Research Article

Vibrational Spectroscopic Investigation and Conformational Analysis of Methacrylamidoantipyrine: A Comparative Density Functional Study

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FT-IR and Raman spectra of methacrylamidoantipyrine (MAAP) have been reported in the region of 4000–10 cm^{-1} and 4000–100 cm^{-1} , respectively. The optimized geometric parameters, conformational analysis, normal mode frequencies, and corresponding vibrational assignments of MAAP ($\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2$) have been examined by means of density functional theory (DFT) method using the Becke-3-Lee-Yang-Parr (B3LYP) exchange-correlation functional and the 6-31G⁺⁺(d,p) basis sets. Vibrational assignments have been made on the basis of potential energy distribution (PED) and the thermodynamics functions, and the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) of MAAP have been predicted. Calculations are carried out with the possible seven (amide-1-5 and imide-1-2) conformational isomers of MAAP. Comparison between the experimental and theoretical results indicates that the B3LYP method provides satisfactory evidence for the prediction of vibrational wavenumbers, and the amide-1 conformational isomer is supposed to be the most stable form of MAAP.

1. Introduction

The MAAP, which has a π electron rich aromatic ring, was first synthesized using antipyrine, a hydroxy radical capture and spectroscopic reagent for phenols, and used for a method described for removal of phenolic compounds with nitrophenol imprinted polymer based on π - π and hydrogen bonding interactions [1]. Then, it was used in analyzing the selective binding behavior of paraoxon and parathion compounds on surface imprinted polymers prepared using both charge transfer (MAAP) and ligand-exchange (MAAP-Gd) monomers [2]. Today, one can easily reach many papers published where it is one of the most important organic chemical product for the molecularly imprinted polymers [1–5]. For instance, it has been used in researching the biomimetic immunoassay based on molecularly imprinted polymer [3], the 8-Hydroxy-2'-deoxyguanosine (8-OHdG), which is one of the most abundant oxidative DNA lesions

resulting from reactive oxygen species, and the 8-OHdG level in blood serum from a breast cancer patient [4], and new 8-OHdG imprinted quartz crystal microbalance sensor [5]. Furthermore, it is taken part in adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents [6].

Vibrational spectroscopy has been widely used as the standard tool for structural characterization of molecular systems together with DFT calculations [7–14]. DFT is popular as it is a cost-effective procedure for studying the physical properties of molecules. Unlike the Hartree Fock theory, DFT recovers electron correlation in the self-consistent Kohn-Sham procedure through the functions of electron density, so it is a cost-effective and reliable method. The DFT/B3LYP model exhibits good performance particularly on vibrational frequencies and geometries of organic compounds [7–14].

Though MAAP has wide applications in science, to the best of our knowledge, there is limited information

available in the literature about its spectroscopic properties. A detailed, quantum chemical study will be useful in making assignments to the fundamental normal modes and in explaining the obtained experimental data of MAAP. Furthermore, theoretically and experimentally presented data may be helpful in the context of the further studies of MAAP. For the above goals, we have reported vibrational spectra of MAAP. Vibrational frequencies with PED values, HOMO and LUMO data, structural parameters, and some thermodynamics functions of MAAP are also calculated for the most stable conformational isomer of MAAP by means of B3LYP/6-31G⁺⁺(d,p) level. The results of the theoretical and spectroscopic studies are reported here.

2. Experimental

MAAP was prepared according to the published procedure [1] and used without further purification. FT-MIR and FIR spectra were recorded in the region of 4000–400 cm⁻¹ and 400–10 cm⁻¹ with Bruker Optics IFS66v/s FTIR spectrometer at a resolution of 2 cm⁻¹. Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 785 nm excitation from a 3B diode laser having 3 cm⁻¹ resolution in the spectral region of 4000–100 cm⁻¹.

3. Calculations

All the calculations were performed using Gaussian 09.A1 program [15] on HP DL380G7 server system, and GaussView 5.0.8 [16] was used for visualization of the structure and simulated vibrational spectra. Many possible conformational isomers could be proposed for MAAP; however, the five amide and two imide conformational isomers of MAAP (Figure 1) were chosen using HF/6-31G(d,p) level by Spartan 10 program [17]. For these calculations, the possible seven conformational isomers of MAAP were first optimized in the gas phase at B3LYP level of theory using 6-31G⁺⁺(d,p) basis set, and no geometric restrictions were applied. Its amide-1 conformational isomer was found more stable than the others (Figure 1). According to the theoretical calculations, the vibrational frequencies and assignments of the two conformational isomers amide-1 and amide-2 are about the same. So, it has been given the data for one of them.

Therefore, after the optimization, harmonic vibrational frequencies and corresponding vibrational intensities for the amide-1 conformational isomer of MAAP were calculated by using the same method and basis set and then scaled by 0.955 (above 1800 cm⁻¹) and 0.977 (under 1800 cm⁻¹) [10, 13]. In order to show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule, PED calculations were carried out by the vibrational energy distribution analysis 4 (VEDA) [18].

4. Results and Discussion

4.1. Geometrical Structures. To clarify the vibrational frequencies, it is essential to examine the geometry of any compound, as small changes in geometry can potentially

cause substantial differences in frequencies. Gibbs free energy and relative stability of the optimized geometries in gas phase for seven conformational isomers of MAAP with B3LYP/6-31G⁺⁺(d,p) method are given in Figure 1. Regarding the calculated free energies, all conformational isomers relative to the amide-1 and amide-2 forms of MAAP could be neglected for the calculation of equilibrium constant since their energy differences are larger than 2 kcal/mol [10–14]. The amide-1 conformational isomer of MAAP is more stable than amide-2 by 0.03 kcal/mol. Consequently, MAAP in the gas phase prefers the amide-1 and amide-2 conformational isomers with preference of 51% and 49%, respectively.

Some of the optimized geometric parameters such as bond lengths and bond angles calculated by B3LYP/6-31G⁺⁺(d,p) are listed in Table 1 for the most stable conformational isomer (amide-1) of MAAP. To the best of our knowledge, experimental data on the geometric structure of MAAP is not available in the literature. However, some geometric parameters for 4-([(1E)-(2-hydroxynaphthyl)methylidene]amino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-one and p-methacryloylaminophenylarsonic acid monomer were identified in previously reported studies [19, 20]. Henceforth, the theoretical results have been compared with data for some parts of the related molecules as given in Table 1.

Generally, it is expected that the bond distances calculated by electron correlated methods are longer than the experimental distance. This situation can be seen in Table 1 as expected. Overall, the calculated bond lengths are in good agreement with experimental results. The mean absolute deviation (MAD) and root mean square deviation (RMSD) of bond lengths are 0.022 and 0.032 Å, respectively. The biggest difference between the experimental and calculated bond distances is 0.061 Å. As can be seen in Table 1, big differences are observed in the calculated C6–N5–C7, C2–C1–N20 and C7–C1–N20 bond angles compared to experimental values. The calculated C2–C1–N20 and C6–N5–C7 bond angles are about 11° smaller than the experimental result whereas the calculated C7–C1–N20 angle is about 11° larger than the experimental value. All the other bond angles are reasonably close to the experimental data.

The MAD and RMSD of bond angles are 3.15 and 4.96°, respectively. The observed differences in bond distances and angles are not due to the theoretical shortcomings, as experimental results are also subject to variations owing to the insufficient data to calculate equilibrium structure which are sometimes averaged over zero point vibrational motion. Furthermore, it can be noted that theoretical results have been compared with available experimental data.

For the optimized geometric parameters, magnitude of dihedral angles, D (10; 11; 12; 13) = 0.70°, D (1; 7; 4; 5) = 177.49°, D (8; 7; 5; 4) = 178.46°, D (20; 1; 2; 4) = 178.68°, D (1; 20; 15; 16) = 165.90°, D (17; 16; 15; 18) = 175.60°, D (14; 9; 5; 4) = 21.60°, D (1; 2; 3; 7) = 173.40°, D (15; 16; 18; 20) = 17.85°, D (1; 20; 15; 19) = 15.35°, and D (15; 16; 17; 19) = 13.24°, indicate that a large part of molecule is nearly in the same plane. In this compound, two intramolecular hydrogen bonds can be observed as N20–H36...O19 and N20–H36...O3. Theoretical results are N20–H36: 3.17 Å/N20–H36–O19: 25.1°

TABLE 1: Some optimized geometric parameters of MAAP.

Parameters	B3LYP/6-31G ⁺⁺ (d,p)		
	Amide-1	Ref. [19]	Ref. [20]
Bond lengths (Å)			
C1–C2	1.457	1.426	
C1–C7	1.362	1.369	
C1–N20	1.400	1.394	1.407
C2–O3	1.232	1.239	
C2–N4	1.400	1.395	
N4–N5	1.414	1.399	
N4–C9	1.420	1.422	
N5–C6	1.474	1.452	
N5–C7	1.406	1.362	
C7–C8	1.494	1.487	
C15–C16	1.508		1.482
C15–O19	1.229		1.227
C15–N20	1.377		1.359
C16–C17	1.506		1.426
C16–C18	1.342		1.403
Bond angles (°)			
C2–C1–N20	117.8	128.8	
C7–C1–N20	133.0	122.0	
C1–C2–O3	128.2	132.3	
C1–C2–N4	105.0	104.8	
O3–C2–N4	126.7	122.9	
C2–N4–N5	109.8	109.4	
C2–N4–C9	125.1	127.1	
N4–N5–C6	113.1	119.6	
N4–N5–C7	106.7	107.5	
C6–N5–C7	117.3	128.9	
C1–C7–N5	109.3	109.2	
N5–C7–C8	119.2	121.7	
C16–C15–O19	121.3		122.1
C16–C15–N20	115.9		115.6
O19–C15–N20	122.8		122.3
C15–C16–C17	114.8		116.3
C15–C16–C18	121.7		120.7
C17–C16–C18	123.4		123.0
C1–N20–C15	126.2	121.4	128.2

and N20–H36: 2.52 Å/N20–H36–O19: 100.6°. The complete set of optimized geometric parameters for the amide-1 conformational isomer of MAAP is given in Table 3. Several thermodynamic parameters (zero point energy, entropy, etc.) calculated by B3LYP/6-31G⁺⁺(d,p) method are also presented in Table S1 (see Supplementary Material available online at <http://dx.doi.org/10.1155/2013/386247>). The total energy and change in total entropy for the amide-1 conformational isomer of MAAP are at room temperature.

4.2. Vibrational Studies of MAAP. To the best of our knowledge, the vibrational wavenumbers and assignments of MAAP in the middle and far infrared regions of the spectrum

have not been reported in the literature. But, a few selected bands of MAAP were reported by Ersöz et al. [1]. The measured and calculated vibrational frequencies for MAAP along with corresponding vibrational assignments and intensities are given in Table 2.

The theoretical and experimental vibrational spectra of MAAP are shown in Figure 2. All calculated frequency values presented in this paper are obtained within the harmonic approximation. This allows us to identify vibrational motion in terms of independent vibrational modes, each of them is governed by a simple one-dimensional harmonic potential. It is difficult to determine the MAAP's vibrational assignments in the observed spectrum due to its low symmetry. Therefore, the assignments of vibrational modes for the amide-1 conformational isomer of MAAP have been provided by VEDA 4 [18] in Table 2. The MAAP molecule consists of 37 atoms having 105 normal vibrational modes, and its most stable form belongs to the point group C_1 with only identity (E) symmetry element or operation. According to the calculations, 18 normal vibrational modes of MAAP are below 400 cm⁻¹ while 87 modes are between 4000 cm⁻¹ and 400 cm⁻¹.

The high wavenumber region contains characteristic wavenumbers of NH stretching that are observed at 3249 cm⁻¹ (IR) and at 3254 cm⁻¹ (R) as strong broad band. The NH infrared band is consistent with previously reported data for MAAP [1] where this band was found as 3260 cm⁻¹. The corresponding scaled theoretical value for this mode is 3426 cm⁻¹. The amide band is the most intense and is predominantly C=O stretch supports also the amide form of MAAP. Hydrogen bonding plays an important role in the broadening of the spectral bands [21]. The broadening of the NH bands is attributed to the intramolecularly bonded hydrogen to the C=O group. The CH stretching region encompasses four and six CH modes in IR and Raman spectrum, respectively. The vibrational bands at 3094, 3059 cm⁻¹ in IR spectrum and 3080, 3044, and 3005 cm⁻¹ in Raman spectrum are attributed to the CH stretching vibrations while the bands at 2969, 2919 cm⁻¹ in IR spectrum and 2968, 2934, and 2863 cm⁻¹ in Raman spectrum are assigned to the CH₂ and CH₃ stretchings. Corresponding scaled calculated values for these bands are found as 3090, 3073, 3062, 3040, 3012, 2971, 2914, and 2892 cm⁻¹. In the high wavenumber region of the spectra, the anharmonicity can explain substantial differences between the experimental and calculated values. Alternatively, these differences may be due to intra/intermolecular interactions or to the laser used for Raman.

Carbonyl stretchings are observed at 1673 cm⁻¹—IR (1683 cm⁻¹—R) and at 1648 cm⁻¹—IR (1631 cm⁻¹—R) as intense bands in the vibrational spectra. The former band is clearly assigned to the carbonyl band at cyclic ketone position, whereas the latter is attributed to the amide carbonyl band. The corresponding scaled theoretical values of these modes are 1703 cm⁻¹ and 1694 cm⁻¹. C=C stretchings are observed at 1620 cm⁻¹—IR and at 1592 cm⁻¹—IR (1605 and 1570 cm⁻¹—R) as a very strong band in the vibrational spectra. The former band is assigned to the methacrylate

TABLE 2: Experimental and calculated vibrational wavenumbers (cm^{-1}) of MAAp.

Mode	P.E.D ($\geq 5\%$)	Experimental		γ^α	B3LYP/6-31G ⁺⁺ (d,p)		
		IR	Raman		γ^β	I_{IR}	I_{R}
ν_1	$\nu\text{NH}(100)$	3249 s, b	3254 s, b	3588	3426	38.29	16.36
ν_2	$\nu\text{CH}(97)$			3239	3093	0.43	12.83
ν_3	$\nu\text{CH}(100)$	3094 w		3235	3090	13.53	17.90
ν_4	$\nu\text{CH}(89)$		3080 vs	3218	3073	3.23	25.29
ν_5	$\nu\text{CH}(89)$	3059 m		3207	3062	25.36	40.11
ν_6	$\nu\text{CH}(90)$			3193	3049	13.87	25.64
ν_7	$\nu\text{CH}(93)$		3044 w	3183	3040	1.14	12.12
ν_8	$\nu\text{CH}(87)$			3172	3029	2.42	13.11
ν_9	$\nu\text{CH}(95)$			3167	3025	8.58	8.38
ν_{10}	$\nu\text{CH}(99)$		3005 s	3154	3012	4.74	32.59
ν_{11}	$\nu\text{CH}(94)$			3136	2995	14.79	17.50
ν_{12}	$\nu\text{CH}(96)$			3132	2991	12.80	14.93
ν_{13}	$\nu\text{CH}(99)$	2969 s	2968 m	3111	2971	12.02	17.64
ν_{14}	$\nu\text{CH}(92)$			3104	2964	12.55	15.67
ν_{15}	$\nu\text{CH}(91)$	2919 s	2934 vs	3051	2914	18.10	52.55
ν_{16}	$\nu\text{CH}(98)$			3042	2905	21.81	39.66
ν_{17}	$\nu\text{CH}(96)$		2863 m	3028	2892	50.02	29.76
ν_{18}	$\nu\text{OC}(74)$	1673 vs	1683 s	1743	1703	152.72	26.56
ν_{19}	$\nu\text{OC}(74)$	1648 vs	1631 vs	1734	1694	363.40	52.85
ν_{20}	$\nu\text{CC}(69)\text{-}5$			1702	1663	40.11	111.41
ν_{21}	$\nu\text{CC}(76)$	1620 vs		1691	1652	100.80	34.41
ν_{22}	$\nu\text{CC}(65) + \delta\text{HCC}(19)$	1592 vs	1605 vs	1647	1609	53.05	79.10
ν_{23}	$\nu\text{CC}(69) + \delta\text{HCC}(10)$		1570 m	1633	1595	2.13	4.99
ν_{24}	$\delta\text{HNC}(58) + \nu\text{CN}(10)$	1491 vs		1556	1520	352.19	41.25
ν_{25}	$\delta\text{HCC}(60) + \nu\text{CC}(10)$			1531	1496	105.42	13.21
ν_{26}	$\delta\text{HCH}(85)$			1515	1481	15.71	6.95
ν_{27}	$\delta\text{HCH}(84)$			1500	1465	2.85	7.29
ν_{28}	$\delta\text{HCC}(81)$	1455 vs	1466 m, sh	1499	1465	68.70	2.59
ν_{29}	$\delta\text{HCC}(60) + \nu\text{CC}(23)$			1491	1457	7.98	1.88
ν_{30}	$\delta\text{HCH}(78)$			1484	1450	4.60	13.15
ν_{31}	$\delta\text{HCH}(87)$			1477	1443	12.74	7.51
ν_{32}	$\delta\text{HCH}(77)$		1446 w	1477	1443	4.71	5.30
ν_{33}	$\delta\text{HCH}(80)$			1456	1423	8.18	7.40
ν_{34}	$\delta\text{HCH}(75)$		1426 s	1454	1421	7.77	21.77
ν_{35}	$\delta\text{HCH}(67) + \nu\text{CC}(11)$			1433	1400	76.53	29.21
ν_{36}	$\delta\text{HCH}(77)$			1414	1382	5.79	5.84
ν_{37}	$\nu\text{CC}(30) + \delta\text{HCH}(19)$	1407 s		1392	1360	178.18	19.77
ν_{38}	$\nu\text{NC}(59)$	1368 s	1368 vs	1371	1339	88.20	122.68
ν_{39}	$\delta\text{HCC}(63) + \nu\text{CC}(22)$			1360	1329	1.59	2.24
ν_{40}	$\nu\text{CC}(52) + \delta\text{HCC}(21)$	1310 vs, sh	1303 s	1340	1309	78.89	32.98
ν_{41}	$\nu\text{CC}(42) + \delta\text{HCC}(18)$			1325	1295	7.14	10.34
ν_{42}	$\nu\text{NC}(39)$	1295 vs 1285 vs	1245 w, sh	1292	1263	218.19	34.06
ν_{43}	$\nu\text{NN}(36) + \nu\text{NC}(11)$	1200 s		1233	1205	85.54	0.69
ν_{44}	$\nu\text{NN}(61) + \nu\text{NC}(12)$		1211 m	1219	1191	43.20	36.30
ν_{45}	$\delta\text{HCC}(71) + \nu\text{CC}(20)$		1170 m	1200	1173	1.88	4.90
ν_{46}	$\delta\text{HCC}(78)$			1184	1157	0.60	4.78
ν_{47}	$\nu\text{NC}(41) + \delta\text{HCN}(16) + \delta\text{HCC}(10)$		1126 w	1164	1138	5.43	2.93
ν_{48}	$\delta\text{HCN}(55)$	1136 s		1156	1130	16.14	8.01
ν_{49}	$\delta\text{HCN}(55) + \nu\text{NC}(10)$	1105 m		1130	1104	14.51	7.56
ν_{50}	$\nu\text{CC}(38) + \delta\text{HCC}(28)$	1074 w	1069 w	1104	1079	12.00	0.64

TABLE 2: Continued.

Mode	P.E.D ($\geq 5\%$)	Experimental		B3LYP/6-31G ⁺⁺ (d,p)			
		IR	Raman	ν^α	ν^β	I_{IR}	I_{R}
ν_{51}	$\nu\text{NC}(35) + \delta\text{HCC}(18)$	1060 m		1082	1058	13.07	0.41
ν_{52}	$\delta\text{HCC}(83)$			1071	1047	0.12	2.18
ν_{53}	$\delta\text{HCC}(26) + \nu\text{NC}(13)$			1060	1035	4.98	1.92
ν_{54}	$\delta\text{HCC}(59)$			1057	1032	0.42	0.55
ν_{55}	$\nu\text{CC}(45) + \delta\text{CCC}(17)$	1026 m	1008 vs	1041	1017	18.61	24.00
ν_{56}	$\delta\text{HCC}(80)$	1001 w		1026	1002	6.02	2.76
ν_{57}	$\delta\text{CCC}(62) + \nu\text{CC}(21)$		973 w	1014	990	0.17	68.48
ν_{58}	$\delta\text{HCC}(95)$			998	975	0.06	0.48
ν_{59}	$\delta\text{HCC}(95)$			980	958	0.21	0.17
ν_{60}	$\delta\text{HCC}(32) + \nu\text{CC}(22) + \nu\text{NC}(11)$	956 vw, sh		970	948	13.72	0.75
ν_{61}	$\nu\text{CC}(87)$	932 s	946 m	954	932	38.98	3.92
ν_{62}	$\nu\text{NC}(28) + \delta\text{HCC}(25)$			943	921	6.80	9.61
ν_{63}	$\delta\text{HCC}(79)$			922	901	3.20	3.83
ν_{64}	$\nu\text{CC}(28) + \delta\text{HCC}(27)$	892 w	902 m	907	886	1.89	20.36
ν_{65}	$\tau\text{HCCN}(95)$	842 m	858 m	848	829	0.20	3.18
ν_{66}	$\tau\text{HNCC}(43)$	806 w		838	819	6.14	4.33
ν_{67}	$\tau\text{HCCC}(53) + \gamma\text{CCCC}(16)$		783 w	803	785	11.75	2.48
ν_{68}	$\tau\text{HCCC}(73)$	763 vs	749 w	772	754	42.94	1.70
ν_{69}	$\gamma\text{OCNC}(81)$	744 m		746	729	13.41	4.16
ν_{70}	$\nu\text{CC}(35) + \delta\text{CNN}(20) + \tau\text{HCCC}(10)$	708 s 703 s	705 vw	728	711	42.51	1.35
ν_{71}	$\tau\text{HCCC}(84)$			701	685	16.44	0.60
ν_{72}	$\delta\text{HCC}(25) + \gamma\text{CCCC}(11)$		685 s	678	662	2.43	13.74
ν_{73}	$\delta\text{HCC}(28) + \delta\text{CNN}(11)$	666 m	656 m	668	653	6.92	5.11
ν_{74}	$\delta\text{CCC}(60)$	641 m		658	643	23.86	5.80
ν_{75}	$\delta\text{CCC}(79)$			630	616	1.15	7.40
ν_{76}	$\tau\text{HNCC}(57)$		603 s	1340	608	56.00	27.67
ν_{77}	$\gamma\text{CCNN}(21)$			1325	590	11.65	5.02
ν_{78}	$\delta\text{CCN}(30) + \gamma\text{CCNN}(20) + \nu\text{CC}(10)$	587 s		1292	575	25.19	15.04
ν_{79}	$\delta\text{CCO}(27) + \tau\text{HNCC}(12) + \gamma\text{CCNN}(10)$			622	564	5.98	4.06
ν_{80}	$\gamma\text{NCCC}(76)$	501 s		604	501	8.72	1.59
ν_{81}	$\delta\text{CCC}(49)$		476 w	588	478	8.40	2.76
ν_{82}	$\tau\text{CCCN}(31)$	436 m		577	447	19.92	15.42
ν_{83}	$\delta\text{CNC}(26) + \tau\text{CCNC}(23)$		423 m	512	417	1.68	4.29
ν_{84}	$\tau\text{CCCC}(94)$	409 w	397 vw	489	409	0.58	1.88
ν_{85}	$\delta\text{CCN}(49)$	373 s		458	383	2.79	7.76
ν_{86}	$\gamma\text{CCCC}(32)$			427	346	0.60	11.02
ν_{87}	$\delta\text{CNN}(57)$	331 m	335 w	419	336	9.39	1.00
ν_{88}	$\delta\text{CCC}(65)$			392	305	1.22	3.69
ν_{89}	$\delta\text{CCN}(49)$	289 s	295 w	354	284	12.51	4.15
ν_{90}	$\delta\text{CCC}(35)$	261 w	275 w	344	271	1.06	1.95
ν_{91}	$\tau\text{CCCN}(41)$			312	244	1.68	3.36
ν_{92}	$\delta\text{CCN}(38) + \nu\text{NC}(11)$	225 vw		290	217	5.16	9.01
ν_{93}	$\tau\text{HCCC}(79)$			277	213	0.40	2.36
ν_{94}	$\delta\text{CCN}(37)$		200 m	250	207	3.45	21.32
ν_{95}	$\tau\text{HCCC}(90)$	169 vw		222	169	0.51	3.26
ν_{96}	$\tau\text{CCCC}(58)$			218	157	1.07	5.37
ν_{97}	$\tau\text{CCNC}(47)$	140 s		212	141	3.32	7.37
ν_{98}	$\tau\text{HCCC}(54) + \tau\text{CCNC}(11)$	134 s		173	134	0.62	23.80
ν_{99}	$\tau\text{CCNC}(27) + \tau\text{HCCC}(14) + \delta\text{HCC}(13)$	111 m		160	113	4.87	17.07
ν_{100}	$\tau\text{CNCC}(58)$			144	77	1.35	138.91

TABLE 2: Continued.

Mode	P.E.D ($\geq 5\%$)	Experimental		B3LYP/6-31G ⁺⁺ (d,p)			
		IR	Raman	ν^α	ν^β	I_{IR}	I_R
ν_{101}	$\tau\text{CNCC}(27) + \tau\text{CCNC}(17) + \delta\text{CCN}(10)$	71 vw		137	68	5.61	39.27
ν_{102}	$\tau\text{CCNN}(80)$	60 vw		115	55	1.93	72.49
ν_{103}	$\tau\text{CNCC}(56)$	50 vw		79	46	2.34	115.46
ν_{104}	$\tau\text{CNCC}(67)$	41 vw		70	39	4.55	83.80
ν_{105}	$\tau\text{CCNC}(49) + \delta\text{CNC}(16)$			57	24	1.74	72.73

ν^α : unscaled wavenumbers, ν^β : scaled with 0.955 above 1800 cm^{-1} and 0.977 under 1800 cm^{-1} . IR and R: calculated infrared and Raman intensities. PED data are taken from VEDA4. v: very, s: strong, m: medium, w: weak, b: broad, and sh: shoulder. ν , δ , τ , and γ denote stretching, bending, torsion, and out modes, respectively.

FIGURE 1: Optimized conformational isomers and numbering of MAAp.

double band, whereas the latter is attributed to the C=C band of rings. The corresponding theoretical values of these modes are 1652 cm^{-1} and 1609 cm^{-1} (1595 cm^{-1}).

The CN stretching modes of the amide group are observed at 1491 cm^{-1} (IR-vs), 1295 cm^{-1} (IR-vs), 1285 cm^{-1} (IR-vs), 1245 cm^{-1} (R-w,sh), and 1060 cm^{-1} (IR-m) while

the present theoretical values are 1520 cm^{-1} , 1263 cm^{-1} , and 1058 cm^{-1} . The CN and NN stretch vibrations at cyclic ketone position are observed at 1368 cm^{-1} (IR-s), 1368 cm^{-1} (R-vs), 1200 cm^{-1} (IR-s), and 1211 cm^{-1} (R-m) while the present theoretical values are 1339 cm^{-1} , 1205 cm^{-1} , and 1191 cm^{-1} . CC or NC stretching, CCC, CCN, CNC or HCC bending,

TABLE 3: Complete set of optimized geometric parameters for amide-1 conformational isomer of MAAP.

B3LYP/6-31G ⁺⁺ (d,p)							
Parameters	Amide-1	Parameters	Amide-1	Parameters	Amide-1	Parameters	Amide-1
Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)		Dihedral angles (°)	
C1-C2	1.457	C2-C1-C7	108.9	C7-C1-C2-O3	-173.4	N4-C9-C10-H27	0.6
C1-C7	1.362	C2-C1-N20	117.8	C7-C1-C2-N4	3.4	C14-C9-C10-C11	-0.2
C1-N20	1.400	C7-C1-N20	133.0	N20-C1-C2-O3	1.9	C14-C9-C10-H27	-179.2
C2-O3	1.232	C1-C2-O3	128.2	N20-C1-C2-N4	178.7	N4-C9-C14-C13	179.5
C2-N4	1.400	C1-C2-N4	105.0	C2-C1-C7-N5	-0.5	N4-C9-C14-H31	-1.4
N4-N5	1.414	O3-C2-N4	126.7	C2-C1-C7-C8	178.3	C10-C9-C14-C13	-0.7
N4-C9	1.420	C2-N4-N5	109.8	N20-C1-C7-N5	-174.9	C10-C9-C14-H31	178.4
N5-C6	1.474	C2-N4-C9	125.1	N20-C1-C7-C8	4.0	C9-C10-C11-C12	0.9
N5-C7	1.406	N5-N4-C9	119.5	C2-C1-N20-C15	139.6	C9-C10-C11-H28	-179.5
C6-H21	1.098	N4-N5-C6	113.1	C2-C1-N20-H37	-19.6	H27-C10-C11-C12	179.9
C6-H22	1.091	N4-N5-C7	106.7	C7-C1-N20-C15	-46.5	H27-C10-C11-H28	-0.6
C6-H23	1.091	C6-N5-C7	117.3	C7-C1-N20-H37	154.3	C10-C11-C12-C13	-0.7
C7-C8	1.494	N5-C6-H21	111.4	C1-C2-N4-N5	-4.9	C10-C11-C12-H29	179.4
C8-H24	1.089	N5-C6-H22	109.1	C1-C2-N4-C9	-158.0	H28-C11-C12-C13	179.8
C8-H25	1.096	N5-C6-H23	108.4	O3-C2-N4-N5	171.9	H28-C11-C12-H29	-0.1
C8-H26	1.095	H21-C6-H22	109.5	O3-C2-N4-C9	161.2	C11-C12-C13-C14	-0.2
C9-C10	1.402	H21-C6-H23	109.7	C2-N4-N5-C6	135.1	C11-C12-C13-H30	-179.4
C9-C14	1.402	H22-C6-H23	108.6	C2-N4-N5-C7	4.7	H29-C12-C13-C14	179.6
C10-C11	1.395	C1-C7-N5	109.3	C9-N4-N5-C6	70.1	H29-C12-C13-H30	0.4
C10-H27	1.083	C1-C7-C8	131.4	C9-N4-N5-C7	20.5	C12-C13-C14-C9	0.9
C11-C12	1.398	C1-C7-N5	109.3	C2-N4-C9-C10	-50.7	C12-C13-C14-H31	-178.2
C11-H28	1.086	N5-C7-C8	119.2	C2-N4-C9-C14	129.1	H30-C13-C14-C9	-179.9
C12-C13	1.397	C7-C8-H24	109.9	N5-N4-C9-C10	158.6	H30-C13-C14-H31	1.0
C12-H29	1.086	C7-C8-H25	111.7	N5-N4-C9-C14	-21.6	O19-C15-C16-C17	31.4
C13-C14	1.396	C7-C8-H26	110.4	N4-N5-C6-H21	-62.2	O19-C15-C16-C18	-144.2
C13-H30	1.086	H24-C8-H25	106.6	N4-N5-C6-H22	58.8	N20-C15-C16-C17	-147.4
C14-H31	1.084	H24-C8-H26	109.3	N4-N5-C6-H23	176.9	N20-C15-C16-C18	37.0
C15-C16	1.508	H25-C8-H26	108.9	C7-N5-C6-H21	62.6	C16-C15-N20-C1	-165.9
C15-O19	1.229	N4-C9-C10	118.9	C7-N5-C6-H22	-176.3	C16-C15-N20-H37	-7.4
C15-N20	1.377	N4-C9-C14	120.9	C7-N5-C6-H23	-58.2	O19-C15-N20-C1	15.4
C16-C17	1.506	C10-C9-C14	120.2	N4-N5-C7-C1	-2.5	O19-C15-N20-H37	173.8
C16-C18	1.342	C9-C10-C11	119.5	N4-N5-C7-C8	1.6	C15-C16-C17-H32	-175.8
C17-H32	1.093	C9-C10-H27	119.6	C6-N5-C7-C1	-130.5	C15-C16-C17-H33	-54.7
C17-H33	1.094	C11-C10-H27	120.9	C6-N5-C7-C8	129.5	C15-C16-C17-H34	63.2
C17-H34	1.097	C10-C11-C12	120.7	C1-C7-C8-H24	-21.7	C18-C16-C17-H32	-0.3
C18-H35	1.086	C10-C11-H28	119.2	C1-C7-C8-H25	96.4	C18-C16-C17-H33	120.9
C18-H36	1.086	C12-C11-H28	120.1	C1-C7-C8-H26	-142.3	C18-C16-C17-H34	-121.2
N20-H37	1.014	C11-C12-C13	119.5	N5-C7-C8-H24	157.1	C15-C16-C18-H35	-1.0
		C11-C12-H29	120.3	N5-C7-C8-H25	-84.8	C15-C16-C18-H36	176.8
		C13-C12-H29	120.3	N5-C7-C8-H26	36.5	C17-C16-C18-H35	-176.2
		C12-C13-C14	120.5	N4-C9-C10-C11	179.6	C17-C16-C18-H36	1.5
		C12-C13-H30	120.2				
		C14-C13-H30	119.3				
		C9-C14-C13	119.6				
		C9-C14-H31	119.7				
		C13-C14-H31	120.7				
		C16-C15-O19	121.3				

TABLE 3: Continued.

Parameters		B3LYP/6-31G ⁺⁺ (d,p)		Parameters		Parameters	
Amide-1		Amide-1		Amide-1		Amide-1	
Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)		Dihedral angles (°)	
		C16-C15-N20	115.9				
		O19-C15-N20	122.8				
		C15-C16-C17	114.8				
		C15-C16-C18	121.7				
		C17-C16-C18	123.4				
		C16-C17-H32	111.0				
		C16-C17-H33	110.1				
		C16-C17-H34	111.0				
		H32-C17-H33	109.3				
		H32-C17-H34	108.6				
		H33-C17-H34	106.7				
		C16-C18-H35	122.9				
		C16-C18-H36	120.8				
		H35-C18-H36	116.2				
		C1-N20-C15	126.2				
		C1-N20-H37	113.2				
		C15-N20-H37	117.5				

FIGURE 2: Experimental ((a), (b)) and theoretical ((c), (d)) vibrational spectra of MAAP.

some torsion, and out modes dominate the regions of 1000–500 cm^{-1} while CCC, CCN, CNC, or CNN bending and CCCN, CCNC, CNCC, CCNN, HCCC, or CCCC torsion modes are seen in the low frequency region. Similar situations have been shown in for calculations. Vibrational modes in the low wavenumber region of the spectrum contain contributions of several internal coordinates and their assignments have reduction approximation to one of two of the internal coordinates.

To make a comparison between the experimental and theoretical frequencies, we have calculated RMSD. This is used to measure the difference between values predicted by a model and those actually observed from the thing being modeled. In this study, RMSD values have been obtained as 29 cm^{-1} (IR) and 32 cm^{-1} (R). Omitting the ν_1 stretch from the analysis results substantially reduced RMSD values as 15 cm^{-1} (IR) and 17 cm^{-1} (R). Furthermore, the correlation values between the experimental and calculated vibrational frequencies are found to be as 0.99898 (IR) and 0.99889 (R). Similarly, omitting the ν_1 stretch from the analysis results substantially reduced correlation values as 0.99963 (IR) and 0.99960 (R). It can be seen that the B3LYP calculation is reliable for both IR and Raman spectra.

Regarding the calculated fundamentals, in general, the computed vibrational intensities are in agreement with the experimental results. Although the calculated vibrational intensities of some modes are about zero, these bands can be seen in the vibrational spectra. The opposite situation has also been observed. Similarly, the ν_{42} and ν_{70} modes are observed as double peaks in the infrared spectrum which can be attributed to molecular interactions (Figure 2). It is also important to note that theoretical studies were conducted for an isolated molecule in the gaseous state contrary to the experimental values recorded for the presence of interactions in the solid phase.

The HOMO and LUMO orbitals are called the frontier orbitals and determine the way the molecule interacts with other species. The HOMO is the orbital that could behave as an electron donor, since it is the outermost orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, as it is the innermost orbital that has room to accept electrons. The transitions can be described from HOMO to LUMO. A single orbital, however, may be both the LUMO and the HOMO. The HOMO is dominated by nitrogen, oxygen, and carbon atoms. The LUMO is located over all atoms except from some CH_3 and NH groups in MAAP. Frontier molecular orbital and their orbital energy are shown in Figure 3 together with the HOMO-LUMO gap. The energy gap given from the ground state to first excited state is calculated at around 4.66 eV. The laser used for Raman analysis in the present study has an energy around half of this gap. Therefore, electronic excitement due to Raman laser seems unlikely.

5. Conclusion

The experimental and theoretical vibrational investigations of MAAP are performed, for the first time, by using FT-IR,

FIGURE 3: Frontier molecular orbitals for MAAP.

Raman, and quantum chemical calculations. In conclusion, the following results can be summarized.

- (1) Results of energy calculations for gas phase indicate that the amide-1 conformational isomer is the most stable conformer of MAAP. Furthermore, relative energies of the other five conformational isomers, except for the amide-2, are larger than 2.0 kcal/mol. Therefore, relative mole fractions of the five forms could be neglected, and these results suggest that the MAAP molecule prefers the amide-1 and amide-2 conformational isomers with preference of 51% and 49%, respectively, and the conformational energy barrier is independent of the imide form.
- (2) The RMSD and correlation values between the experimental and calculated vibrational frequencies indicate that B3LYP/6-31G⁺⁺(d,p) method is reliable, and this theoretical approximation makes the understanding of vibrational spectrum of MAAP easier.

Conflict of Interests

The authors declare that no conflict of interests exists.

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