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MOLECULAR STRUCTURE, VIBRATIONAL SPECTRA AND THERMODYNAMICAL PROPERTIES OF 4-(4-N-HEXYLOXYPHENYL)-2-METHYL-3-BUTYN-2-OL (4HP2M3B)

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ABSTRACT

4-(4-n-hexyloxyphenyl)-2-methyl-3-butyn-2-ol compound single point energy was calculated for optimized the compound which helps the accurate path for the further computational studies. Structural, vibrational spectroscopic studies are obtained using the computational methods. Total Energy Distribution assignments are tabulated for all vibrations. This intermediate compound used as the connecting agent for laboratory reagent. Thermodynamical properties like entropy, enthalpy, Gibbs free energy are used to determine the thermal equilibrium of the compound.

KEYWORDS: 4-(4-n-hexyloxyphenyl)-2-methyl-3-butyn-2-ol, Total Energy Distribution, Gibbs free energy, enthalpy.

INTRODUCTION

Over the last decades there has been an increasing interest and research activity on Electrical and vibrational properties of organic systems. In organic materials, electrons are more accessible and optical arise from the interaction between light and electrons within individual molecular units, giving greater and faster responses. J.L. Bredas et al demonstrated that the electronic properties of organic materials develop from the interaction between light and electrons within the individual molecular units and rapid responsiveness due to the highly delocalized π electron system connecting the donor and acceptor that increase the asymmetric polarization[1]. H.S.Nalwa et al analyzed the behaviuor of π-electrons that are easily affected by an external optical field as they are relatively loosely bound to the nucleus[2]. P.N.Prasad et al showed that the delocalized orbitals may be extended over the entire molecule giving large and fast polarization[3]. It can be used to dramatically reduce the transmittance of a device exposed to high energy

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inputs[4]. It is the base for all the photonic technologies. J.Zyss et al synthesized the organic compounds with large dipole moment which depicts the nonlinear susceptibilities of organic materials far larger than the inorganic optical materials[5].The high optical non linearity makes them a promising material for optoelectronics and nonlinear optical applications[6].

2-methyl-3-butyn-2-ol and their derivatives are known for their importance in biology and material science. The interesting properties of 2-methyl-3-butyn-2-ol (2M3BY) fascinate the agrochemical and specialty chemical industrialists. It is exploited as an acetylene precursor in the synthesis of suicide inactivators of monoamine oxidase for Mannich reaction[7]. It was reported that 2-methyl-3-buten-2-ol is effectively replaced with MBY in baits for trapping IPS typographus and also[8]. V. V. Brei et al correlated the strength of the basic sites of the catalyst and their activity[9].Their properties are determined by the triple bond and involved in 99semihydrogenation of nanoparticles [10, 11, 12].

The target compound was synthesized on reacting 4-iodophenol with 1-bromohexane in the presence of anhy.K_2CO_3 undergo O-Alkylation gave the ether, which was then coupled with 2-methyl-3-butyn-2-ol in Sonogashira reaction conditions to provide the protected phenylacetylene[13].

The present letter 4HP2M3B have been inspected by both observed and calculation method. The literature review concluded that, there are no publications of the title compound 4HP2M3B using the theoretical methods. From the equilibrium molecular structure, parameters and vibrational assignments help to determine the results of the interior properties of the molecules. Thermo dynamical properties are predicted using the DFT methods using the hybrid basis set.

COMPUTATIONAL DETAILS

The GAUSSIAN 09W program is used to predict the quantum computational calculations of 4HP2M3B with the original version along with three parameters functional by way of applying Becke-Lee-Yang-Parr hybrid method [14] level with different basis sets on Intel Core i3 1.9GHz processor personal computer to derive the complete geometry optimization. Gaussian software is a super positioning tool for developing fields of computational physics like structural analysis, reaction mechanisms, potential energy values, charge distributions and excitation energies of the compound [15]. The single point energy calculation is computing the energies of specific molecular structures and the allied molecular properties are predicted initially. Geometry optimizations calculating equilibrium structure of molecules, optimizing transition structures and energy minimizations at dynamic basic sets. The spectra are computerized using the B3LYP with 6-31+G (d, p) basic set and the output spectra are monitored threw Gauss sum program, which gives the Raman intensities spectra directly. This program equating the intensity theory of Raman scattering derived relationship and produces the modified Raman intensities data.

Scaling factors initiated by a least square optimization of the computed to the experimental data to fit both the experimental as well as theoretical results. Vibrational frequencies range of wave numbers above 2319cm^{-1} are scaled as 0.9959 and below 2319cm^{-1} scaled as 0.9963 for B3LYP[16]. After scaled with the scaling factor, the deviation from the experiments is less than 10cm^{-1} with a few exceptions. The vibrational assignments with Total Energy Distribution (TED) were calculated and explained using the Scaled quantum mechanical program using Vibrational Energy Distribution Analysis VEDA 4.0 Software [17, 18, 19]. An elevated degree of precision as the customary consideration along with obtainable linked by the GAUSSVIEW program are made by the molecules vibrational frequency assignments.

The electronic oscillatory frequency and electronic properties such as HOMO (higher occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbital energy distribution, Mulliken atomic charge distribution and thermo dynamical parameters are resolute by the time-dependent DFT (TD-DFT)[20]. The energy absorption spectra and energy gap plot drawn from Gauss view 5.0 programs [21]. Molecular Electrostatic Potential (MEP) map had been drawn. The polarizability and hyperpolarizability is calculated to understand the frequency doubling of the Second Harmonic Generation (SHG) behavior of 4HP2M3B. At last, investigations are conducted to find the density of states of different atoms, total density of states and band gap studies are found using theoretical replicas.

STRUCTURAL PARAMETERS

Synthesized compound structure was drawn by input software Gauss View 09W. The structure was optimized via some of hybrid basis sets in Gaussian 09W. Global minimization energy of -812.687 a.u got from basis set of B3LYP/6-31(d,p) which is a good one, while comparing with other basis sets. Optimized structure of 4HP2M3B is shown in Fig. 1. Optimized parameters are given in Table 1. C1 point

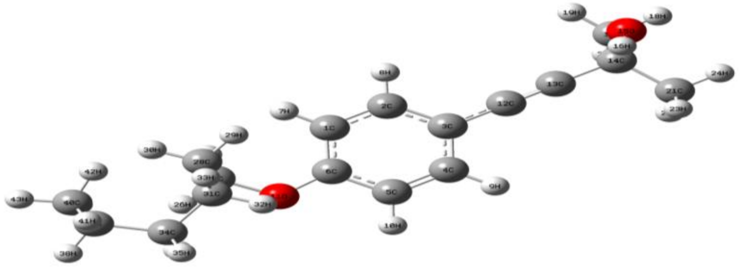


Fig. 1. Optimized structure of 4HP2M3B

group symmetry fit into 4HP2M3B compound. Carbon and carbon bond lengths have some differentiations were placed. The greater value found for CC bond length which connects with oxygen. Other combination bonds are not greater than oxygen combo for CC bond. Oxygen carbon is smaller value of all bond length. Hexyloxy group was attached to para position of benzene ring which can exist in variety of conformations. The interaction of alkyne group of 2-methyl-3-bytyn -2-ol with the substituent on the ring is of great importance in determining its structural and vibrational properties. The changes in charge distribution on the carbon atom can change in the frequency or bond length of CH bond to the benzene ring [22, 23].

VIBRATIONAL ASSIGNMENTS

In the current research, the IR and Raman spectroscopy for title compound computed through hybrid method. Fig. 2 & 3 has shown the IR & Raman spectra respectively. 123 modes of normal vibrations found by the VEDA software and tabulated in Table 2. Table illustrated the 69 CH modes, 42 υ modes, 41 β modes and 40 τ modes of vibrations in every atom. TED assignments demonstrated and computerized in this portion will help the researchers for our feature criteria.

CH aroma vibrations

The bands between 3100-3000cm^{-1} are CH heterocyclic aromatic compounds which are very close to the benzene rings. This article compound contains the 3000-3800cm^{-1} range for this particular heterocyclic aroma vibration in the DFT level. Swarnalatha et al. proposed, position and nature of the compound should not have more change by the proxy compounds when compared to others [24]. Hetero aroma CH modes in-plane and Out-of-plane lie on the region 1500-1000cm^{-}

^{1}and 1000-750cm^{-1} respectively[25]. The thirty four β vibrations and nineteen torsion (τ) vibrations are found for the title compound. The calculated frequency values at 936-1552cm^{-1} and 714-1425cm^{-1} are assigned in carbon hydrogen β vibration (mode no.28-77) and τ vibration (mode no.43-88), respectively.

C-C and C-C-C vibrations

Benzene ring has almost the same length of the all carbons bond and minimum deviation and Hexyloxy and alkyne groups are substituent for ring. The twenty four stretching (mode no. 25, 26, 40, 52, 54, 55, 63, 64, 65, 66, 67, 72, 73, 75, 77, 78, 79, 80, 84, 85, 86, 89, 90, 110) carbon vibrations slouch in the region 500-1850 cm^{-1} and twenty bending of vibrations slouch above the region 1300cm^{-1} [26]. In general, the bands around 1400–1650 cm^{-1} in benzene derivatives are assigned to skeletal stretching CC bands [27, 28]. Experimental IR data observed at

2230 and 1601cm^{-1} range for this current study which has good agreement with theoretical range of 2319, 1658, 1603 cm^{-1}. The spectral computerized values of C-C-C bending modes at 1028, 832, 774, 660, 623, 566, 487, 461, 447, 379, 328, 290, 272, 249, 160, 112, 47 cm^{-1} calculated.

CCCC torsional vibrations

The ring torsions have been assigned in region at below 800cm^{-1} which is discussed in present paper referred by earlier reports[29.] These peaks have been calculated at the region at 725, 566, 538, 447, 425, 421, 387, 249, 146, 99, 60, 53, 38, 17cm^{-1} by B3LYP methods which are well merge with observed values. And these wavenumbers are mixed with CCCO torsions in the investigated molecules.

C-O vibrations

The observed region 1260–1000 cm^{-1} is the best frequency vibration for carbonyl group [30]. For the reason that of its sky-scraping intensity [31, 32] and the comparative interference-free province in which it occurs, this band is logically effortless to distinguish. The computed regions 1275, 1200, 1099, 1062, 972, 923, 774 cm^{-1} are tabulated by hybrid methods for carbonyl group vibrations.

Methyl group

At about 1426-1406 cm^{-1} range are calculated in the deformations of these methyl group rocking modes. In the research paper, moieties are incorporate with methyl group and nigh on the equivalent enormity and intensity. Dealing of skeletal stretching modes, the methyl rocking was susceptible and variable in position [33]. Typically, destitute ranges are monitored at 1120-1050 cm^{-1} and 900-800 cm^{-1} [34, 35].

The destitute bands at 1217 and 1036 cm^{-1} by the major involvement to the β Rtrigd and Rtrigd were corresponding for the β and δ rocking modes, respectively. Twisting of CH_3 modes are anticipated underneath 421 cm^{-1}. This mode was computed for two basis sets at the modes 51 and 95 devoid of sustain by TEDs.

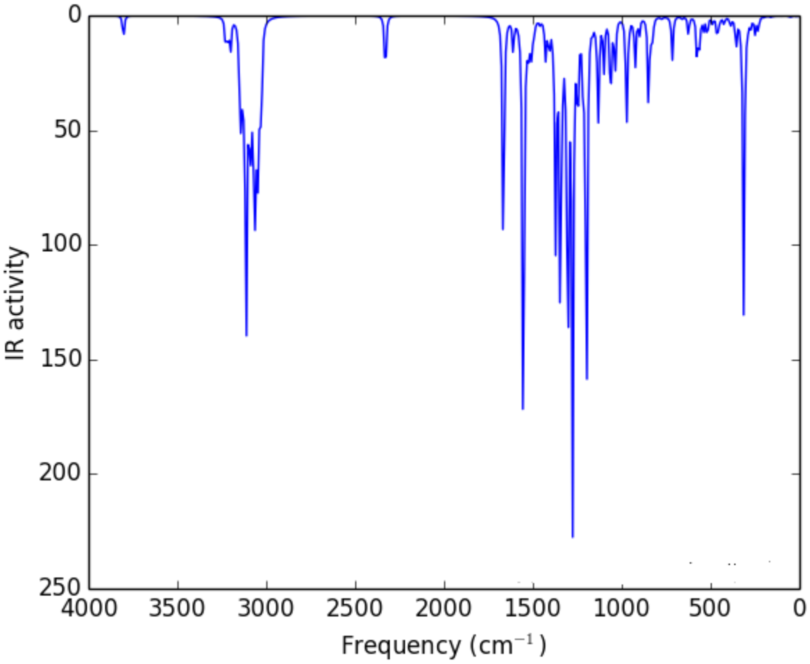
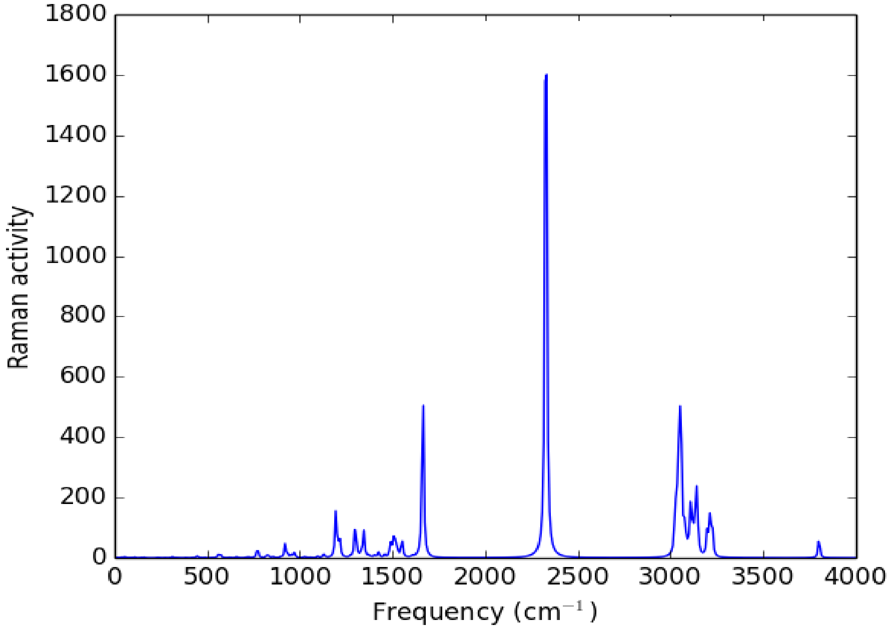


Fig. 2. FTIR spectra for 4HP2M3B

Fig. 3. FTR spectra for 4HP2M3B

THERMODYNAMIC PARAMETERS

The theoretical harmonic frequencies and the quantities are tabulated in Table 3. The standard statistical thermodynamic functions: Self consistent field energy, Zero-point vibrational energy, Rotational constants, Rotational temperatures, standard heat capacities, entropies, enthalpy and Gibbs free energy for the title compounds[36]. The margin values of 4HP2M3B gives the changes in the total entropy at room temperature. The energies of whole molecules, the change in the self-consistent field energy of 4HP2M3B are tabulated.



CONCLUSION

The research the experimental FT-IR, FTR spectroscopic studies are investigated for the first time. The theoretical spectra are predicted using computational methods and well agreed with experimental results. The molecular structure was characterized by ^{1}H Nuclear Magnetic Resonance Spectroscopy, Infrared Spectroscopy, Mass Spectroscopy and Elemental Analysis. Structure of the compound is confirmed using the computational spectral studies and geometrical parameters. This study is helpful for further studies like thermo dynamical studies. The vibrational assignments of the 4HP2M3B are assigned with TED value. Thermodynamic parameters also tabulated.

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TABLE 1 Selected Optimized Geometrical Parameters of 4HP2M3B

Bond Length		Bond Angle		Dihedral Angel	
C1-C2	1.401	C2-C1-C6	119.95	C6-C1-C2-C3	-2.32
C1-C6	1.400	C2-C1-H7	120.08	C6-C1-C2-H8	177.82
C1-H7	1.070	C6-C1-H7	119.97	H7-C1-C2-C3	178.21
C2-C3	1.402	C1-C2-C3	119.96	H7-C1-C2-H8	-1.65
C2-H8	1.070	C1-C2-H8	119.98	C2-C1-C6-C5	3.88
C3-C4	1.402	C3-C2-H8	120.05	C2-C1-C6-O11	-175.41
C3-C12	1.543	C2-C3-C4	120.00	H7-C1-C6-C5	-176.65
C4-C5	1.403	C2-C3-C12	119.88	H7-C1-C6-O11	4.06
C4-H9	1.070	C4-C3-C12	120.12	C1-C2-C3-C4	-0.70
C5-C6	1.402	C3-C4-C5	119.98	C1-C2-C3-C12	179.27
C5-H10	1.071	C3-C4-H9	119.99	H8-C2-C3-C4	179.16
C6-O11	1.423	C5-C4-H9	120.03	H8-C2-C3-C12	-0.87
O11-C25	1.423	C4-C5-C6	119.85	C2-C3-C4-C5	2.16
C12-C13	1.213	C4-C5-H10	120.13	C2-C3-C4-H9	-178.19
C13-C14	1.533	C6-C5-H10	120.02	C12-C3-C4-C5	-177.81
C14-O15	1.433	C1-C6-C5	120.14	C12-C3-C4-H9	1.84
C14-C17	1.544	C1-C6-O11	119.65	C2-C3-C14-O15	12.81
C14-C21	1.544	C5-C6-O11	120.20	C2-C3-C14-C17	-104.92
O15-H16	0.958	C6-O11C25	113.00	C2-C3-C14-H21	133.02
C17-H18	1.062	C13-C14-O15	109.43	C4-C3-C14-O15	-169.42
C17-H19	1.061	C13-C14-C17	109.51	C4-C3-C14-C17	72.85
C17-H20	1.064	C13-C14-C21	109.34	C4-C3-C14-H21	-49.21
C21-H22	1.070	O15-C14-C17	109.45	C3-C4-C5-C6	-0.60
C21-H23	1.071	O15-C14-C21	109.42	C3-C4-C5-H10	179.43
C21-H24	1.072	C17-C14-C21	109.67	H9-C4-C5-C6	179.75
C25-H26	1.063	C14-C15-H16	109.79	H9-C4-C5-H10	-0.21
C25-H27	1.062	C14-C17-H18	109.81	C4-C5-C6-C1	-2.42
C25-C28	1.532	C14-C17-H19	109.41	C4-C5-C6-O11	176.87
C25-C37	1.670	C14-C17-H20	109.84	H10-C5-C6-C1	177.54
C25-H39	1.146	H18-C17-H19	109.26	H10-C5-C6-O11	-3.17
H26-C34	0.891	H18-C17-H20	109.19	C1-C6-O11-C25	-106.81
H26-C37	1.059	H19-C17-H20	109.32	C5-C6-O11-C25	73.90
C28-2H9	1.063	C14-C21-H22	85.21	C6-O11-C25-H26	177.52
C28-H30	1.072	C14-C21-H23	81.49	C6-O11-C25-H27	56.95
C28-C31	1.532	C14-C21-H24	140.55	C6-O11-C25-C28	-63.55
C31-H32	1.063	H22-C21-H23	138.38	C6-O11-C25-C37	137.43
C31-H33	1.065	H22-C21-H24	86.38	C6-O11-C25-H39	106.03
C31-C34	1.531	H23-C21-H24	79.63	C13-C14-O15-H16	60.33
C34-H35	1.074	O11-C25-H26	109.07	C17-C14-O15-H16	-179.66

C34-H36	1.062	O11-C25-H27	110.27	C21-C14-O15-H16	-59.46
C34-C37	1.538	O11-C25-C28	109.20	C13-C14-C17-H18	177.02
C37-H38	1.077	O11-C25-C37	107.49	C13-C14-C17-H19	57.12
C37-H39	1.077	O11-C25-H39	82.57	C13-C14-C17-H20	-62.89
C37-C40	1.544	H26-C25-H27	109.74	O15-C14-C17-H18	57.06
C40-H41	1.037	H26-C25-C28	108.93	O15-C14-C17-H19	-62.85
C40-H42	1.099	H27-C25-H39	75.21	O15-C14-C17-H20	177.15
C40-H43	1.055	H27-C25-C28	109.61	C21-C14-C17-H18	-62.99

TABLE 2 Selected Experimental and Theoretical Ted Vibrational Assignments for 4HP2M3B Along With Their Intensities

Normal Modes	Symmetry spices	Experimental (cm^{-1})	Wavenumbers(cm^{-1}) B3LYP/6-31G(d,p)		Wavenumbers(cm^{-1}) B3LYP/6-31G(d,p)		Vibrational assignments
		FT-IR	Scaled	Un Scaled	IR Intensity (Km/mol)	Raman Intensity	
1	A		3787	3803	11.081	74.463	νCH(100)
2	A	3363	3214	3227	13.353	196.525	νCH(99)
3	A		3202	3216	7.256	217.694	νCH(99)
23	A	2929	3016	3028	23.267	242.889	νCH(93)
24	A	2864	3013	3026	24.873	103.317	νCH(96)
25	A	2230	2319	2329	29.736	12188.609	νCC(93)
26	A		1658	1665	120.063	7544.074	νCC(54)
27	A	1601	1603	1609	14.722	52.492	νCC(60)+βCCC(13)
28	A		1547	1552	224.971	938.764	βHCC(55)+βCCC(21)
29	A		1521	1527	3.660	277.034	βHCH(69)
30	A		1520	1525	7.875	44.178	βHCH(76)
31	A		1514	1519	0.945	136.410	βHCC(11)+βHCH(32)+τHCCC(28)
32	A		1512	1518	5.484	339.689	βHCC(10)+βHCH(11)+τHCCC(31)
33	A		1505	1511	1.647	391.667	βHCH(70)
38	A		1486	1492	1.202	94.404	βHCH(64)+τHCCC(22)
39	A		1483	1488	1.800	467.597	βHCH(77)
40	A		1453	1459	1.822	129.960	νCC(56)+βHCC(21)
41	A		1425	1430	4.361	77.581	βHCC(24)+βHCH(46)
42	A		1421	1426	4.610	67.169	βHCH(27)+βHCC(20)+τCHHH(31)
43	A		1420	1425	10.085	196.001	βHCO(11)+βHCC(14)+δCHCH(34)+τHCCC(10)
44	A		1404	1409	0.492	36.994	βHCC(43)
45	A		1401	1406	12.694	27.160	βHCH(16)+βHCC(10)+δCHHH(56)
46	A		1397	1402	0.824	82.641	τHCCC(32)
47	A		1378	1383	4.732	68.209	βHCC(15)+τHCCC(31)
48	A		1369	1374	9.188	22.271	τHCCH(28)+τHCCC(10)

49	A		1365	1370	93.514	101.563	βHOC(49)
50	A		1341	1346	65.903	1526.521	δCHCH(11)+βHCC(12)+νCC(10)
52	A		1324	1329	13.050	229.508	νCC(18)+βHCC(68)
53	A		1304	1309	31.917	65.430	βHCO(17)+βHCC(14)
56	A		1270	1275	219.545	89.795	νOC(20)+βHCO(12)
57	A		1241	1246	44.093	17.188	βHCO(22)+βHCC(12)
60	A		1195	1200	51.560	615.333	νOC(10)+τHCCC(28)
61	A		1191	1195	136.064	3793.031	βHCC(37)
62	A		1157	1162	2.402	13.393	δCCOH(10)+τHCCH(10)
63	A		1137	1141	3.299	33.103	νCC(10)
64	A		1132	1136	5.628	36.542	νCC(10)+βHCC(32)
65	A		1125	1129	43.020	299.979	νCC(30)+βHOC(26)+βHCC(24)
66	A		1095	1099	22.719	175.893	νOC(15)+νCC(25)
67	A		1058	1062	40.351	63.492	νOC(37)+νCC(30)
68	A		1043	1047	2.650	22.953	βHCC(10)+δCCOH(21)
69	A		1032	1036	23.562	50.458	δCCCH(16)+βHCC(15)+νOC(10)
70	A		1024	1028	0.595	44.730	βCCC(76)
71	A		1021	1025	0.408	92.396	βHCC(29)+δCHCH(39)+τHCCC(10)
72	A		969	972	39.861	608.809	νOC(21)+νCC(12)+βHCC(10)
73	A		964	967	15.057	188.132	νCC(39)+τHCCH(13)
74	A		961	965	0.047	89.161	δCCCH(55)+τHCCO(34)
75	A		952	956	1.918	166.188	νCC(14)+δCCOH(11)
76	A		948	951	0.174	178.438	δCCCH(57)+τHCCO(25)
77	A		933	936	0.842	418.796	νCC(32)+βHCC(26)+τHCCC(12)
78	A		920	923	21.914	2287.427	νCC(16)+νOC(31)
79	A		896	899	7.999	171.741	νCC(27)+δCCCH(13)
81	A		845	848	41.966	71.493	δCCCH(22)+τHCCO(55)
83	A		821	824	6.800	260.194	δCCOH(23)+τHCCO(63)
84	A		818	821	0.877	346.165	νCC(31)+βHCC(11)
85	A		771	774	1.274	2605.629	νOC(11)+νCC(11)+βCCC(11)
87	A		722	725	0.737	321.119	τCCCC(55)+δOCCC(21)
88	A		711	714	19.042	123.706	δCCCH(35)+τHCCC(11)
89	A		658	660	1.311	502.114	νCC(10)+βCCC(45)
91	A		573	576	17.098	1230.140	βCCO(22)+δOCCC(10)
92	A		564	566	6.361	795.819	βCCC(15)+τCCCC(23)+τCCCO(24)
94	A		536	538	5.661	94.077	βCCO(15)+τCCCC(34)+δOCCC(13)

TABLE 3 Theoretically Computed Energies (A.U.), Zero Point Vibrational Energies, Rotational Constants, Entropies and Dipole Moment for 4HP2M3B.

Thermodynamic parameters	**B3LYP**
Self-consistent field energy (a.u)	-3012.667
Zero point vibrational energy (kcal/mol)	75.916
Rotational constant (GHz)	1.591
	0.398
	0.319
Rotational temperature (K)	0.076
	0.019
	0.015
Thermal energy (kcal/mol)	
Total	82.311
Translational	0.889
Rotational	0.889
Vibrational	80.533
Specific heat capacity at constant volume (cal/mol K)	
Total	36.744
Translational	2.981
Rotational	2.981
Vibrational	30.783
Dipole moment (Debye)	2.1511Debye
Lumo(eV)	-1.99
Homo(eV)	-6.82
Energy gap(eV)	-4.83
Entropy(S)(cal/mol K)	
Total	101.468
Translational	41.943
Rotational	31.744
Vibrational	27.781
Gibbs Free Energy	0.084
Enthalpy	-3012.549