The title molecule 6MQ is used in fragrances for soaps, perfumes and creams and also used as an intermediate in pharmaceutical manufactures [5].

A large number of works has been reported in the literature dealing with vibrational analysis of methyl derivatives of quinoline [6-12]. Yusuf ZALAOGLU et al had reported vibration studies of 6-methyl-1,2,3,4-tetrahydroquinoline[11] and the structure and vibrational spectra of 2,4–diaminoquinoline and 4-Amino-2-methylquinoline were recorded by V. and Krishnakumar John Xavier[13]. The total energy distribution of 2-,4-,6-methyl quinoline had been discussed in detail by Aysen E.Ozel [12] only based on theoretical work but not experimentally. The present research work was undertaken to study the vibrational modes and also to carry out HOMO-LUMO, Polarizability, Hyper polarizability, Mullikan's charge density and thermodynamical properties for the title molecule.

MATERIALS AND METHODS

Experimental setup and measurements

2.1 Spectral details

The fine sample of 6MQ provided by the Sigma Aldrich Chemical Co.(USA), with a stated purity of greater than 98%, was used as such for the spectral measurements. At the room temperature a Fourier transform IR spectrum of the title compound was measured in 3700-100 cm^{-1} region at a resolution of ± 2 cm^{-1} using Bruker IFS -66V Fourier transform spectrometer. The FT-Raman spectrum of 6MQ was recorded on the same instrument equipped with an FRA -106 FT–Raman accessory. The spectrum was recorded in the 4000-50 cm^{-1} with Nd: YAG laser operating at 200 mW power. The reported wave numbers are expected to be accurate within ± 2 cm^{-1}.

2.2 Computational Details

Using the version of Gaussian 09W (revision B.01) program, the DFT calculations of the title compound were carried out on intel core2 duo /2.20 Ghz processor. Becke-3-lee-yang-parr (B3LYP) functions were used to carry out ab-initio analysis with the standard 6-311++G and 6-311++G(d.p) basis sets. The normal coordinate analysis of the compound 6-methylquinoline has been computed at the fully optimized geometry by assuming c_1 point group symmetry. 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.

The animation option of the Gauss view 05 graphical interface for Gaussian program was employed for the proper assignment of the title compound and to check whether the mode was pure or mixed. The idea of using multiple scale factors in the recent literature (17, 18) has been adapted for this study and it minimized the deviation between the computed and the experimental frequencies. Most of the scale factors are much closer to the unity for DFT studies which implies that DFT B3LYP/6-311++G (d, p) computations yield results much closer to the experimental values.

RESULTS AND DISCUSSION

3.1 Molecular Geometry

The optimized molecular geometry of 6MQ obtained by the DFT computational analysis is shown in Figure (i). The optimized geometrical parameters of 6MQ are presented in Table (i).

In this title compound C7-C6, C8-C10, C9-C5, C9-C4, C2-C2 bond lengths are found to be about 1.42 Å and they are found to be coincident with values shown by Singh Rajeev et al [19]. C9-N1 and C2-N1 bond lengths are 1.354 and 1.2916 Å respectively. The inner bond angles of C8-C9-C10, C9-C10-C5 and C10-C4-C3 are found to be 119^0 and the outer bond angles of C8-C7-H16, C6-C7-H16, C7-C6-C11, C10-C4-H14, C2-C3-H13 and C3-C2-H12 are also found to be same as inner angle. The methyl group attached to the ring shows deviation angle as 108^0.The bond angles C9-N1-C2 which calculated as 118^0 by DFT methods are higher than methyl group angle. The dihedral angles of C9-C10-C4-H14, C10-C4-C3-C14 and C4-C3-C2-H12 are 180^0 which suggest that the title molecule is a planar molecule.

Fig (i) : The molecular structure of 6-methyl Quinoline

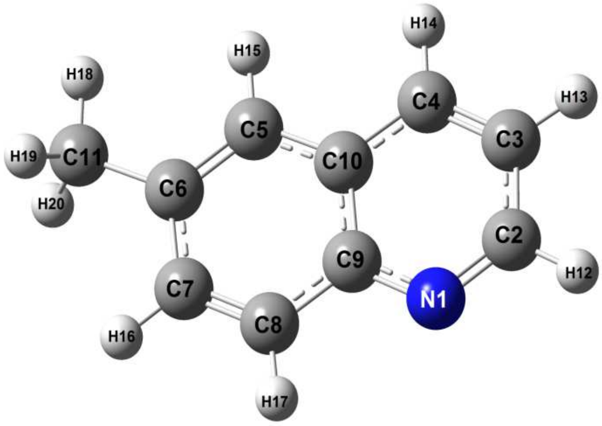

Table (i) : Optimized geometrical parameters of 6-methylquinoline obtained from B3LYP (6-311++G) density functional calculations.

Parameters	DFT(B3LYP) 6-311++G(d,p)	Parameters	DFT(B3LYP) 6-311++G(d,p)
Bond length (Å)		**Dihedral angle (°)**	
C_7-C_8	1.3718	C_6-C_7-C_8-C_9	0.000
C_7-C_6	1.4237	C_6-C_7-C_8-H_{17}	-180.000
C_7-H_{16}	1.0857	H_{16}- C_7-C_8-C_9	-180.000
C_8-C_9	1.419	H_{16}-C_7-C_8-H_{17}	0.000
C_8-H_{17}	1.0836	C_8-C_7-C_6-C_5	0.000
C_{10}-C_9	1.4282	C_8-C_7-C_6-C_{11}	-180.000
C_9-N_1	1.3631	H_{16}-C_7-C_6-C_5	180.000
C_{10}-C_5	1.4194	H_{16}-C_7-C_6-C_{11}	0.001
C_{10}-C_4	1.4161	C_7-C_8-C_9-C_{10}	0.000
C_5-C_6	1.3768	C_7-C_8-C_9-N_1	180.000
C_5-H_{15}	1.0862	H_{17}-C_8-C_9-C_{10}	-180.000
C_6-C_{11}	1.5081	H_{17}-C_8-C_9-N_1	0.000
C_4-C_3	1.3729	C_8-C_9-C_{10}-C_5	0.000
C_4-H_{14}	1.0855	C_8-C_9-C_{10}-C_4	180.000
C_3-C_2	1.4157	N_1-C_9-C_{10}-C_5	180.000
C_3-H_{13}	1.0837	N_1-C_9-C_{10}-C_4	0.000
C_2-H_{12}	1.0876	C_8-C_9-N_1-C_2	-180.000
C_2-N_1	1.3155	C_{10}-C_9-N_1-C_2	0.000
C_{11}-H_{18}	1.0947	C_9-C_{10}-C_5-C_6	0.000
C_{11}-H_{19}	1.0947	C_9-C_{10}-C_5-H_{15}	-180.000
C_{11}-H_{20}	1.0916	C_4-C_{10}-C_5-C_6	-180.000
Bond angle (°)		C_4-C_{10}-C_5-H_{15}	0.000
C_8-C_7-C_6	121.648	C_9-C_{10}-C_4-C_3	0.000
C_8-C_7-H_{16}	119.565	C_9-C_{10}-C_4-H_{14}	180.000
C_6-C_7-H_{16}	118.787	C_5-C_{10}-C_4-C_3	180.000
C_6-C_5-C_{10} C7-C8-C9	120.534	C_5-C_{10}-C_4-H_{14}	0.000
C_7-C_8-H_{17} C7-C8-H17	121.641	C_{10}-C_5-C_6-C_7	0.000
C_9-C_8-H_{17}	117.825	C_{10}-C_5-C_6-C_{11}	180.000
C_8-C_9-C_{10}	118.467	H_{15}-C_5-C_6-C_7	180.000
C_8-C_9-N_1	118.890	H_{15}-C_5-C_6-C_{11}	-0.001
C_{10}-C_9-N_1	122.644	C_7-C_6-C_{11}-H_{18}	-59.544
C_9-C_{10}-C_5	119.370	C_7-C_6-C_{11}-H_{19}	59.546
C_9-C_{10}-C_4	117.324	C_7-C_6-C_{11}-H_{20}	-179.999
C_5-C_{10}-C_4	123.306	C_5-C_6-C_{11}-H_{18}	120.457
C_{10}-C_5-C_6	121.480	C_5-C_6-C_{11}-H_{19}	-120.453
C_{10}-C_5-H_{15}	118.502	C_5-C_6-C_{11}-H_{20}	0.002
C_6-C_5- H_{15}	120.018	C_{10}-C_4-C_3-C_2	0.000
C_7-C_6-C_5	118.502	C_{10}-C_4-C_3-H_{14}	-180.000
C_7-C_6-C_{11}	119.691	H_{14}-C_4-C_3-C_2	-180.000
C_5-C_6-C_{11}	121.807	H_{14}-C_4-C_3-H_{13}	0.000
C_{10}-C_4-C_3	119.335	C_4-C_3-C_2-H_{12}	180.000
C_{10}-C_4-H_{14}	119.579	C_4-C_3-C_2-N_1	0.000
C_3-C_4-H_{14}	121.086	H_{13}-C_3-C_2-H_{12}	0.000
C_4-C_3-C_2	118.790	H_{13}-C_3-C_2-N_1	-180.000
C_4-C_3-H_{13}	121.423	C_3-C_2-N_1-C_{10}	0.000
C_2-C_3-H_{13}	119.787	H_{12}-C_2-N_1-C_{10}	180.000
C_3-C_2-H_{12}	119.589		
C_3-C_2-N_1	124.047		
H_{12}-C_2-N_1	116.364		
C_9-N_1-C_2	117.860		
C_6-C_{11}-H_{18}	111.086		
C_6-C_{11}-H_{19}	111.086		
C_6-C_{11}-H_{20}	111.480		
H_{18}-C_{11}-H_{19}	107.087		
H_{18}-C_{11}-H_{20}	107.959		
H_{19}-C_{11}-H_{20}	107.959		

3.2 Assignment of Spectra

The detailed analysis of the fundamental modes of vibration with FTIR and FT Raman experimental frequencies, IR intensity and Raman activity of 6MQ using B3LYP method with 6-311++G (d, p) basis set is reported in Table (ii). Since 6MQ has 20 atoms, it is expected to exhibit 54 normal modes of vibrations (3N-6). Of these, 37 (2N-3) vibrations are planar (A') and 17 (N-3) vibrations are non-planar (A''). For visual comparison, the experimental spectra and simulated spectra in the infrared region are shown in Figure (ii) and the corresponding Raman spectra

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are given in Figure (iii). Even though the calculated vibrational frequencies are scaled down by the appropriate multiple scale factors to suit the experimental values, it may be noted that the simulated IR and Raman spectra are drawn for unscaled frequencies. The correlation diagram between the scaled and the experimental frequencies of the 6MQ shown in the Figure (iv) illustrates the resultant reduced deviation between the experimental and calculated vibrational frequencies.

Fig (ii) : Comparison of observed and simulated Infrared spectra of 6-methylquinoline

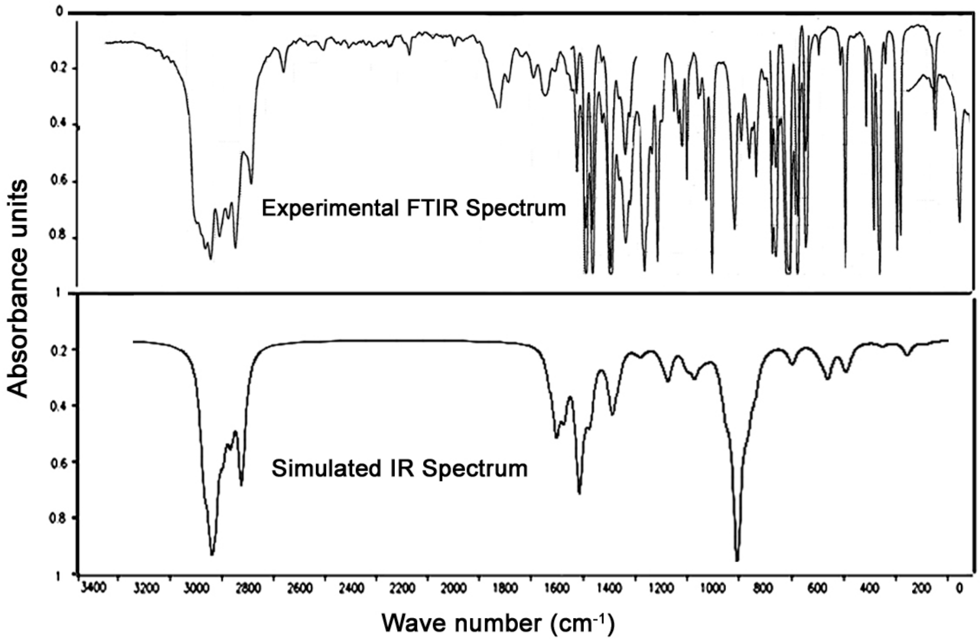


Fig (iii) : Comparison of observed and simulated Raman spectra of 6-methyl quinoline

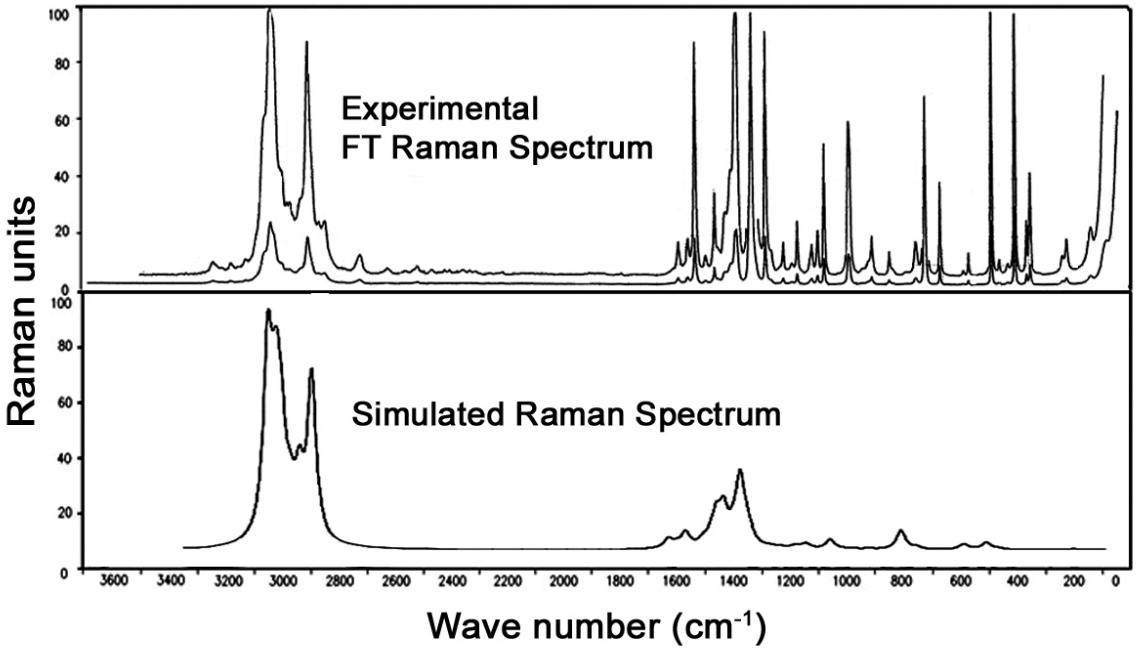


Table (ii) : Experimental and Calculated Frequencies, IR & Raman intensities and assignments for 6-Methylquinoline

Mode of Vibrations.	Observed frequency (cm^{-1})				Calculated frequency(cm^{-1}) B3LYP /6311++G(d,p)				Assignment
	IR		Raman		Unscaled	Scaled	IR Intensity	Raman Activity	
1			3161	W	3192	3160	54.253	0.013	ν_s CH
2	3140	W			3187	3155	2.06	0.032	ν_s CH
3			3082	S	3161	3098	0.163	0.033	ν_s CH
4			3057	VS	3158	3063	6.29	0.034	ν_s CH
5	3027	VS			3152	3026	8.43	0.034	ν_{as} CH
6	3008	VS	2985	S	3137	3011	0.663	0.039	ν_{as} CH
7	2968	VS			3104	2979	3.719	0.143	ν_{as} CH (CH_3)
8	2936	S	2924	VS	3069	2946	3.467	0.157	ν_{as} CH (CH_3)
9	2912	VS			3022	2900	0.004	0.161	ν_s CH (CH_3)
10			1665	M	1666	1663	0.116	0.162	ν CC
11	1623	M	1625	VW	1635	1618	12.732	0.166	ν CC+C-N
12	1579	VS	1571	VS	1601	1584	9.967	0.275	ν CC+ β CH
13	1546	VS			1534	1533	1.07	0.402	δ_{as} C-H of CH_3+νCC
14	1500	M			1507	1507	5.112	0.495	δ_{as} C-H of CH_3+νCC
15			1499	W	1486	1485	6.718	0.621	δ_{asy} CH_3
16	1485	VS			1485	1484	0.081	0.662	δ_{asy} CH_3 + C=N
17	1442	VS			1456	1440	2.564	0.747	CC + CN + δ_{asy} CH_3
18			1423	VS	1416	1416	5.28	0.859	δ_{asy} CH_3
19			1380	VS	1394	1380	2.159	1.085	δ CC + β CH
20	1361	VS			1385	1357	3.023	1.611	CC_{sy}+δ CH + δ_{sy} CH_3
21	1337	M	1322	VS	1361	1334	0.084	1.646	CCC + β CH
22	1295	VS			1285	1285	1.169	1.684	β CH + νC-N
23	1249	W	1255	VW	1263	1250	2.658	1.855	β CH + νC-N
24	1233	M			1239	1239	2.296	2.359	CCC+ β CH + νC-N
25	1177	S			1187	1174	0.77	2.588	β CH
26	1159	M	1140		1165	1152	0.693	2.86	β CH
27	1110	VS		S	1141	1141	0.045	4.843	R_{symd}+CC str
28			1043	VS	1063	1062	0.64	5.127	ν C-CH_3+ν CC+ β C-N-C
29			1023	VS	1051	1026	19.475	6.761	R1asymd
30			1021	M	1024	1024	3.429	8.759	symdCH_3
31	995	M	1007	M	992	991	8.546	9.696	γ CH + β CH+ CCC
32			978	M	987	977	7.37	10.534	γ CH + β CH+ CCC
33	967	M			967	967	0.338	10.814	R_{symd}+ CH wagging
34	943	M	949	VW	961	942	34.98	12.238	CH of R2
35	893	VS	891	w	906	897	0.126	14.64	R_{symd}(Ring breathing)
36	863	VS			893	892	4.792	18.84	R2symdef + ν C-CH_3
37	820	VS			849	832	1.645	19.705	ω CH + γ CCC
38	799	VS	793	VS	808	791	0.888	25.682	ω CH + γ CCC
39	782	VS			781	781	5.235	28.944	ω CH + β CNC + β C-N-C
40			703	M	778	703	13.146	31.313	ω CH
41	675	vw			723	694	1.08	39.86	νC-CH3 +R_{asymd}
42			635	VW	646	639	10.032	42.014	νC-H + β CC
43	615	VS			631	611	7.102	50.04	R_{asymd}
44	525	M	538	VW	544	538	15.974	67.213	R_{symd} + CCC
45			508	VS	517	506	12.419	69.22	CC + ω CH
46	498	VS	485	VS	489	488	0.46	71.315	CC + ω CH
47	451	VW	452	VW	457	452	12.452	93.132	γ CCC
48			421	VS	420	419	6.4	103.193	γ CC
49	408	VS	395	M	408	408	10.84	103.989	γ CCC + R2-symd
50			280	W	284	284	15.836	116.045	δas C-CH_3
51	269	M	266	VW	271	270	6.309	149.701	t CH_3
52	172	S	185	W	174	173	23.436	159.731	Butterfly
53	126	M			126	125	18.993	247.113	t CH_3
54	94	S			97	95	33.522	344.662	τ CH3

vs– *Very strong;* ***s*** *– strong;* ***m*** *– medium;* ***w*** *– weak;* ***vw*** *– very weak*
ν_{as} *– asymmetric stretching;* ν_{sym} *– symmetric stretching;* ***δ*** *– scissoring; ρ – rocking;*
τ*–torsion;* ***t****–twisting; β – in-plane bending; γ – out-of-plane bending;*
symd *– symmetric deformation,* ***asymd*** *– assymmetric deformation*

3.2.1Methyl Group Vibrations

The methyl group (CH_3) attached with the benzene ring at sixth position in the title molecule can have the following types of vibrations: symmetric and asymmetric stretching, symmetric and asymmetric scissoring, twisting, wagging and rocking. Sundaraganesan et al [20] verified that the CH_3 stretching vibration in pyridine ring occurs at lower frequencies than those of aromatic ring (3000-3100 cm^{-1}). The anti-symmetric stretching mode of CH_3 is expected around 2980 cm^{-1} and symmetric stretching mode of CH_3 is expected at 2870 cm^{-1} [21]. In line with these, the sharp peaks found in the FTIR at 3027 and 3008 cm^{-1} shows very strong asymmetric stretching vibrations of CH_3 whereas the band at 2924 cm^{-1} in FT Raman is assigned to symmetric stretching mode. These assignments found support from the normal modes of animation option of Gauss View 05 which indicates the theoretical three peaks at 3026, 3011 and 2946 cm^{-1} as the corresponding frequencies. These assignments are agreed well with the literature values [20-23].

For most of the compounds the asymmetric scissoring appears at fairly constant range of 1400-1460 cm^{-1}[24]. The vibrations observed at 1499 and 1423 cm^{-1} in Raman and 1485 and 1442 cm^{-1} in FTIR shows asymmetrical scissoring vibration and 1021 cm^{-1} seen in Raman is assigned to symmetrical scissoring vibration. The symmetrical scissoring mode falls little below the expected region and it may be because the symmetrical scissoring indicated by Alpert et al [21]. The correctness of the assignments was also verified with the Gauss view using the computed values.

The CH_3 rocking vibrations of the compound are identified at 967 cm^{-1} in the IR spectra .The rocking vibrations counterpart of 967 cm^{-1} is not observed in the FT Raman. CH_3 twisting modes are observed at 269 and 126 cm^{-1} in FTIR and at 94 cm^{-1}, it shows the CH_3 torsion mode of vibration. A very strong peak in Raman at 1043 cm^{-1} shows symmetric stretching mode of C-CH_3 and also scissoring asymmetric vibrations of C-CH_3 is identified at 280 cm^{-1} in Raman spectrum.

3.2.2 Ring Vibrations

C-N Vibrations

The presence of nitrogen in the ring of benzene structure gives rise to two C=N stretching vibrations and identifying these vibrations is a little hectic task as their vibrational frequency lies within the C-C stretching region [22,23]. Sundaraganesan [17] proposed C-N stretching vibrations in the region 1382-1266 cm^{-1} to C-N stretching vibrations in the compound 2-Amino-5-methyl pyridine. In the present work, the very strong vibration at 1485 cm^{-1} in IR shows symmetric C=N stretching vibration. Symmetric C-N stretching vibrations are found at 1295, 1249 and 1233 cm^{-1} for IR spectrum. Very strong vibrations of IR at 782 cm^{-1} and for Raman at 1043 cm^{-1} shows the in-plane bending of C-N-C vibrations. By invoking Gauss view visualization option, these vibrations are cross checked and found to be correct. The ab -initio calculations yielded 1484 cm^{-1} and 1285, 1250, 1239 cm^{-1} as scaled C=N and C-N stretching vibrations. The calculated frequencies for Raman and IR values of C-N-C vibrations are verified at 1043 and 782 cm^{-1}. These assignments are supported from the works of Sundaraganesan et al [24] and Peak et al [25].

C-H Vibrations

The hetero aromatic structure shows the presence of C-H asymmetric stretching vibrations in the region 3100-3000 cm^{-1} and 3100-2950 cm^{-1} is suggested for symmetric stretching modes of vibrations [26-29].

In the present exploration the symmetric stretching of aromatic C-H vibrations in Raman spectrum is found at the frequencies 3161, 3082, 3057 and 635 cm^{-1}. Similarly the symmetric stretching of C-H vibrations in FTIR is found at 3140 cm^{-1} and the C-H stretching vibrations corresponding to 3161, 3082 and 3057 cm^{-1} are found to be missing in the FTIR spectrum. The very strong asymmetric C-H stretching vibrations in FTIR spectrum are found in the frequencies 3027 and 3008 cm^{-1} and the corresponding asymmetric C-H stretching vibrations for the same are found to be missing in the Raman spectrum.

The theoretical computation gives the frequency values for symmetric and asymmetric C-H vibrations at 3160,3155,3098,3063 and 639 cm^{-1} and 3026 and 3011 cm^{-1} as indicated in Table 2. Generally, in the substituted benzene, apart from stretching vibrations some bending vibrations also can occur. These bending vibrations can also be obtained in two ways such as in- plane bending and out- of- plane bending. The in-plane C-H bending vibrations appears in the range 1300-1000 cm^{-1} and out- of- plane bending vibration occurs in the range of 1000-750 cm^{-1} [30].

The experimental frequencies of 6MQ at 1579,1295,1177,1159 and 995 cm^{-1} in FTIR spectrum show C-H in- plane bending vibrations. Similarly in FT Raman the frequency at 1255 and 978 cm^{-1} are assigned to C-H in- plane bending vibrations [31].

The types of vibrations like scissoring, rocking, torsion, twisting and wagging are identified as out-of- plane bending modes in vibrational spectroscopy. The scissoring vibrations of C-H bonds are identified at 1360 cm^{-1}. The very strong out of plane wagging vibrations of C-H are found at 820,799 and 782 cm^{-1} in FTIR spectrum and these kinds of wagging vibrations are assigned for the frequencies 485,508,703 and 949 cm^{-1} for FT Raman spectrum. Like these ring C-H vibrations, we can find some C-H vibrations in methyl group also and the frequencies at 2968 and 2936 cm^{-1} are assigned to asymmetric stretching of C-H in methyl group. The very strong symmetric vibrations of C-H in methyl group are found in 2912 cm^{-1} in FTIR spectrum. Similarly asymmetric scissoring modes of vibrations of C-H in the methyl group are found at the frequencies 1546, 1500 cm^{-1} in FTIR spectrum. These assignments support the calculated frequencies found at the frequencies of 2979, 2946, 2900 cm^{-1} and 1533, 1507 cm^{-1}.

C-C Vibrations

The C-C aromatic stretching vibrations give rise to characteristic bands in both the IR and Raman spectra covering the spectral range from 1600-1400 cm^{-1}[32-35].The IR bands at 1623, 1579, 1546 and 1500 cm^{-1} and the corresponding Raman bands at 1665 and 1380 cm^{-1} are in excellent agreement with experimental values.

The C-C-C in plane bending vibrations have given rise to weak bands across the low frequency region, That is to say, below 1000 cm^{-1} [36] and in line with this the very strong IR bands at 820 ,451,408 cm^{-1} and in Raman band at 793,421 cm^{-1} have been assigned to out –of-plane bending vibrations in the title molecule 6MQ [35] and the in-plane bending vibrations are observed at 995 cm^{-1} in FTIR and 978 and 635 cm^{-1} in Raman.

Apart from these ring vibrations, we can observe some kind of other vibrations for whole rings of the molecules in our present work. Ring symmetric deformations occur at the frequencies 1110,893,863,525 and 408 cm^{-1} in FTIR spectrum. This resembles the calculated frequencies 1141,897,892,538 and 408 cm^{-1} obtained from Gaussian. Similarly ring asymmetric deformations are found at 1023,675,615 cm^{-1} and gets support from the calculated values of 1051,723,631 cm^{-1}. The ring breathing and butterfly vibrations of 6MQ are being confirmed at the frequencies 893 and

172 cm^{-1} in IR spectrum and these frequency values are correlated with the calculated frequencies at 897 and173 cm^{-1}.

3.3 Non linear optical effects

The interactions of electromagnetic radiation in some molecules can give a non-linear optical (NLO) effect which shows the some alterations in- phase, frequency and amplitude from the incident field [37]. NLO is an important concept in current research scenario because of its vast applications to telecommunications, optical switching and signal processing [38-41].

The mean polarizability (α_0), the total static dipole moment (μ) and the first order hyper polarizability (β_0) are calculated by using x,y,z components.

$$\mu = (\mu x^2 + \mu y^2 + \mu z^2)^{1/2}$$

$$\alpha_0 = 1/3\,(\alpha xx + \alpha yy + \alpha zz)$$

$$\beta_0 = (\beta x2 + \beta_y^2 + \beta_z^2)^{1/2}$$

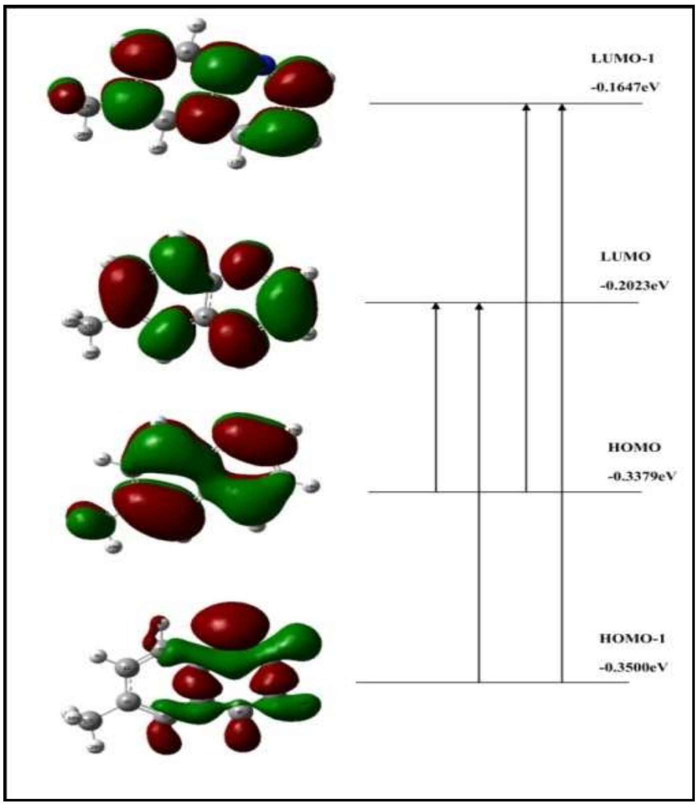
$$= [(\beta_{XXX} + \beta_{XYY} + \beta_{XZZ})^2 + (\beta YYY + \beta_{YXX} + \beta_{YZZ})^2 + (\beta_{ZZZ} + \beta_{ZXX} + \beta_{ZYY})^2]^{1/2}$$

The α and β values of the Gaussian 05 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u) (α : 1 a.u = 0.1482×10^{-24}esu; for β : 1 a.u =8.639×10^{-33} esu;) and these above polarizability values are listed in Table (iii). To study the NLO properties of molecule the value of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison. The first hyperpolarizability of the title molecule is found to be two times greater than the urea [μ and β of urea are 1.3732 Debye and $0.3728\times10^{-30} cm^5/esu$] [42] and from the resultant values we identify the title compound as a good NLO material. By knowing the dipole moment in a molecule we can study the dipole–dipole interactions which occur inside the atoms of that molecule and the inter-molecular interactions are getting stronger when the dipole moment is high.

Table (iii): The electric dipole moment, polarizability and first order hyperpolarizability of 6-methylquinoline.

Parameters	**DFT(B3LYP)6-311++G(d,p)**
β_{XXX}	269.982041
β_{XXY}	-35.0762567
β_{XYY}	-6.79988488
β_{YYY}	-5.35309903
β_{XXZ}	-0.00288419862
β_{XYZ}	-0.0000520944151
β_{YYZ}	0.000599396551
β_{XZZ}	-0.847327320
β_{YZZ}	0.133578615
β_{ZZZ}	-0.000491910495
β_{TOTAL} (e.s.u)	2.22130×10^{-30} e.s.u
α_{XX}	186.943504
α_{XY}	-6.21446537
α_{YY}	124.639710
α_{XZ}	-0.000956284994
α_{YZ}	0.000612208426
α_{ZZ}	67.7208876
α_0	126.4347 a.u

Fig (v) : Frontier molecular orbitals of 6-methylQuinoline.



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3.4 Frontier molecular orbital analysis:

The molecular orbital (MO) is an important concept in chemistry and molecular orbital theory is employed extensively to describe chemical behavior. Not only does the MO theory become a ubiquitous set of tools used to explain chemical behavior, such as reactivity and kinetics, but it also provides an indispensable conceptual construct for the description of other phenomenon involving molecular electronic structure including charge- transfer processes, photo excitation, magnetism, and molecular electronics. In fact, it is quite common to extract trends in molecular behavior based on simple MO properties. For example, molecules with large HOMO-LUMO gaps are generally stable and un reactive; while those with small gaps are generally reactive. Thus the stability of a molecule can be affected by the factors of total energy, dipole moment and energy gap between HOMO-LUMO levels. The computed values of HOMO-LUMO of 6mq are -0.33789 and -0.20228 respectively. The intra molecular charge transfer (ICT) from HOMO-LUMO occurs through π-conjugated path. Here LUMO is an electron acceptor and HOMO represents the ability to donate an electron. The energy gap is a parameter to determine the molecular electrical transport property because it is a measure of electron conductivity. The frontier orbital picture is given in

Figure (v).The filled orbital (HOMO) is located in the entire molecule except hydrogen atoms in 6MQ whereas the unfilled orbitals (LUMO) are localized except methyl and hydrogen atoms.

The larger the HOMO-LUMO energy gap the harder the molecule [46-50]. The global hardness is $\eta = ½ (\varepsilon_{LUMO}- \varepsilon_{HOMO})$. 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, $\mu=½ (\varepsilon_{LUMO} + \varepsilon_{HOMO})$. The global electrophilicity index, $\omega = \mu^2/2 \eta$ is also calculated and these values are listed in Table (iv).

Table (iv) : Calculated energy values of 6-methylquinoline in its ground state.

Molecular properties	**B3LYP/6-311++G(d,p)**
E_{LUMO+1} (eV)	**-0.1647**
E_{LUMO} (eV)	**-0.2023**
E_{HOMO} (eV)	**-0.3379**
E_{HOMO-1} (eV)	**-0.3500**
$\Delta E_{HOMO-LUMO}$ (eV)	**0.1357**
$\Delta E_{HOMO-LUMO+1}$ (eV)	0.1632
$\Delta E_{HOMO-1 - LUMO}$ (eV)	0.1477
$\Delta E_{HOMO-1 - LUMO+1}$ (eV)	0.1853
Global hardness(η)	0.0678
Electronic chemical potential(μ)	-0.2700
Global electrophilicity index(ω)	-0.1350

3.5 Mullikan's charge analysis

The atomic population and charge distribution in the molecule can be obtained from Mullikan's analysis and this charge distribution has been calculated by B3LYP/6-311 ++ G (d.p) level theory and the carbon atomic charges are found to be either positive or negative and they change from -0.008925 to 0.262847. The magnitudes of the hydrogen atoms have both positive and negative values and the nitrogen atom has high positive charge (0.044173) than other atoms and it acts as acceptor atom and 8C atom with maximum negative charge (-0.008925) acts as a donor atom. The atomic charge values for each atom are listed in Table (v).

Table (v) : Mulliken atomic charges of 6 Methylquinoline for B3LYP with 6-311++G(d,p) basis sets.

Atom with IUPAC Numbering	**B3LYP 6-311++G(d,p)**
1N	0.044173
2C	0.120229
3C	-0.441778
4C	0.275890
5C	-0.637699
6C	0.817536
7C	-0.182059
8C	-0.653169
9C	-1.862481
10C	1.566358
11C	-0.509805
12H	0.198459
13H	0.177357
14H	0.164348
15H	0.089657
16H	0.166165
17H	0.192509
18H	0.157024
19H	0.157028
20H	0.160258

2.6 Thermodynamic properties

On the basis of vibrational analysis of DFT studies at B3LYP/6-311++G and 6-311++G(d.p) levels some of the thermodynaimc parameters [51] are calculated and presented in Table (vi).These parameters are listed out based on the statistically thermodynamic functions : heat capacity(C), enthalpy changes(H) and entropy (S) for the title compound. The Zero point and total energy are also calculated for each function.

Table (vi) : Theoretically computed Dipole moment(Debye), energy(au), zero point vibrational energy(kcal mol^{-1}), entropy(cal mol^{-1}k^{-1}), rotational temperature(Kelvin), rotational constant(GHz), thermal energy(Kcal/Mol) and Molar capacity at constant volume(Cal/Mol-Kelvin)of 6-methylquinoline.

Parameters	**B3LYP-6-311++G**
Dipole moment	2.4064
Total energy	-441.35931841
Zero point energy	426080.1
Entropy	
Total	90.182
Translational	40.786
Rotational	29.716
Vibrational	19.680
Rotational temperature	
	0.13701
	0.04019
	0.03120
Rotational constants	
	2.85479
	0.83735
	0.65005
Thermal Energy	
Total	107.150
Translational	0.889
Rotational	0.889
Vibrational	105.372
Molar capacity at constant volume	
Total	34.048
Translational	2.981
Rotational	2.981
Vibrational	28.086

CONCLUSION

The equilibrium geometries of 6MQ were investigated and analyzed at DFT at B3LYP/6-311++G (d, p) level. The thermodynamic properties and Mullikan’s charges are also analyzed. The first order hyper polarizability and dipole moment results identified that the title compound is a good NLO material. The calculated Homo-Lumo energies show that charge transfer occurs within the molecule. Thus from the knowledge of the physical and chemical properties of these kinds of drug materials may lead to improve the properties of the tested molecules of the drugs by applying little modifications of the structure.

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