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QUANTUM MECHANICAL STUDY ON VIBRATIONAL AND ELECTRONIC TRANSITIONS, HOMO-LUMO, NBO, UV
AND NMR ANALYSIS OF (S)-3-AMINOMETHYL HEXONIC ACID

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ABSTRACT

(S)-3-aminomethyl hexonic acid (S3AMH) is a well known antiepileptic drug that controls epileptic seizures. In the present study FTIR and FT-Raman spectra of the drug S3AMH have been recorded for the identification of the functional groups. The structure, geometry optimization, vibrational frequencies and vibrational assignments have been made for the stable conformer of the molecule using semi empirical PM6 method, Abinito Restricted Hartree Fock (RHF), Density Functional theory based on Becke 3-lee-yang-parr (B3LYP) and (B3PW91) functional with standard 6-311++G(d,p) basis set. Detailed investigation of the observed fundamental vibrational frequencies of the molecule and calculated results by PM6, RHF, B3LYP and B3PW91 methods indicates that B3PW91 is superior for molecular vibrational problems. The HOMO and LUMO energy level, Natural population analysis and the thermodynamic functions have also been calculated for the title molecule using the PM6, RHF, B3LYP and B3PW91 methods. B3PW91 based UV and experimental spectral analysis of the molecule have been performed. The RHF, B3LYP and B3PW91 methods based NMR calculation procedure has been used to assign the ¹H NMR and ¹³C NMR chemical shift of S3AMH.

Keywords – FTIR; FT Raman; PM6; RHF; DFT-B3LTP and B3PW91

1. INTRODUCTION

(S)-3-aminomethyl hexonic acid (S3AMH) belongs to antiepileptic or anticonvulsant drug group in the treatment of epileptic seizures, bipolar diseases and as mood stabilizer¹. S3AMH is the pharmacologically active S- enantiomer of racemic 3- isobutyl γ- amino butyric acid with structure analogue to GABA A or B receptors or influence GABA uptake. Hence, the title molecule is of considerable interest in the field of medicinal and pharmaceutical science. The present study is devoted to perform a detailed calculation of the molecular structure using PM6, Ab-initio Restricted Hartree Fock (RHF), Density Functional theory based on Becke 3-lee-yang-parr (B3LYP) and (B3PW91) functional with standard 6-311++ G(d,p) basis set^{2,3} and also to predict the infrared, UV spectra, ¹H NMR and ¹³C NMR chemical shifts and the thermodynamic parameters like entropy, heat capacity and energy have been evaluated.

2. EXPERIMENTAL

The spectroscopically pure grade sample of S3AMH was purchased from a reputed Pharmaceutical company, Chennai, India and was used as such for the spectral measurements. FTIR spectrum of the title compound has been recorded in the range 4000 - 450 cm^{-1} at SAIF, IIT Madras, Chennai, India. The FT Raman spectrum of S3AMH was recorded in the range 5000 - 50 cm^{-1} on a computer interfaced BRUKER IFS 66V model Interferometer at IITM, Chennai. UV-Visible spectral measurements have been made using Cary 5E –UV-VIS spectrophotometer in the wavelength region 200-300 nm at IIT, Chennai. All sharp bands observed in the spectra are expected to have an accuracy of $\pm 1\text{cm}^{-1}$. Quantum chemical methods have proved to be an essential tool for interpreting the vibrational spectra. Hence in this study PM6, RHF, Density functional theory by B3LYP and B3PW91 based on Becke 3-Lee-Yang-parr and Becke 3-Perdew and Wang's 1991 have been performed to support the vibrational spectra of S3AMH.

3. COMPUTATIONAL DETAILS

All the theoretical computations were performed at PM6, Restricted Hartree Fock level, B3LYP and B3PW91 on a Pentium IV/1.6 GHz personal computer using the Gaussian 09W program package⁴. The geometry optimization was carried out using the initial geometry generated from standard geometrical parameters at PM6, RHF, B3LYP and B3PW91 methods adopting 6-311++G(d,p) basis set to characterize all stationary points as minima. In the quantum methods, Becke's three parameters exchange–functional (B3)^{5,6} combined with gradient-corrected correlation functional of Lee, Yang and Parr (LYP)⁷ by implementing the split-valance polarized 6-31G (d, p) basis set have been utilized for the computation of molecular structure optimization and vibrational frequencies. The optimized geometry was used in the vibrational frequency calculations at the PM6, RHF, B3LYP and B3PW91 level to characterize all stationary points as minima. Finally, calculated normal mode vibrational wave numbers provide thermodynamic properties by way of statistical mechanics. The vibrational frequency assignments were made with a high degree of accuracy with the help of Chem. craft software program⁸.

4. RESULTS AND DISCUSSION

4.1 Molecular geometry

The optimized geometry of S3AMH, obtained by the PM6, RHF, B3LYP and B3PW91 levels of calculation, is provided in (Tables-1 and 2) accordance with the atom numbering scheme given in (Fig.1).

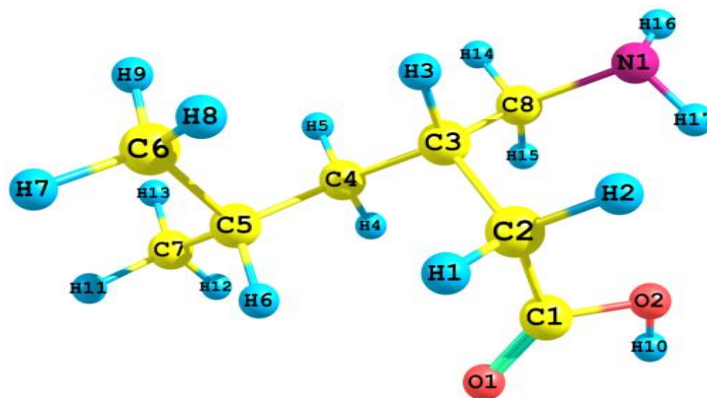


Fig.1: Atom numbering of S3AMH

Table-1: Selected bond lengths (Å) for S3AMH

Bond	PM6	RHF	B3LYP	B3PW91	Expt
C ₁ -C ₂	1.493	1.507	1.51	1.504	1.51
C ₁ -O ₇	1.209	1.185	1.207	1.226	1.22
C ₁ -O ₈	1.383	1.332	1.38	1.354	1.36
C ₂ -C ₃	1.544	1.534	1.538	1.531	1.51
C ₄ -H ₁₅	1.107	1.087	1.099	1.097	1.1
C ₄ -H ₁₆	1.108	1.086	1.095	1.095	1.1
C ₅ -C ₆	1.534	1.531	1.534	1.539	1.54
C ₅ -C ₉	1.535	1.531	1.535	1.529	1.53
C ₅ -H ₁₇	1.119	1.091	1.099	1.1	1.1
C ₆ -H ₁₉	1.19	1.085	1.090	1.093	1.1
C ₂ -H ₁₂	1.15	1.086	1.091	1.096	1.1
C ₃ -C ₁₀	1.546	1.535	1.541	1.535	1.53
C ₄ -C ₅	1.544	1.538	1.541	1.536	1.53
O ₈ -H ₂₁	0.991	0.945	0.969	0.967	0.96
C ₉ -H ₂₃	1.094	1.086	1.094	1.094	1.1
C ₉ -H ₂₄	1.195	1.088	1.195	1.095	1.1
C ₁₀ -N ₁₁	1.491	1.458	1.49	1.463	1.47
C ₁₀ -H ₂₆	1.117	1.089	1.098	1.099	1.1
N ₁₁ -H ₂₇	1.015	0.999	1.013	1.013	1.04
N ₁₁ -H ₂₈	1.014	1	1.015	1.014	1.04

Table- 2: Selected bond angles (°) for S3AMH

Bond	PM6	RHF	B3LYP	B3PW91	Expt
C ₂ -C ₁ -O ₇	131.98	127.2	127.39	125.31	124.2
C ₂ -C ₁ -O ₈	109.38	111.19	111	110.07	109.4
O ₇ -C ₁ -O ₈	118.62	121.6	121.59	121.6	121.5
C ₁ -C ₂ -C ₃	113.33	116.32	115.97	115.85	116.7
C ₁ -C ₂ -H ₁₂	110.44	106.59	107.46	107.53	109.5
H ₁₂ -C ₂ -H ₁₃	105.36	106.36	106.26	106.21	109.4
C ₃ -C ₄ -C ₅	113.48	115.35	115.41	111.26	109.5
C ₅ -C ₄ -H ₁₅	110.17	109.35	109.3	109.32	108.3
C ₄ -C ₅ -C ₆	111.66	113.38	113.24	111.09	109.5
C ₄ -C ₅ -C ₉	110.18	110.18	110.34	110.34	109.5
C ₆ -C ₅ -H ₁₇	108.29	108.29	107.64	107.28	108.3
C ₅ -C ₆ -H ₂₀	111.69	111.69	110.88	109.86	108.3
C ₁ -O ₈ -H ₂₁	112.87	112.87	108.85	106.5	107
H ₂₂ -C ₉ -H ₂₃	107.34	107.34	107.84	107.90	108.5
H ₂₃ -C ₉ -H ₂₄	107.54	107.54	107.64	108.59	108.5
C ₃ -C ₁₀ -N ₁₁	109.09	109.09	111.09	110.07	109.5
N ₁₁ -C ₁₀ -H ₂₅	109.16	109.16	108.14	107.30	107.8
N ₁₁ -C ₁₀ -H ₂₆	113.3	113.3	112.97	113.24	-
C ₁₀ -N ₁₁ -H ₂₈	110.67	110.67	111.13	111.02	111.2
H ₂₇ -N ₁₁ -H ₂₈	107.15	107.15	107.09	106.9	106.8

Tables-1 and 2 compares the bond lengths and bond angles of S3AMH with those experimentally available from X-ray diffraction data⁹. From the calculated values, it is observed that most of the optimized values are slightly varies with the experimental values. The deviation of theoretical parameters of optimized geometry from the experimental values is due to fact that the theoretical calculations belong to molecule in the gaseous phase while the experimental results belong to the molecule in liquid state. The calculated geometrical parameters represent a good approximation and they are the basis for calculating vibrational frequencies and thermodynamic parameters. The calculated bond lengths by PM6, RHF, B3LYP methods are slightly deviated, while the value of B3PW91 method is much closer with experimental values. This indicates that B3PW91 method estimate the electron correlation effect well than the PM6, RHF and B3LYP methods.

4.2 Vibrational Assignment

The FTIR and FT-Raman spectra of S3AMH are given in (Fig.2 and3). The calculated and experimental wave numbers and intensities of the normal mode of vibrations and the corresponding vibrational assignment for S3AMH are given in (Table-3).

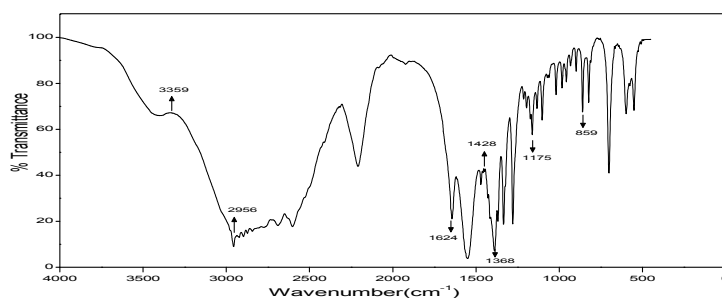


Fig. 2: FTIR spectrum of S3AMH

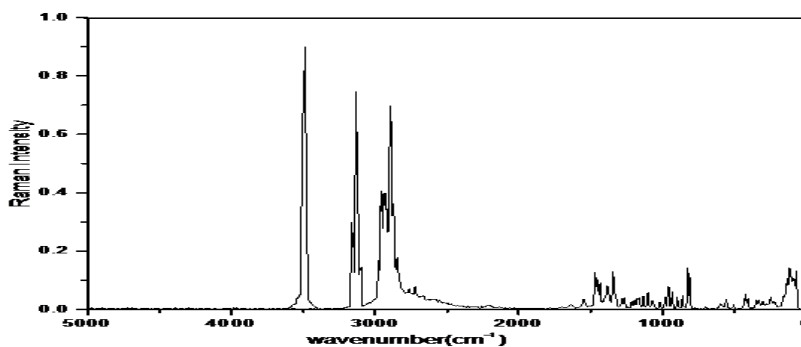


Fig. 3: FT Raman spectrum of S3AMH

The presence of hydrogen bonding, carboxylic acids in the liquid and solid phases exhibit a broad band at 3400- 2500 cm^{-1} due to the OH stretching vibrations, which some times in the lower half of the frequency range has two or three weak bands superimposed on it¹⁰. A band at 3359 cm^{-1} in FTIR spectrum and at 3589 cm^{-1} in FT Raman spectrum has been assigned for the carboxylic acid OH stretching vibration.

The predominant contribution¹¹ of in plane bending vibration of OH groups is always centered at around 1500 cm^{-1} . Thus the strong band appeared in the FTIR spectrum at 1428 cm^{-1} and a very weak band at 1436 cm^{-1} in the FT Raman spectrum has been attributed to in plane bending vibration of OH group. The out of plane bending mode of hydroxyl group is assigned at 1278 cm^{-1} in FT Raman spectra.

The carbonyl group is important and its characteristics frequency has been extensively used to study wide range of compounds. It is contained in a large number of different classes of compounds for which a strong absorption band is observed in the region 1800-1550

cm⁻¹ ¹². Because of its high intensity and the relatively interference free region in which it occurs, this band is reasonably easy to recognize. In the present work the bands observed at 1549, 1624 cm⁻¹ in the FTIR spectrum and at 1624 cm⁻¹ in the FT Raman spectrum are assigned to C=O stretching mode of vibrations.

For the assignment of CH₃ group frequencies, fifteen fundamental vibrations can be associated to CH₃ groups. Nine stretching, three bending and three rocking vibration modes are designed to the motion of methyl group. The CH₃ asymmetric and symmetric stretching frequencies are established at 2956 cm⁻¹ in infrared spectrum. The methyl hydrogen deformation modes are also well established in the spectrum. We have observed the methyl deformation mode at 1334, 1530, 1624 cm⁻¹ in the infra red spectrum and 1344, 1436 cm⁻¹ in FT Raman spectrum.

Table – 3: Calculated and Experimental wave numbers (cm⁻¹) for S3AMH

Frequency (cm ⁻¹)		PM6		RHF		B3LYP		B3PW91		Vibrational Assignment
FTIR	FT Raman	Freq. (cm ⁻¹)	IR Intensity KM/Mole	Freq. (cm ⁻¹)	IR Intensity KM/Mole	Freq. (cm ⁻¹)	IR Intensity KM/Mole	Freq. (cm ⁻¹)	IR Intensity KM/Mole	
		21	1.015	35	0.678	33	0.579	35	0.597	C-C Deformation
		31	0.166	43	0.241	43	0.066	43	0.091	C-C Deformation
		58	0.264	65	0.157	67	0.262	68	0.382	C-C Deformation
		281	0.689	304	1.828	372	1.835	370	1.554	CH ₂ Rocking
		353	6.879	364	0.452	391	2.58	389	2.634	C-H Stretching
		409	1.001	377	1.041	402	1.519	397	1.708	C-C Bending
508vw	550w	439	3.8	472	0.551	514	7.655	515	23.632	CH ₂ Rocking +C-C Bending+NH ₂ Twisting
822w		857	22.993	791	4.091	835	12.531	834	11.636	C-O Stretching +C-H Deformation
859w		883	67.733	815	3.261	870	12.37	872	12.402	NH ₂ Wagging +CH ₂ Twisting
	876m	928	29.996	851	1.675	895	3.15	900	2.41	CH ₂ Wagging+NH ₂ Wagging
898vw		950	24.001	867	3.769	905	2.377	902	3.91	NH ₂ Wagging
	914w	988	37.713	876	0.576	937	2.987	939	0.647	CH ₂ Rocking
932w		997	13.597	904	5.443	940	0.1	944	2.078	CH ₂ Twisting
956w	958m		41.697	910	3.606	973	4.29	976	4.822	C-C Stretching
1019m		1047	10.433	949	2.824	1005	8.789	1015	4.978	C-C Stretching
1071w		1111	13.343	1016	3.385	1065	1.217	1062	30.745	C-N Stretching +C-N Deformation
1133w		1125	8.586	1037	2.398	1116	12.461	1109	80.536	C-H Stretching +O-H Deformation
1162w		1187	24.28	1074	8.486	1160	2.528	1174	13.637	CH ₂ Scissoring
1180vw		1231	74.797	1117	1.1	1170	13.335	1217	2.491	C-C Stretching+NH ₂ Scissoring
1278m		1266	11.621	1227	4.597	1288	0.989	1284	4.151	CH ₃ Twisting +OH Deformation
1334vs	1344s	1315	52.618	1289	2.076	1366	7.31	1366	25.843	C-H Deformation +OH Deformation
1368vs	1362s	1333	17.228	1317	0.743	1385	15.845	1382	38.341	NH ₂ Rocking +CH ₂ Rocking
1388vs	1384m	1345	0.734	1336	3.262	1417	17.642	1409	19.715	CH ₂ Rocking
1428s	1436vw	1409	18.984	1368	1.153	1446	0.574	1443	0.778	NH ₂ Rocking+CH ₂ Wagging+ OH Deformation
1440s				1390	3.549	1458	4.698	1460	13.223	CH ₃ Wagging +C-C Stretching
1470s				1409	9.12	1483	4.077	1475	3.95	CH ₂ Scissoring +CH ₃ Scissoring
1549s				1448	4.947	1549	4.087	1610	34.754	CH ₃ Scissoring +C=O Stretching
1624s	1624 m	1602	3.954	1572	2.633	1614	3.331	1775	25.951	NH ₂ Scissoring +C=O Stretching
2956vs	2956s	2446	2.731	2841	5.646	2994	4.115	2988	24.013	CH ₃ Symmetric Stretching
3359m	3589s	2772	5.653	3339	6.861	3491	1.927	3517	2.555	NH ₂ Symmetric Stretching +OH Stretching

vw- very weak, w- weak, m- medium, s- strong, vs- very strong

The NH₂ group in the sample under investigation gives rise to two symmetric and two asymmetric stretching vibrations. The frequency of asymmetric vibration is higher than that of symmetric one. It has frequency range of 3300 cm⁻¹ to 3700 cm⁻¹¹³. In addition, NH₂ group has scissoring, rocking, wagging modes. The NH₂ scissoring mode has been suggested to lie in the region 1550 cm⁻¹ to 1650 cm⁻¹. In the present work NH₂ wagging band occurs at 859, 898 cm⁻¹ in the FTIR spectrum and at 876 cm⁻¹ in FT Raman spectrum. Similarly NH₂ rocking vibration occurs at 1368 cm⁻¹ in the FTIR spectrum. NH₂ twisting vibration occurs at 508 cm⁻¹ in FTIR spectrum and corresponding FT Raman band is observed at 550 cm⁻¹. The theoretically computed values for different functional groups falls in the region mentioned above by PM6, RHF, B3LYP and B3PW91 methods.

4.3 HOMO and LUMO Energy gap

Highest occupied molecular orbital and lowest unoccupied molecular orbital are very important parameters for quantum chemistry¹⁴. The ionization potential (I) is the negative of the highest occupied molecular orbital (HOMO) energy, i.e. $I = -E_{\text{HOMO}}$, and affinity potential (A) is the negative of the lowest unoccupied molecular orbital (LUMO) energy, i.e. $A = -E_{\text{LUMO}}$. The HOMO energy of the drug under study are -8.321AU (PM6), -9.203 (RHF), -5.732 (B3LYP) and -7.3988AU (B3PW91) and LUMO energy are 0.618AU (PM6), 4.999AU (RHF), 0.409AU (B3LYP) and 0.2844AU (B3PW91). The energy difference between HOMO and LUMO orbital's is called as energy gap and is calculated by various methods are 8.982AU (PM6) and 14.202AU (RHF) and 5.323AU (B3LYP) and 7.6831AU (B3PW91). The 3D plots of HOMO and LUMO are shown in (Fig. 4).

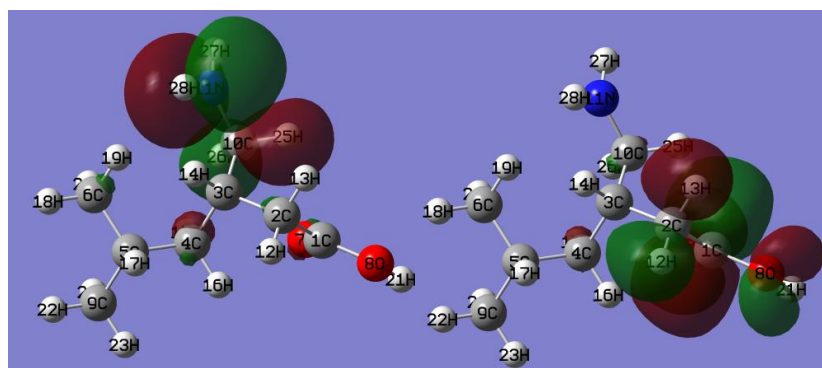


Fig. 4: Homo and LUMO energy structure of S3AMH

4.4 Natural population analysis

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems¹⁵. An attempt has been made to describe the electron distribution in S3AMH using RHF, B3LYP and B3PW91 quantum chemical methods. The calculated natural atomic charges values from the natural population analysis (NPA) and Mulliken population analysis (MPA) procedures using RHF, B3LYP and B3PW91 methods are listed in (Table-4) and the graphical representation of the same is given in (Fig.5).

The NPA from the natural bonding orbital (NBO) method is better than the MPA scheme. The NPA of S3AMH shows the presence of oxygen atom $O_1 = -0.719$ (RHF), -0.612 (B3LYP) and -0.603 (B3PW91) imposes positive charge on the carbon atom $C_1 = 0.994$ (RHF), 0.83 (B3LYP) and 0.800 (B3PW91). The carbon atoms $C_1, C_2, C_3, C_4, C_5, C_6, C_7,$ and C_8 possess large negative values due to the electropositive hydrogen atoms attached to them. The large negative charge on the nitrogen atom N_1 imposes more positive charge on the hydrogen atoms H_{16} and H_{17} . Moreover there is no difference in charge distribution observed on all hydrogen atoms except the H_{10} atom $H_{10} = 0.538$ (RHF), 0.517 (B3LYP) and 0.500 (B3PW91) which arises due to the negative charge accumulated on the O_2 atom.

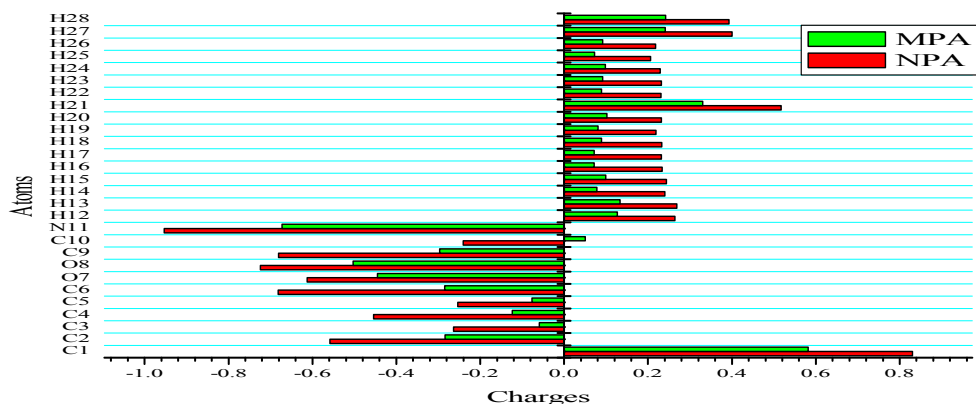


Fig. 5: Graphical representation of Mulliken and Natural charge distribution of S3AMH

Table- 4: Mulliken and Natural Atomic charges of S3AMH

Atom with numbering	MPA			NPA		
	RHF	B3LYP	B3PW91	RHF	B3LYP	B3PW91
C1	0.775	-0.13	0.109	0.994	0.83	0.8
C2	-0.32	-0.523	-0.65	-0.537	-0.558	-0.487
C3	-0.137	1.678	1.075	-0.249	-0.263	-0.245
C4	-0.161	-0.961	-1.009	-0.422	-0.454	-0.384
C5	-0.139	-0.33	-0.495	-0.238	-0.253	-0.235
C6	-0.3	-0.662	-0.814	-0.644	-0.681	-0.588
C7	-0.31	-0.732	-0.119	-0.642	-0.68	-0.583
C8	0.084	-0.768	-0.771	-0.183	-0.24	-0.173
O1	-0.562	-0.235	-0.261	-0.719	-0.612	-0.603
O2	-0.641	-0.23	-0.119	-0.807	-0.724	-0.698
N1	-0.802	-0.554	-0.341	-0.997	-0.953	-0.904
H1	0.152	0.283	0.249	0.252	0.264	0.235
H2	0.16	0.396	0.283	0.256	0.268	0.241
H3	0.115	0.368	0.237	0.226	0.239	0.21
H4	0.125	0.301	0.224	0.232	0.243	0.214
H5	0.102	0.29	0.195	0.218	0.233	0.204
H6	0.096	0.279	0.183	0.216	0.232	0.184
H7	0.103	0.298	0.172	0.219	0.232	0.204
H8	0.09	0.217	0.166	0.208	0.218	0.193
H9	0.111	0.257	0.185	0.22	0.232	0.205
H10	0.379	0.281	0.279	0.538	0.517	0.5
H11	0.102	0.335	0.174	0.217	0.231	0.202
H12	0.104	0.273	0.15	0.218	0.231	0.203
H13	0.107	0.257	0.164	0.217	0.229	0.201
H14	0.089	0.278	0.242	0.192	0.206	0.169
H15	0.111	0.233	0.172	0.207	0.218	0.18
H16	0.282	0.32	0.252	0.406	0.4	0.378
H17	0.281	0.377	0.23	0.399	0.392	0.372

4.5. UV spectral analysis

Electronic transition energies and oscillator strength (f), wavelength of absorption (λ) and spectral assignments of S3AMH was calculated employing Time Dependent method using B3PW91 for which the optimized geometry obtained from B3PW91 calculations was used. The results of the theoretical calculations of electronic transition energies along with the band assignment are presented in the (Table-5) and they are compared with the experimental data of S3AMH. The (Fig.6) shows the UV spectrum of S3AMH. The present experiment revealed three absorption bands at 209, 222 and 250nm in the UV region.

Table - 5: Assignment of observed electronic transitions

B3PW91					λ Expt. (nm)
S. No	λ calc (nm)	Energy (e V)	F	State Transitions	
1	250	4.958	0.0170	H \rightarrow L H \rightarrow L+1 H \rightarrow L+2 H \rightarrow L+4	267
2	222	5.569	0.0038	H \rightarrow L H \rightarrow L+1 H \rightarrow L+2 H \rightarrow L+3	238
3	209	5.931	0.0077	H \rightarrow L H \rightarrow L+1 H \rightarrow L+3 H \rightarrow L+5	218

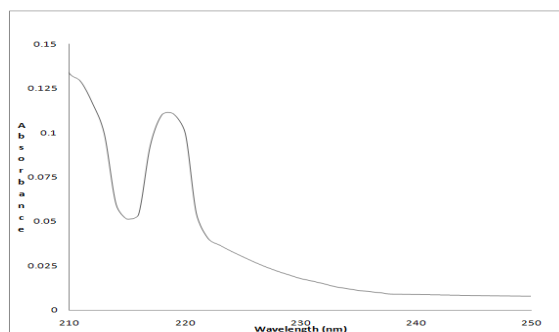


Fig. 6: UV Spectrum of S3AMH

The experimental and theoretical studies of the electronic absorption spectrum of S3AMH were used to explain each observed band, which was not done earlier. The theoretical calculated values are higher than the observed electronic absorption bands of S3AMH. However electronic absorption bands calculated closely agrees with the experimental results.

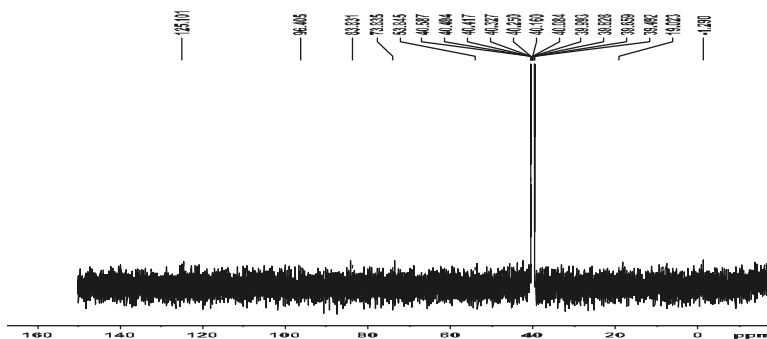


Fig. 10. Experimental ¹³C NMR spectrum of S3AMH

The spectrum of S3AMH showed a singlet at 7 ppm for the oxygen atom (O₂). A doublet is predicted at 2.4ppm for the methylene group of hydrogen atoms (H₄, H₅, H₁₄, and H₁₅). Another doublet at 2.00 ppm is predicted for the proton of the amine group (H₁₆, H₁₇). Two doublet peaks at 1.3ppm mark the methyl groups are mainly due to the carbon atoms (C₇ and C₆).

Table - 6: The calculated ¹³C and ¹H NMR chemical shifts of S3AMH.

Atom number	¹³ C Chemical shift					Atom number	¹ H Chemical shift				
	RHF	B3LYP	B3PW91	Chem. Ultra	Exp		RHF	B3LYP	B3PW91	Chem. Ultra	Exp
1	122.4	127.61	130.7	128.9	125.2	1	3.06	3.62	3.61	2.25	4.22
2	38.54	51.68	58.67	39.8	40.32	2	3.29	3.8	3.83	2.00	3.64
3	35.69	52.99	59.8	31.6	40.25	3	1.51	2.07	2.03	2.04	1.88
4	52.15	68.8	77.01	41.4	73.83	4	2.65	3.21	3.04	1.21	3.47
5	27.72	43.16	50.66	25.3	39.82	5	2.57	3.27	3.14	1.21	3.64
6	25.76	37.82	44.1	23.5	39.49	6	1.7	2.33	2.2	1.62	1.00
7	26.45	38.02	43.86	23.5	19.02	7	2.1	2.43	2.43	0.91	1.88
8	55.25	71.09	78.3	45.7	73.83	8	2.73	3.25	3.23	0.91	1.88
						9	1.75	2	1.93	0.91	1.88
						10	7.06	7.02	7.01	11.00	14.10
						11	2.13	2.48	2.49	0.91	1.88
						12	2.09	2.41	2.4	0.91	1.00
						13	1.74	2.02	1.96	0.91	1.00
						14	3.72	4.61	4.55	4.73	4.22
						15	4.14	4.92	4.89	4.48	3.64
						16	1.09	1.06	1.61	5.11	4.22
						17	1.26	1.26	1.53	5.11	4.22

(Table-6) gives the ¹³C NMR the experimental and predicted chemical shift values obtained by the RHF, B3LYP and B3PW91 and Chem Draw Ultra10.0 software program along with assignment. The carbon atom C₁ appearing at very higher chemical shift value 122.4 ppm in RHF, 127.61ppm in B3LYP, 130.7ppm in B3PW91 and 128.9 ppm in ChemDraw Ultra and 125.2 in experimental due to negative charge of oxygen atom(O₁). The carbon atom C₁ is electropositive and possess more positive charges than the other carbon atoms, and hence shielding is very small and appears up field. The theoretical and ChemDraw Ultra methods revealed that the more electron rich atoms are C₅, C₆ and C₇ and they are highly shielded atoms and hence appear at downfield (lower chemical shift). In this study a good correlation between atomic charges and chemical shift was made. It is concluded that the predicted chemical shift values

of B3PW91 are in closer agreement with the experimental chemical shift values of the structurally related molecules for both ¹H-NMR and ¹³C-NMR chemical shift methods.

4.7 Thermodynamic properties

Several calculated thermodynamic parameters such as Rotational constants, Enthalpy, Gibbs free energy and dipole moment at room temperature are presented in (Table-7).

Table - 7: Thermodynamic parameter of S3AMH

Parameters	PM6	RHF	B3LYP	B3PW91
Rotational constants(GHz)				
A	1.2978	1.3992	1.3625	1.3733
B	0.6594	0.6275	0.629	0.6353
C	0.5115	0.4872	0.4852	0.4901
ZPVE(Kcal/mol)	142.622	167.191	156.241	156.578
Energy(Kcal/mol)				
Translational	0.889	0.889	0.889	0.889
Rotational	0.889	0.899	0.889	0.889
Vibrational	149.533	173.42	162.938	163.045
Total	151.31	175.197	164.716	165.046
Heat capacity(Kcal/mol-Kelvin)	49.789	45.913	49.104	49.06
Entropy(Cal/mol-Kelvin)	119.37	112.879	116.398	116.141
Dipole moment (Debye)				
μ _x	1.9948	0.8107	0.8523	0.8315
μ _y	0.6959	0.8665	0.8098	0.8057
μ _z	-0.7324	-0.9836	-0.8216	-0.8145
μ	2.2299	1.541	1.434	1.4156

Scale factors have been recommended for an accurate prediction in determining the zero- point vibrational energies and the entropy S¹⁷. The biggest value ZPVE of S3AMH is 167.191kcal/mol obtained by RHF method whereas the smallest value is 142.622 kcal/mol obtained by PM6 method. The dipole moment of the molecule was also calculated by PM6, RHF, B3LYP and B3PW91 methods with 6-311++G (d, p) basis set. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions.

Therefore, it can be used as descriptor to depict the charge movement across the molecule depending upon the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. As a result of calculations by different methods the highest dipole moments was observed for PM6 whereas the smallest one was observed for B3PW91 in S3AMH.

The study on the variation of thermodynamic parameters with temperature provides information for the further study on the S3AMH and also can be used to compute the other thermodynamic energies according to the relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics. The standard thermodynamic functions: heat capacity, entropy and enthalpy at various temperature for S3AMH are listed in the (Table-8) and the corresponding variation spectrum is represented in the (Fig.11).

Table -8: Variation of Thermodynamic parameters with temperature of S3AMH

Temperature (K)	S (calmol ⁻¹ K ⁻¹)	C _p (cal mol ⁻¹ K ⁻¹)	H (kcalmol ⁻¹)
100	325.77	101.27	6.72
200	413.87	157.78	19.75
298.15	487.12	213.76	37.94
300	488.45	214.86	38.33
400	558.39	273.74	62.79
500	625.32	326.87	92.88
600	689.02	371.92	127.89
700	749.28	409.73	167.03
800	806.13	441.75	209.64
900	859.79	469.12	255.22
1000	910.46	492.69	303.34

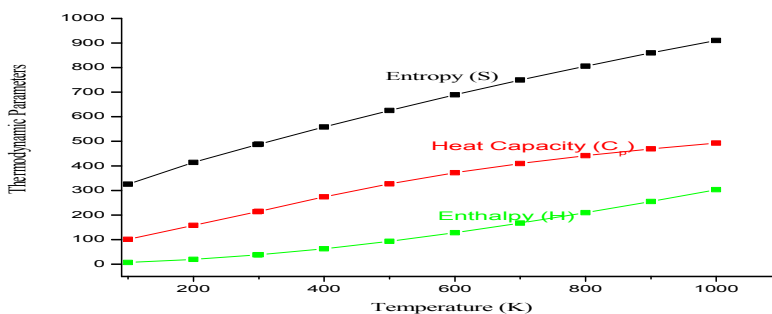


Fig.11: Thermodynamic functions graph of S3AMH.

5. CONCLUSION

The geometry of S3AMH was optimized with PM6, RHF, B3LYP and B3PW91 methods. The molecular structure, vibrational frequencies, ¹H-NMR and ¹³C-NMR of S3AMH has been studied. On the basis of the calculated and experimental results, assignment of the fundamental frequencies were examined. The available experiment results were compared with theoretical data. Theoretical ¹H-NMR and ¹³C NMR chemical shift values were reported and compared with experimental data, showing a good agreement both for ¹H and

¹³C. Thus, the present investigation provides vibrational assignments, structural information and thermodynamic properties of the compound which may be useful to upgrade the knowledge on S3AMH.

6. ACKNOWLEDGEMENT

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