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A Combined Experimental and Theoretical Study on Vibrational Spectra of 2-Phenylcyclopropan-1-Amine

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Abstract

In this work, a combined experimental and theoretical study on molecular structure, vibrational spectra and natural bond orbital (NBO) analysis of 2-phenylcyclopropan-1-amine (2PCP1A) have been reported. The optimized molecular structure, atomic charges, vibrational frequencies and natural bond orbital analysis of 2PCP1A have been studied by performing DFT/B3LYP/6-31G(d,p),6-311++G(2d,3p)and 6-31G(3df,3pd) levels of theory. The FT-IR, FT-Raman spectra were recorded in the region of 4000–400cm^{1} and 3500-100cm^{1} respectively. The harmonic vibrational frequencies were scaled and compared with experimental values. The observed and the calculated frequencies are found to be in good agreement. The UV–visible spectrum was also recorded and compared with the theoretical values. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Natural Population Analysis (NPA) was used for charge determination in the title molecule. Besides, molecular electrostatic potential (MEP), frontier molecular orbitals (FMO) analysis were investigated using theoretical calculations.

Keywords: FTIR; FT-Raman; DFT; MEP; NBO; NLO

Introduction

2-phenylcyclopropan-1-amine (2PCP1A) compound belongs to the class of organic compounds known as aralkylamines. These are alkylamines in which the alkyl group is substituted at one carbon atom by an aromatic hydrocarbyl group. This monoamine oxidase inhibitor is effective in the treatment of major depression, dysthymic disorder, and atypical depression. It also is useful in panic and phobic disorders. Phenycycloproane and its derivatives are studied by several authors. Influence of Reactant Polarity on the course of (4+2) Cycloadditions was investigated by Sustmann [1]. Density Functional Theory Study of the Cycloaddition Reaction of Furan Derivatives with Masked o-Benzoquinones is carried out by Domingo [2]. Resonance Raman studies of phenylcyclopropane radical cations are studied by Godbout [3]. Weak hydrogen bridges: a systematic theoretical study on the nature and strength of C--H...F--C interactions is done by Kryspin [4]. Lysine demethylase inhibitors for myeloproliferative or lymphoproliferative diseases or disorders are studied by Mathewet [5].

In the present work, harmonic-vibrational frequencies are calculated for 2-phenylcyclopropan-1-amine (2PCP1A) using B3LYP/6-31G(d,p), 6-311++G(2d,3p) and 6-31G(3df,3pd) methods. The calculated spectra of the compound are compared to that of experimentally observed FT-IR and FT-Raman spectra. The redistribution of electron density (ED) in various bonding and antibonding orbitals and E(2) energies have been calculated by natural bond orbital (NBO) analysis by DFT method to give clear evidence of stabilization originating from the hyper conjugation of various intramolecular interactions. The HOMO and LUMO analysis have been used to elucidate information regarding ionization potential (IP), electron affinity (EA), electronegativity (), electrophilicity index (), hardness () and chemical potential () are all correlated. These are all confirming the charge transfer within the molecule and also molecular electrostatic potential (MESP) shows the various electrophilic and nucleophilic region of the title molecule.

Experimental

The compound under investigation 2PCP1Awas purchased from Aldrich chemicals, USA. The FT-IR spectrum of 2PCP1A was recorded in the region 400-4000 cm^{1} on IFS 66 V spectrophotometer using KBr pellet technique as shown in

Figure 1(b). The FT-Raman spectrum of 2PCP1A has been recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 3500-100cm^{1}on a Thermo Electron Corporation model Nexus 670 spectrophotometer equipped with FT-Raman module accessory as shown in Figure 2(a). The ultraviolet absorption spectra of 2PCP1A were examined in the range 200–400 nm using SHIMADZU UV-1650 PC, UV–VIS recording spectrometer using water as solvent.

Computational Details

DFT method is very much useful for the Quantum mechanical calculations of energies, geometries and vibrational wave numbers of organic chemical system. The gradient corrected density functional theory (DFT) [6] with the three-parameter hybrid functional Becke3 (B3) [7,8] for the exchange part and the Lee-Yang-Parr (LYP) correlation functional [9], calculations have been carried out in the present investigation, using 6-31G(d.p), 6-311++G(2d,3p) and 6-31G(3df,3pd) basis sets with Gaussian-03 [10] program, invoking gradient geometry optimization [11]. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to true energy minima. The optimized structural parameters of 2PCP1A were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies. The vibrational assignments of the normal modes were made on the basis of the potential energy distribution (PED) calculated by using the VEDA 4 program [12].

Results and Discussion

Molecular geometry

The first task for the computational work is to determine the optimized geometries of the title compound. The optimized molecular structure of 2PCP1A with the numbering scheme of the atoms is shown in Figure 1(a). The optimized structural parameters such as bond length and bond angles are determined by B3LYP method with 6-31G(d,p),6-311++G(2d,3p) and 6-31G(3df,3pd) as basis sets. The geometry of the molecule is considered by possessing C1 point group symmetry. From the structural data given in Table 1, it is observed that the various benzene ring CC bond distances and the CH bond lengths of title compound are found to be almost the same at all levels of calculations.

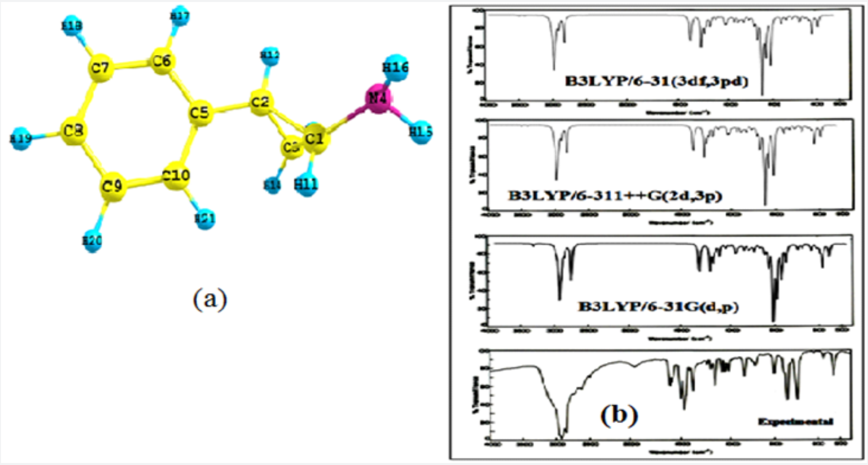

Figure 1: a) Optimized structure of 2PCP1A and b) FT-IR spectra of 2PCP1A.

Table 1: Optimized geometrical parameters with bond length and bond angle of 2PCP1A.

Bond length(Å)	B3LYP		
	6-31G(d,p)	6-311++G(2d,3p)	6-31G(3df,3pd)
C1-C2	1.52	1.50	1.51
C1-C3	1.49	1.48	1.49
C1-N4	1.44	1.43	1.44
C1-H11	1.09	1.08	1.08
C2-C3	1.51	1.50	1.51
C2-C5	1.48	1.49	1.48
C2-H12	1.08	1.08	1.08
C3-H13	1.08	1.08	1.08
C3-H14	1.08	1.09	1.08
N4-H15	1.01	1.02	1.01
N4-H16	1.01	1.02	1.01
C5-C6	1.40	1.41	1.40
C5-C10	1.40	1.41	1.40
C6-C7	1.39	1.40	1.39
C6-H17	1.08	1.09	1.08
C7-C8	1.39	1.38	1.39
C7-H18	1.08	1.07	1.08
C8-C9	1.39	1.40	1.39
C8-H19	1.08	1.09	1.08
C9-C10	1.39	1.40	1.39
C9-H20	1.08	1.08	1.08

C10-H21	1.08	1.08	1.08
Bond angle()			
C2-C1-N4	116.8	116.8	116.9
C2-C1-H11	114.6	114.8	114.8
C3-C1-N4	117.1	117.1	117.1
C3-C1-H11	115.9	115.9	116.1
N4-C1-H11	118.7	118.4	118.3
C1-C2-C5	122.0	122.1	121.9
C1-C2-H12	113.3	113.3	113.2
C3-C2-C5	122.5	122.4	122.5
C3-C2-H12	114.3	114.5	114.3
C5-C2-H12	114.4	114.5	114.4
C1-C3-H13	116.9	116.8	117.0
C1-C3-H14	118.6	118.5	118.6
C2-C3-H13	116.7	116.5	116.8
C2-C3-H14	117.9	117.8	117.8
H13-C3-H14	115.1	115.2	115.1
C1-N4-H15	110.2	110.3	110.5
C1-N4-H16	110.3	110.5	110.6
H15-N4-H16	106.9	106.8	106.8
C2-C5-C6	119.3	119.2	119.3
C2-C5-C10	122.7	122.5	122.7
C6-C5-C10	117.9	117.8	1117.9
C5-C6-C7	121.2	121.3	121.2
C5-C6-H17	119.1	119.2	119.0
C7-C6-H17	119.6	119.5	119.6
C6-C7-C8	120.2	120.5	120.1
C6-C7-H18	119.6	119.5	119.6
C8-C7-H18	120.1	120.1	120.1
C7-C8-C9	119.2	119.2	119.2
C7-C8-H19	120.3	120.2	120.3
C9-C8-H19	120.3	120.3	120.3
C8-C9-C10	120.4	120.4	120.4
C8-C9-H20	120.0	120.0	120.0
C10-C9-H20	119.5	119.5	119.5
C5-C10-C9	120.9	120.9	120.9
C5-C10-H21	119.9	120.0	120.0
C9-C10-H21	119.0	118.9	118.9

Vibrational Assignments

Table 2: Vibrational Assignments of 2PCP1A.

Experimental frequency		B3LYP			Vibrational Band Assignments (PED%)
FT-IR(cm^{-1})	FT-R(cm^{-1})	6-31G(d,p)	6-311++G(2d,3p)	6-31G(3df,3pd)	
3568	3566	3568	3565	3564	NH$_{2(asym)}$ (100)
3488	3492	3484	3488	3492	NH$_{2(sym)}$(99)
3228	3234	3234	3228	3207	CH$_{2(asym)}$(92)
3185	3197	3204	3198	3185	CH(11)
3192	3190	3192	3185	3172	CH(92)
3172	3173	3185	3172	3163	CH(95)
3152	3153	3175	3166	3152	CH(49)
3149	3150	3172	3158	3149	CH(92)
3146	3147	3169	3150	3146	CH(99)
3129	3128	3143	3130	3120	CH$_{2(sym)}$(94)
3064	3063	3068	3063	3061	CH(10)
1662	1663	1664	1662	1660	CC(18)+NH$_2$(35)
1659	1660	1662	1658	1649	HCH(38)+NH$_2$(44)
1636	1637	1636	1625	1622	HCH(62)
1532	1533	1544	1539	1532	HCH(52)
1510	1510	1512	1501	1498	HCH(91)
1473	1472	1486	1465	1473	HCH(30)
1437	1437	1442	1437	1430	HCH(48)
1372	1373	1374	1360	1365	HCH(13)
1365	1366	1365	1352	1354	HCH(64)
1330	1332	1331	1329	1322	HCH(52)
1271	1270	1271	1270	1267	NH$_2$(52)+HCH(10)
1250	1250	1249	1248	1244	HCH(68)

1222	1223	1226	1222	1219	HCH(19)
1215	1214	1212	1210	1205	HCH(34)
1178	1179	1186	1180	1178	HCH(29)
1165	1168	1171	1167	1166	HCH(23)
1122	1122	1125	1123	1119	HCH(29)
1110	1111	1108	1110	1107	HCH(46)
1095	1095	1092	1090	1087	HCH(52)
1062	1063	1063	1060	1062	HCH(22)
1056	1056	1058	1056	1053	HCH(41)
1013	1012	1014	1013	1011	HCCH(31)
995	994	998	995	996	HCNH(21)
977	978	992	990	977	HCCH(41)
965	964	966	965	972	HCCH(28)
945	943	945	947	941	HCH(52)
910	909	909	910	909	HCH(37)
901	899	901	899	901	HCH(52)
856	855	853	858	856	HCH(52)
848	846	848	845	848	HCH(52)+NH_2(11)
814	813	814	813	814	HCH(38)+NH_2(14)
763	762	770	763	766	HCH(72)
751	751	760	752	751	HCH(33)+NH_2(10)
639	640	641	648	637	HCH(67)
635	634	634	635	631	HCCH(31)
582	583	586	588	582	HCCH(26)
515	514	538	520	515	HCH(32)
439	440	441	448	439	HCH(28)
402	402	417	402	399	HCH(22)
375	375	377	375	375	HCH(44)
340	341	339	340	336	HCH(42)
298	297	312	308	298	HCH(44)+NH_2(10)
240	241	239	240	232	HCH(34)+NH_2(14)
162	162	162	159	162	HCH(56)
106	108	107	106	106	HCH(22)
48	49	49	48	47	HCH(24)

The molecule 2PCP1A belongs to C1 point group symmetry, and its 57 fundamentals are distributed amongst the symmetry species as, all these modes are found to be active both in the Raman scattering and infrared absorption. The detailed vibrational assignment of fundamental modes of 2PCP1A along with the calculated IR and Raman frequencies and normal mode descriptions (characterized by PED) are reported in Table 2. For visual comparison, the observed and calculated FT-IR and FT-Raman spectra of 2PCP1A at DFT–B3LYP method using 6-31G(d,p), 6-311++G(2d,3p) and 6-31G(3df,3pd) basis sets are shown in Figures 1(b) and 2(a) respectively. The main focus of the present investigation is the proper assignment of the experimental frequencies to the various vibrational modes of 2PCP1A in corroboration with the calculated harmonic vibrational frequencies at B3LYP level using the standard 6-31G(d,p),6-311++G(2d,3p) and 6-31G(3df,3pd) basis sets. Comparison of the frequencies calculated by DFT-B3LYP method with the experimental values reveals the overestimation of the calculated vibrational modes due to neglect of an harmonicity in real system.

CH vibrations

The aromatic structure shows the presence of CH stretching vibration in the region 3200–3000cm^{1} which is the characteristic region for the identification of CH stretching vibration [13]. In this region, the bands are not affected appreciably by the nature of the constituents. For our title molecule the bands corresponding to CH stretching vibrations at 3204,3185 and

3172cm^{1} by DFT methods show excellent agreement with the literature data and also with the band observed in the recorded FT-IR spectrum at 3172cm^{1} [14,15]. The PED corresponding to this vibration is pure mode of contributing more than 90% as shown in Table 2. Ring Vibrations. Many ring modes are affected by the substitutions in the ring of midodrine. The actual position of these modes are determined not so much by the natural of the substituents but by the form of substitution around the ring system [16]. In our present study the wave number computed 1663, 1662 and 1660cm^{1} by B3LYP methods are assigned to CC stretching vibrations for the title molecule shows good agreement with recorded spectra. The in-plane and out-of-plane bending vibration are computed by DFT/6-31G(d,p), 6-311++G(2d,3p) and 6-31G(3df,3pd) methods show good agreement with literature [18,19] and recorded spectral data.

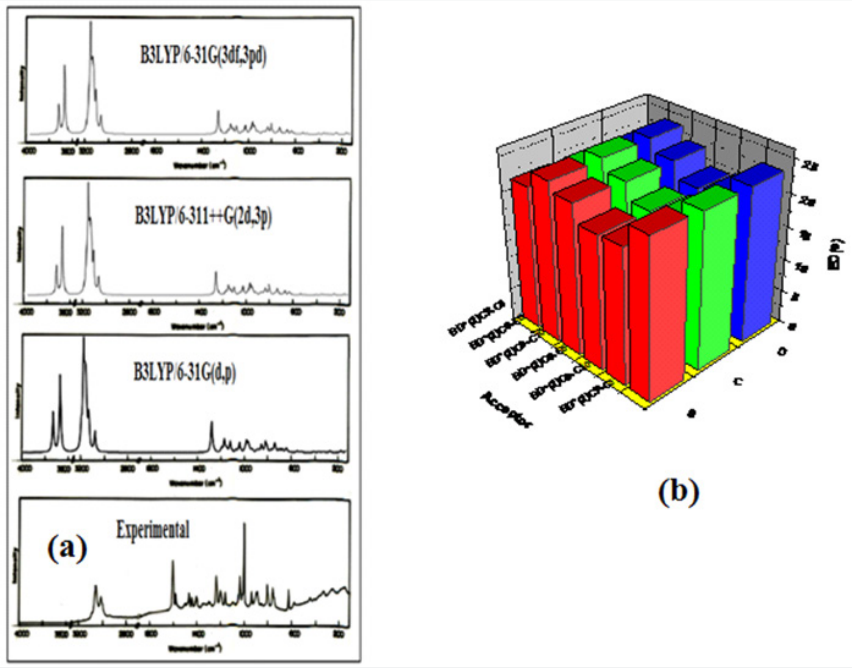

Figure 2: a) FT-Raman spectra of 2PCP1A and b) NBO analysis of 2PCP1A.

NH$_2$ Vibrations

Primary aliphatic amides absorb in the region 3520-3320cm^{-1} [17]. The position of absorption in this region depends upon the degree of hydrogen bonding and the physical state of the sample or the polarity of the solvent. The NH$_2$ asymmetric and symmetric stretching modes are 3568, 3564cm^{-1} and 3488, 3484cm^{-1} by B3LYP basis sets, while the experimental values are 3568 and 3566cm^{-1} in FT-IR and FT-Raman spectrum respectively. They are presented in Table 2. The PED contributions are 100% for stretching mode.

NBO Analysis

Natural bond analysis gives the accurate possible natural Lewis structure picture of because all orbitals are mathematically chosen to include the highest possible percentage of the electron density. Interaction between both filled and virtual orbital spaces information correctly explained by the NBO analysis could enhance the analysis of intra- and intermolecular interactions. The second order Fock matrix was carried out to evaluate donor (i) and acceptor (j) i.e. donor level bonds to acceptor level bonds interaction in the NBO analysis [18]. The result of interaction is a loss of occupancy from the concentrations of electron NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor(i) and acceptor(j), the stabilization energy E(2) associated with the delocalization ij is estimated a where qi is the donor orbital occupancy, εi and εj are diagonal elements and F (i, j) is the off diagonal NBO Fock matrix element.

Natural bond orbital analysis is used for investigating charge transfer or conjugative interaction in the molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy results from the second-order micro-disturbance theory are reported [19,20]. The larger E(2) value the more intensive is the interaction between electron donors and acceptors, i.e. the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [21]. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbitals correspond to a stabilization donor–acceptor interaction. NBO analysis has been performed on the 2PCP1A molecule at the DFT levels in order to elucidate the intramolecular interaction within the molecule.

The intramolecular interaction is formed by the orbital overlap between bonding BD(2)C5C6, BD(2)C9-C10 and antibonding BD*(2)C7-C8, BD*(2)C5-C6 orbital, which results in the intramolecular charge transfer causing stabilization of the system. The second-order perturbation theory of Fock matrix in the NBO analysis shows strong intramolecular hyperconjugative interactions and the results are shown in Table 3. The most important interactions observed are BD(2)C9C10BD*(2)C5-C6 and BD(2)C5-C6BD*(2)C7-C8 and the corresponding energies are 24.30 and 23.78kJ/mol respectively. This larger energy provides the stabilization to the molecular structure. Graphical representation NBO analysis is shown in Figure 2(b).

Table 3: Second order perturbation theory analysis of Fock matrix in NBO analysis and UV-Vis excitation energy (E) of 2PCP1A.

Donor(i)	Acceptor(j)	Calculated E(2)a(kJ/mol)		
		6-31G(d,p)	6-311++G(2d,3p)	6-31G(3df,3pd)
BD(2)C5-C6	BD*(2)C7-C8	23.78	23.46	23.47
	BD*(2)C9-C10	20.39	20.38	20.34
BD(2)C7-C8	BD*(2)C5-C6	20.17	19.98	19.96
	BD*(2)C9-C10	22.77	22.50	22.45
BD(2)C9-C10	BD*(2)C5-C6	24.10	24.30	24.29
	BD*(2)C7-C8	21.63	21.65	21.54

a E(2) means energy of hyper conjugative interaction (stabilization energy)

States	TD-B3LYP/6-31G(d,p)				Expt.	Major Contributions
	Gas phase		Water			
	cal	E(eV)	cal	E(eV)		
S1	227.27	5.4553	230.61	5.3764	225	HOMO->LUMO (94%)
S2	219.09	5.6589	222.11	5.5820	220	HOMO->L+1 (92%)
S3	213.88	5.7968	214.22	5.7876	210	H-2->LUMO (-16%), H-2->L+1 (-19%)

Molecular Electrostatic Potential (MEP)

The MEP is a useful feature to study reactivity given that an approaching electrophile will be attracted to negative regions (where the electron distribution effect is dominant). The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading and is very useful in research of molecular structure with its physicochemical property relationship [22,23]. The resulting surface simultaneously displays molecular size, shape and electrostatic potential value. In the majority of the MEP, while the maximum negative region which preferred site for electrophilic attack indications as red color, the maximum positive region which preferred site for nucleophilic attack symptoms as blue color. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue.

In this study, the color code of the map is in the range between -0.01054a.u. (deepest red) and 0.01054a.u. (deepest blue) in the studied compound, where blue indicates the strongest attraction and red indicates the strongest repulsion. The MEPs of 2PCP1A molecule in 3D plots are represented in Figure 3(a). As can be seen from the MEP map shown in figure, although the regions having the negative potential are over the carbon and nitrogen (the electronegative atoms) and also the regions having the positive potential are over hydrogen atoms localized a maximum positive region. From these results, we can say that the ring, the nitrogen atom and all hydrogen atoms (especially H16 atom) indicate the strongest attraction and C3 and N4 atoms indicate the strongest repulsion.

Molecular Orbitals Transport Properties

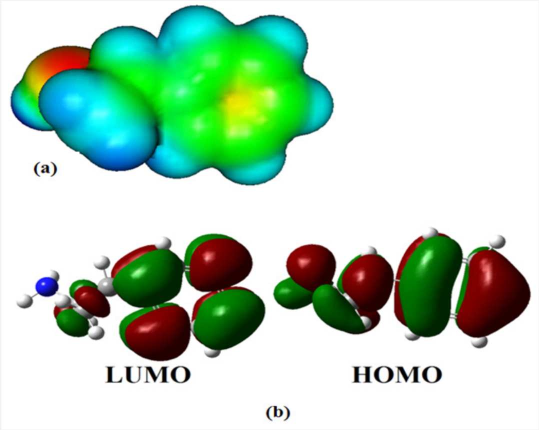

Figure 3: a) Electrostatic potential of 2PCP1A and b) Frontier molecular orbital of 2PCP1A.

The HOMO-LUMO gap results in a significant degree of electric excitation and charge transfer. In most cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice versa. Changes in the HOMO-LUMO gap by connecting with some noble metal or semiconductor or some other means result in the change of the charge transfer degree, intensity and position of the peak.

The HOMO–LUMO gap estimated to be 6.04eV at the B3LYP/6-31G(d,p) level and the frontier orbitals are illustrated in Figure 3(b).The experimental and theoretical UV–Vis spectra are shown in Figure 4(a). Theoretical and experimental maximum absorption wavelengths and excitation energy are collected in Table 3. The observed peaks were found at 225nm in the water phase. The calculated peaks were found at 227nm in the gas phase. The calculated peaks were thus 2nm higher than the observed peaks, and this error may have been caused by the error of PCM modeling.

Natural Population Analysis

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems [24]. Our interest here is in the comparison of different methods to describe the electron distribution in 2PCP1A as broadly as possible, and assess the sensitivity of the calculated charges to changes in (i) the choice of the basis set and (ii) the choice of the quantum mechanical method. Mulliken charges, calculated by determining the electron population of each atom as defined in the basis functions. The Mulliken charges calculated at different levels basis sets are listed in Table 4. The corresponding Mulliken's plot with B3LYP different basis sets are shown in Figure 4(b).

Table 4: Mulliken atomic charges and Molecular properties of 2PCP1A.

Atoms	**B3LYP**		
	6-31G(d,p)	**6-31++G (2d,3p)**	**6-31G (3df,3pd)**
C1	0.026589	0.030345	0.128448
C2	-0.015955	-0.160519	0.303033
C3	-0.212656	-0.213333	-0.347465
N4	-0.597307	-0.605409	-0.540817
C5	0.194118	0.195278	0.087696
C6	-0.140398	-0.140516	-0.074285
C7	-0.084941	-0.084638	-0.153163
C8	-0.089668	-0.089638	-0.278256
C9	-0.086862	-0.086972	-0.089999
C10	-0.149335	-0.150573	-0.230494
H11	0.082292	0.094466	0.069303
H12	0.106929	0.096682	0.081655
H13	0.126486	0.117570	0.090952
H14	0.113109	0.116024	0.088046
H15	0.239854	0.244086	0.163166
H16	0.236448	0.239490	0.158355
H17	0.079777	0.067663	0.101850
H18	0.082257	0.073013	0.111664
H19	0.078718	0.082042	0.107057
H20	0.079439	0.091732	0.106178
H21	0.074704	0.083206	0.117076
Molecular Properties	**B3LYP**		
	6-31G(d,p)	**6-311++ G(2d,3p)**	**6-31G (3df,3pd)**
HOMO(eV)	-5.9715	-6.2888	-6.0877
LUMO(eV)	0.0938	-0.3613	-0.0389
(H-L) (eV)	6.0653	5.9275	6.0488
Ionization potential(I)	5.9715	6.2888	6.0877
Electron affinity(A)	0.0938	0.3613	0.0389
Chemical hardness()	2.9388	2.9637	3.0244
Chemical potential()	-3.0326	-3.3250	-3.0633
Electronegativity()	3.0326	3.3250	3.0633
Electrophilicity index()	4.5983	5.5278	4.6919
Softness(S)	0.3402	0.3374	0.3306

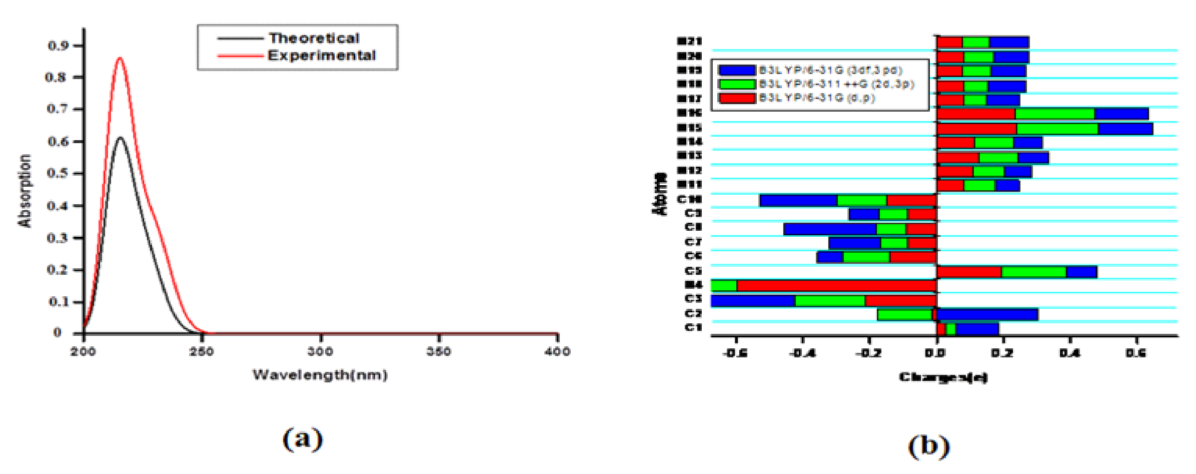

Figure 4: a) UV-Visible spectrum of 2PCP1A and b) Natural population analysis of 2PCP1A.

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Global Reactivity and Charge Reactivity Descriptors

The other electronic properties as the chemical potential (), electronegativity (), electrophilicity index () and chemical hardness () are given in Table 4. The, and are important tools to study the order of stability of molecular systems. Using HOMO and LUMO energies, the and have been calculated. The chemical hardness and the chemicalpotential are given by the following expression,(IA)/2, (IA)/2. The, which measures the stabilization energy, has been given by the following expression, in terms of electronic chemical potential and the chemical hardness: 2/2 electro negativity (),(IA)/2or where I and A are ionization potential and electron affinity of a molecular system [25-28].

Thermodynamics Properties

On the basis of vibrational analysis at B3LYP/6-31G(d,p), 6-311++G(2d,3p) and 6-31G(3df,3pd)levels and several thermodynamic parameters are calculated and are compared in Table 5. The zero point vibration energies (ZPVE) and the entropy, S_{vib} (T) are calculated with B3LYP methods are to the extent of accuracy and the variations in ZPVEs seem to be insignificant. The dipole moment calculated using B3LYP/6-31G(d,p), 6-311++G(2d,3p) and 6-31G(3df,3pd) basis sets are found. The total energies and the change in the total entropy of2PCP1A at room temperature are found to be marginal.

Table 5: Thermodynamic functions of 2PCP1A.

Parameters	B3LYP		
	6-31G(d,p)	6-311++G(2d,3p)	6-31G(3df,3pd)
ZPVE(KJ/mol)	113.05	112.30	112.29
Rotational constant x	3.531	3.533	3.542
y	0.743	0.742	0.745
Z	0.679	0.680	0.681
Thermal Energy (kJ/mol)	0.188	0.188	0.187
Entropy (cal/mol -1K-1)			
Total	92.17	92.51	92.69
Translational	40.57	40.58	40.57
Rotational	29.57	29.52	29.56
Vibrational	22.02	22.03	22.54
Dipole moment (Debye)			
µx	-0.6341	0.1800	-0.5402
µy	-0.1856	-0.6571	-0.6539
µz	-1.0036	-0.8871	-0.5228
Total	1.6778	1.1186	0.9963
Heat capacity(CV)			
Total	34.68	35.10	35.09
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	28.72	29.15	29.13
Enthalphy(E)			
Total	118.55	117.87	117.86
Translatioanal	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	116.77	116.10	116.09

Conclusion

A complete vibrational analysis of 2PCP1A was performed by B3LYP/6-31G(d,p), 6-311++G(2d,3p) and 6-31G(3df,3pd) basis sets. This study demonstrates that the DFT (B3LYP) calculations are powerful approach for understanding the vibrational spectra of the title molecule. FT-IR, FT-Raman and UV-spectral studies of 2PCP1A were carried out. The molecular structure analysis has been performed based on the quantum mechanical approach by DFT calculation. The vibrational modes are assigned on the basis of PED percentage. NBO analysis indicates the strong intramolecular hyperconjugative interaction within the molecule and stability of the molecule. Mulliken charges on 2PCP1A at different levels were calculated and the results discussed. HOMO, LUMO energies and HOMO-LUMO energy gap was also calculated. The maximum absorption peak$_{max}$ in the UV-Vis spectrum has been observed at 304nm. The MEP map shows that the negative potential sites are on nitrogen and some of the carbon atoms as well as the positive potential sites are on the hydrogen and carbon atoms in the molecule.

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