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Vibrational spectroscopic investigation of 1-pyrrolidino-1-cyclohexene: A comparative density functional study

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HIGHLIGHTS

- Infrared, Raman and quantum chemical calculations of 1pych.
- Potential energy surface of 1pych.
- Mixture of envelope and twist forms of 1pych is supposed to be the most stable form.
- B3-LYP method is provides satisfactory results for the prediction vibrational data.

GRAPHICAL ABSTRACT
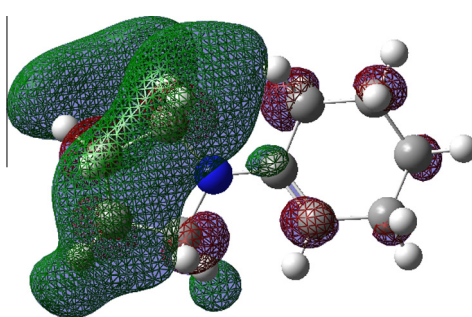
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ABSTRACT

Infrared and Raman spectra of 1-pyrrolidino-1-cyclohexene (1pych) have experimentally been reported in the region of 4000–100 cm^{-1}. The conformational analysis, optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of 1pych ($C_{10}H_{17}N$) have theoretically been examined by means of the Becke-3–Lee–Yang–Parr (B3-LYP) density functional theory (DFT) method together with the 6-31++G(d,p) basis set. Furthermore, reliable vibrational assignments have been made the basis of potential energy distribution (PED) and the thermodynamics functions, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of 1pych have been predicted. Angular distribution of the probability density of populations of its conformational isomers is determined by analysis of the potential energy surface (PES). Comparison between the experimental and theoretical results indicates that B3-LYP method is provides satisfactory results for the prediction vibrational wavenumbers and structural parameters and the mixture of envelope and twist conformers is supposed to be the most stable form of 1pych.

Introduction

It has been reported that many pyrrolidine derivatives are of great interest in medicinal and pharmaceutical chemistry [1–6]. 1-Pyrrolidino-1-cyclohexene (1pych) is a pyrrolidine derivative and referred to in the literature by different synonyms such as 1-(1-cyclohexen-1-yl)pyrrolidine, N-cyclohexenylpyrroli-dine, N-(1-cyclohexen-1-yl)pyrrolidine. 1pych has been used for the recyclisation of carbo- and heterocyclic compounds involving malononitrile and its derivatives [7], in the reduction of enamines [8], for analysis of the transition metal catalyzed hydroboration of enamines [9], and for expedient synthesis of a novel class of pseud-oaromatic amino acids [10].

Vibrational spectroscopy has widely been used as a standard tool for structural characterization of molecular systems together with DFT calculations [11–14]. DFT has big popularity as a cost effective general procedure for studying the physical properties

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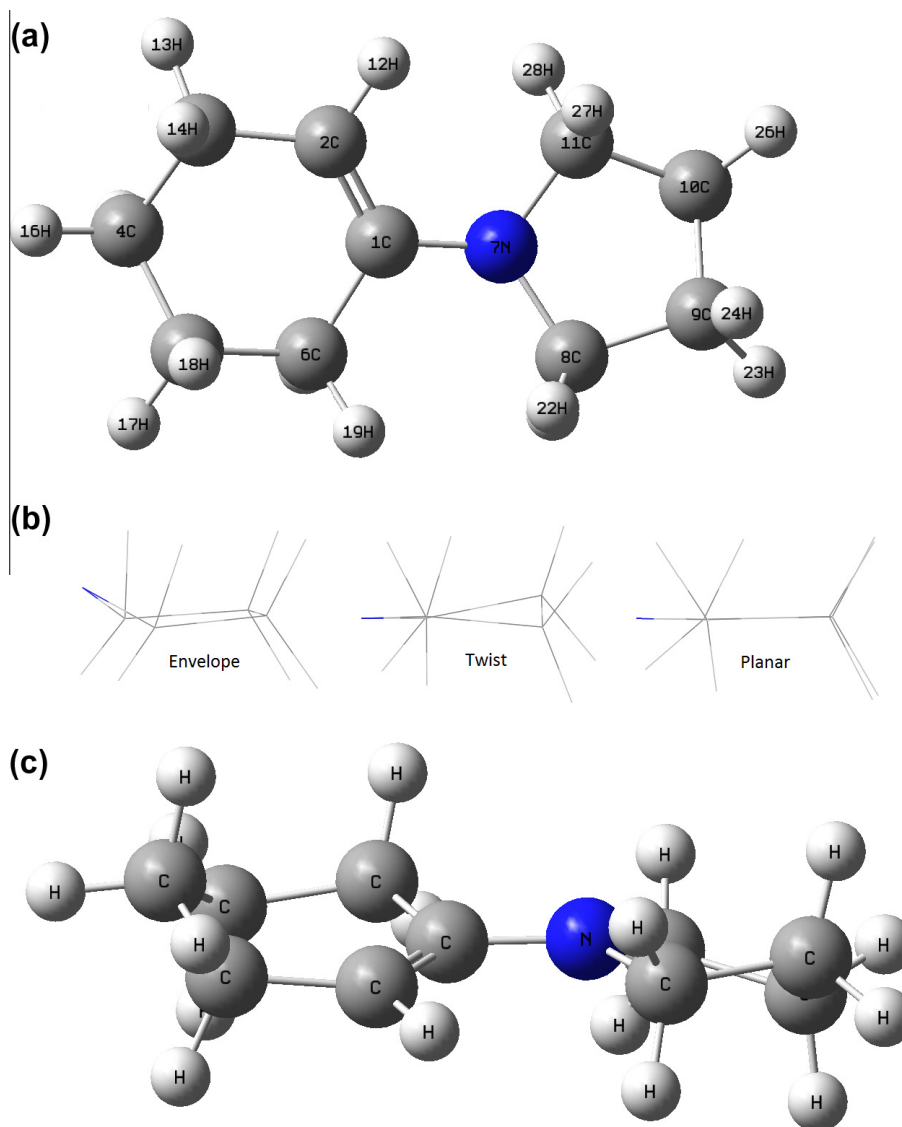E-mail address: cparlak@dpu.edu.tr (C. Parlak).

Fig. 1. Numbering of 1pych (a), possible stable conformations of pyrrolidine (b), optimized structure (conformer 8) for 1pych (c).

of molecules. Unlike Hartree Fock (HF) 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 [11–14]. The DFT/B3-LYP model exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of organic compounds [11–20].

Even though, 1pych has wide applications in many areas of science, to the best of our knowledge, there is no any information present in literature about its vibrational spectroscopic properties. A detailed quantum chemical study will aid in making definitive assignments to the fundamental normal modes and in clarifying the obtained experimental data of 1pych. Furthermore, all data presented may be helpful in the context of the further studies of 1pych. For the above goals, we have reported vibrational spectra of 1pych. The vibrational frequencies with PED values, HOMO and LUMO data and conformational analysis of 1pych are also investigated for its most stable conformer by means of B3-LYP/6-31++G(d,p) level. The results of the theoretical and spectroscopic studies are reported here.

Experimental

A commercial sample of 1pych in liquid phase was purchased (Sigma Aldrich, %97) and used without further purification. FT-MIR and FT-FIR spectra of 1pych in liquid phase were recorded in the region of 4000–400 cm^{-1} and 400–10 cm^{-1} with a Bruker Optics IFS66v/s FTIR spectrometer with a nominal resolution of 2 cm^{-1}. Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation from a 3B diode laser having 3 cm^{-1} resolution in the spectral region of 4000–100 cm^{-1}.

Calculations

All the calculations were performed using Gaussian 09.A1 program [21] on HP DL380G7 server system and GaussView 5.0.8 [22] was used for visualization of the structure and simulated vibrational spectra. Many possible conformational isomers could be proposed for 1pych, but here, for the theoretical conformational
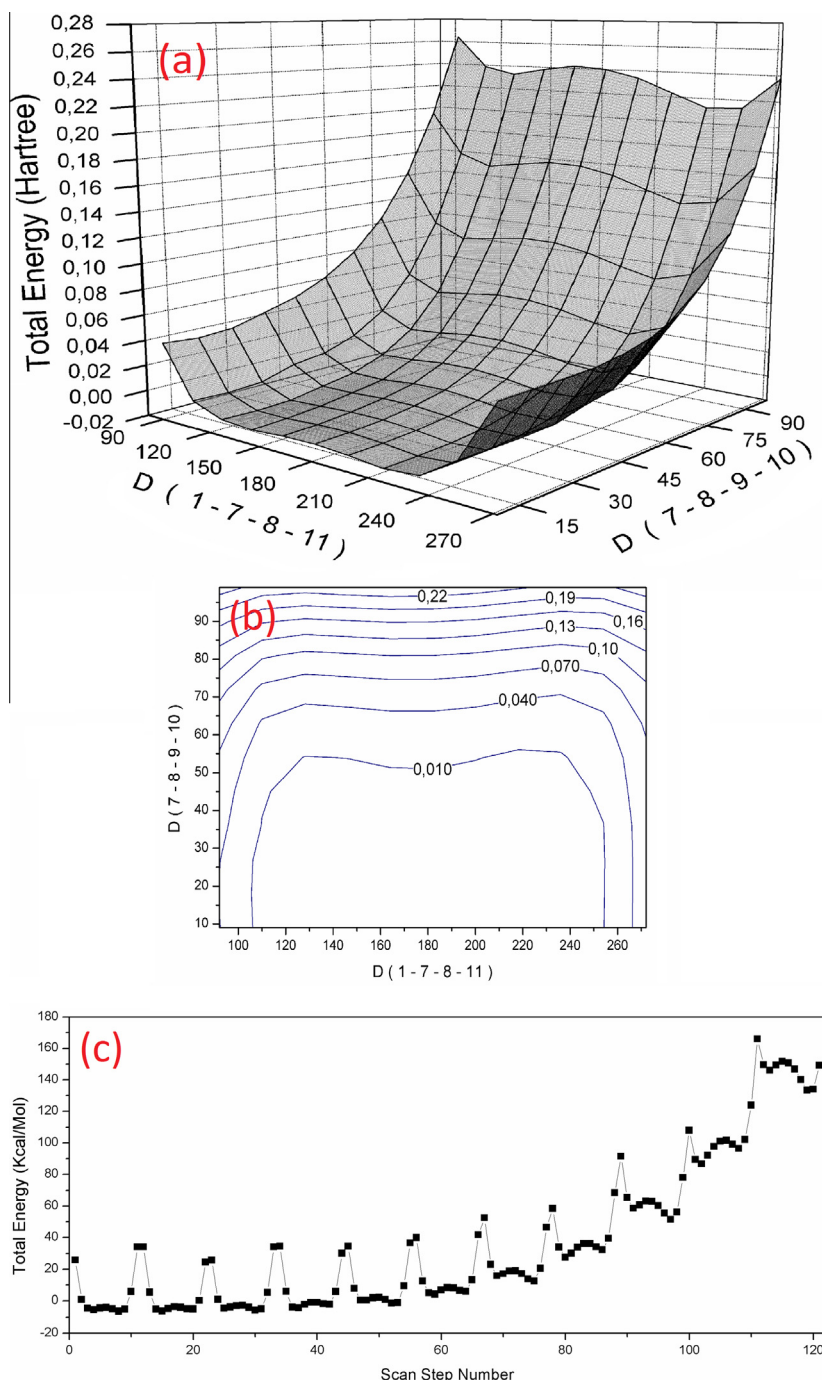
Fig. 2. PES (a), contour (b) and scan/energy (c) graphics of 1pych.

analysis, it was first investigated the rotation in its C1—N7—C8—C11 and N7—C8—C9—C10 (Fig. 1a) dihedral angles scanning from 0 to 90 and 120–270°, respectively, in 10 degrees increments, which was calculated in the gas phase at semi-empirical Austin Model 1 (AM1). Fig. 2 shows PES graphics for the title molecule. Scan process has conducted for 121 different conformational isomers of 1pych and it has been found that 1pych is the most stable in conformer 8 (Fig. 2c, Table S1). Since pyrrolidine has different possible conformers such as the planar, envelope and twist conformations [23], the conformer 8 for 1pych may be called as the mixture of twist and envelope forms due to its geometric parameters (Fig. 1c). Analysis of PES allowed us to determine the

conformational composition of 1pych with a high accuracy and showed that 1pych exists as the mixture of twist and envelope forms, which are seen from Fig. 1c. For the optimization calculation, the mixture of twist and envelope forms of 1pych were first optimized in the gas phase at the B3-LYP level of theory using the 6-31++G(d,p) basis set and no geometric restrictions were applied. After the optimization, in order to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies, harmonic vibrational frequencies and corresponding vibrational intensities of the same conformer of 1pych were calculated by using analytic second derivatives with the same method and basis set under the keyword freq = Raman, pop = full

Table 1
Some optimized geometric parameters for the most stable form of 1pych.

Bond lengths (Å)	B3-LYP/6-31G++(d,p)	Py [27]	Cych [28]	Bond angles (°)	B3-LYP/6-31G++(d,p)	Py [27]	Cych [28]
C—N, py	1.466	1.469		C8—C9—C10	104.30	109.4	
C8—N7	1.474			C9—C10—C11	102.47	109.4	
C11—N7	1.458			C8—N—C11	110.98	105.2	
C—H, py	1.096	1.090		N—C8—C9	104.62	104.6	
C8—H22	1.099			N—C11—C10	103.27	104.6	
C8—H21	1.098			H21—C8—H22	107.38	106.0	
C9—H23	1.094			H27—C10—H28	107.38	106.0	
C9—H24	1.096			H23—C9—H24	107.45	106.0	
C10—H25	1.096			H25—C10—H26	108.08	106.0	
C10—H26	1.094			C2—C1—C6	121.42		123.5
C11—H27	1.106			C3—C4—C5	110.07		111.0
C11—H28	1.096			C1—C6—C5	113.04		112.1
C—C, py	1.538	1.543		H15—C4—H16	106.95		109.2
C8—C9	1.544			H13—C3—H14	105.37		105.6
C9—C10	1.539			C1—C6—H19	110.16		109.5
C10—C11	1.531			C2—C3—H13	110.13		109.7
C—H cych	1.097		1.093	C6—C5—H17	109.45		109.7
C2—H12	1.086			C6—C5—H18	109.41		109.3
C3—H13	1.099			C4—C5—H17	111.04		109.2
C3—H14	1.103			C4—C5—H18	109.05		108.4
C4—H15	1.099			C4—C3—H13	109.76		110.2
C4—H16	1.097			Dihedral angles (°)			
C5—H17	1.097			C11—N7—C1—C2	−0.62		
C5—H18	1.099			C11—C7—C1—C6	174.91		
C6—H19	1.096			C2—C1—N7—C8	151.59		
C6—H20	1.101			C6—C1—N7—C8	−23.86		
C1—C2	1.356		1.335	C9—C8—N7—C11	−5.45		
C1—C6	1.519		1.504	C9—C8—N7—C1	−160.15		
C2—C3	1.512		1.504	C8—C9—C10—C11	35.45		
C3—C4	1.534		1.515	C3—C2—C1—C6	−2.47		
C4—C5	1.531		1.550	C5—C6—C1—C2	13.04		
C5—C6	1.536		1.515	C2—C3—C5—C6	−14.02		
C1—N7	1.396			C2—C3—C4—C5	45.25		
				C3—C4—C5—C6	−61.47		
				C10—C11—C9—C8	34.88		
				C8—C11—C9—C10	34.88		
				C9—C8—C11—C1	7.65		
				C8—C9—C10—C11	35.45		
				C9—C8—C11—N7	6.4		

and then scaled with 0.955 (above 1800 cm^{-1}), 0.977 (under 1800 cm^{-1}) [16,17,19,20] and scaled quantum mechanics (SQM) methodology [18,11,24].

PED calculations, which show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule and thus make it possible to describe the character of each mode numerically, were carried out by the VEDA 4 (Vibrational Energy Distribution Analysis) [25]. Calculated Raman activities are converted to relative Raman intensities using the relationship derived from the intensity theory of Raman scattering [18,26].

Results and discussion

The results of the calculations on the molecular conformers and geometrical parameters of 1pych are discussed first. A brief discussion of the experimental and theoretical vibrational frequencies and intensities is then presented.

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 changes in frequencies. Gibbs free energy and some thermodynamic parameters of the optimized geometry of the mixture form of envelope and twist conformer for 1pych calculated with B3-LYP/6-31++G(d,p) are given as supplementary

materials (Table S2). Regarding the calculated free energies, 108 forms of 121 geometric structures relative to the most stable form 8 could be neglected for the calculation of equilibrium constant since their energy differences are larger than 2 kcal/mol [15–20]. However, after optimizations, the rest 12 isomers tend to reshape them close to mixture of envelope and twist forms. Consequently, 1pych in the gas phase prefers mostly mixture of envelope and twist forms with almost a preference of 100%.

Some of the optimized geometric parameters (bond lengths, bond and dihedral angles) calculated by B3-LYP/6-31++G(d,p) are listed in Table 1. To the best of our knowledge, the experimental data on geometric structure of 1pych is not available in the literature. Therefore, the theoretical results of the mixture of envelope and twist forms for 1pych have been compared together with pyrrolidine [27] and cyclohexene [28] as given in Table 1. Theoretically calculated structural data for 1pych are consistent with its fragments' (pyrrolidine and cyclohexene) previously reported structural data. The mean absolute deviation (MAD) of bond lengths is 0.012 Å. Similarly, the correlation value of bond lengths between the experimental and theoretical data is found to be 0.99405. The biggest difference between the experimental and calculated bond distances is 0.021 Å. One can see that the length of the C1=C2 double bond increases more than other bonds in 1pych when compared to free cyclohexene which is possibly due to interactions of lone pair electrons of N7 and π electrons of C1=C2 double bond.

As it can be seen from Table 1, some differences of are observed in the calculated C8—C9—C10, C9—C10—C11 and C8—N7—C11 bond angles compared to experimental values according to the free

Table 2
Vibrational frequencies (cm^{-1}) for the most stable form of 1pych.

Mode	Assignments	Experimental		B3-LYP/6-31++G(d,p)				
	PED ($\geqslant$10%)	IR	Raman	ν^{α}	ν^{β}	ν^{φ}	I_{IR}	I_R
ν_1	ν CH (99)	3050 m	3072 m	3184	3041	3048	24.69	15.07
ν_2	ν CH (94)	3020 w	–	3111	2971	2978	52.24	23.42
ν_3	ν CH (93)	2965 w	–	3100	2961	2968	38.03	37.88
ν_4	ν CH (91)	–	2942 w	3072	2933	2940	61.21	16.15
ν_5	ν CH (84)	2928 vs	–	3066	2928	2935	51.46	51.56
ν_6	ν CH (88)			3066	2928	2935	69.21	22.51
ν_7	ν CH (89)			3065	2927	2933	38.74	25.68
ν_8	ν CH (88)			3056	2918	2925	43.22	24.63
ν_9	ν CH (87)			3051	2914	2920	17.93	21.88
ν_{10}	ν CH (86)			3029	2893	2900	65.68	38.15
ν_{11}	ν CH (83)			3029	2893	2899	51.05	26.08
ν_{12}	ν CH (88)	–	2885 vw	3023	2887	2893	20.10	22.04
ν_{13}	ν CH (88)			3014	2879	2885	18.14	23.16
ν_{14}	ν CH (89)	2870 m	–	3007	2872	2878	31.36	31.13
ν_{15}	ν CH (89)			3001	2866	2872	61.77	21.82
ν_{16}	ν CH (96)	2827 m	2837 w	2975	2841	2847	71.13	57.8
ν_{17}	ν CH (98)		–	2933	2801	2807	78.11	30.32
ν_{18}	ν CC (71)	1717 s						
		1641 vs	1651 vs	1687	1648	1676	125.74	55.42
ν_{19}	δ HCH (85)	1549 w	1500 m	1541	1506	1511	9.55	5.25
ν_{20}	δ HCH (88)	1486 vw	–	1526	1491	1494	1.99	0.39
ν_{21}	δ HCH (89)			1507	1473	1480	4.75	4.72
ν_{22}	δ HCH (87)			1506	1472	1478	2.51	5.99
ν_{23}	δ HCH (90)			1496	1462	1467	2.99	8.31
ν_{24}	δ HCH (87)			1494	1460	1467	5.52	7.2
ν_{25}	δ HCH (89)	1450 m	1456 s	1491	1457	1462	2.74	8.16
ν_{26}	δ HCH (89)	1435 w	–	1481	1447	1452	6.89	13.65
ν_{27}	δ HCH (34) + ν NC (12)	1392 vs	–	1422	1389	1399	78.18	5.69
ν_{28}	δ HCC (59)			1391	1359	1363	12.88	0.6
ν_{29}	δ HCC (65)			1384	1352	1356	9.92	0.68
ν_{30}	δ HCC (67)	1346 s	1348 m	1382	1350	1351	47.54	5.96
ν_{31}	δ HCC (62)			1372	1340	1345	4.51	7.82
ν_{32}	δ HCC (67)	–	1324 m	1364	1333	1335	24.94	6.14
ν_{33}	δ HCC (67)			1348	1317	1324	1.52	1.02
ν_{34}	δ HCC (65)			1342	1312	1310	4.87	2.21
ν_{35}	ν NC (32) + δ HCC (12)	1304 s	–	1330	1300	1302	87.62	3.62
ν_{36}	δ HCN (70)			1326	1295	1299	0.53	0.63
ν_{37}	δ HCC (69)	1260 w	1274 m	1288	1259	1251	17.88	4.93
ν_{38}	δ HCC (58)			1272	1242	1238	19.24	14.45
ν_{39}	δ HCC (64)	1243 vw	1239 vw	1268	1239	1231	1.44	1.9
ν_{40}	δ HCC (69)	1221 vw	1226 vw	1251	1222	1219	5.45	6.33
ν_{41}	ν NC (31)	1186 w	1194 s	1220	1192	1202	21.48	8.28
ν_{42}	δ HCC (64)			1198	1170	1178	11.94	3.59
ν_{43}	δ HCC (41) + ν CC (10)			1192	1165	1169	11.79	9.25
ν_{44}	δ HCC (45) + ν NC (18)	1155 m	1150 vw	1176	1149	1154	16.45	0.54
ν_{45}	δ HCC (83)			1160	1133	1126	5.32	1.08
ν_{46}	δ HCN (66)	1118 vw	–	1143	1117	1115	1.74	1.07
ν_{47}	δ HCC (62)	1082 vw	1083 s	1100	1075	1081	0.19	3.64
ν_{48}	ν CC (40) + δ HCC (11)	1061 vw	–	1094	1069	1069	2.36	2.91
ν_{49}	ν CC (60) + δ HCC (11)	–	1055 s	1074	1049	1062	0.99	3.72
ν_{50}	ν CC (54)			1055	1031	1045	0.75	11.85
ν_{51}	δ HCC (24) + δ CCC (22)	989 s	1001 m	1005	982	989	8.81	3.71
ν_{52}	δ HCC (41) + ν CC (20)			992	970	976	2.16	3.29
ν_{53}	ν CC (37) + δ HCC (28)	931 w	926 vs	950	928	935	1.79	6.04
ν_{54}	ν CC (40) + δ HCC (21)	912 vs	–	937	916	925	1.39	1.67
ν_{55}	δ HCC (40) + ν CC (23)			926	905	917	1.97	1.7
ν_{56}	ν CC (71)			922	901	911	2.37	13.53
ν_{57}	ν CC (72)			918	897	907	2.87	1.47
ν_{58}	δ HCN (40) + δ CCC (11)	–	886 vw	890	870	881	2.75	3.06
ν_{59}	δ HCC (27) + ν CC (20)+δ CCC (10)	864 vw	854 s	860	840	852	1.34	1.71
ν_{60}	ν CC (46) + δ HCC (11)	827 m	–	846	826	841	2.07	7.9
ν_{61}	δ HCC (59)			839	820	825	2.67	3.17
ν_{62}	γ HCCC (70)	762 s	781 vs	788	770	785	26.24	7.83
ν_{63}	ν CC (38)			779	762	775	0.11	13.77
ν_{64}	δ CCC (46) + δ HCC (14)	670 vw	660 m	701	684	690	1.41	0.72
ν_{65}	δ CCC (53) + δ HCN (16)	588 m	–	592	578	584	0.98	2.09
ν_{66}	δ CCC (41) + γ NCCC (22)	531 w	543 s	540	528	528	1.74	3.91
ν_{67}	γ NCCC (36) + δ CCC (26)	510 vw	477 m	522	510	513	2.41	
		488 vw						7.12
ν_{68}	δ CCC (48)	462 w	451 w	464	453	456	2.34	
		441 vw						5.8
ν_{69}	δ CCC (57) + γ NCCC (12)	–	413 w	428	418	419	0.11	3.84
ν_{70}	δ CCC (42) + τ CCCC (15) + ν NC (14)	340 m	329 s	333	325	328	0.78	15.82

Table 2 (continued)

Mode	Assignments	Experimental		B3-LYP/6-31++G(d,p)				
	PED (⩾10%)	IR	Raman	ν^α	ν^β	ν^φ	I_{IR}	I_R
ν_{71}	τ HCCC (63)	292 w	–	316	309	308	2.24	2.05
ν_{72}	τ CCCN (76)	279 w	255 s	271	264	263	1.48	4.4
ν_{73}	τ CCCC (66)	242 s	–	239	233	230	1.33	16.66
ν_{74}	δ CNC (51) + τ CNCC (24) + τ CCCC (10)	188 s	179 w	180	176	176	0.74	4.17
ν_{75}	τ CNCC (45) + CNC (28)	–	158 w	158	154	153	2.91	17.47
ν_{76}	τ CCCN (81)			109	106	105	2.47	29.85
ν_{77}	γ CCCN (80)	81 m		73	71	69	0.58	10.13
ν_{78}	τ CNCC (77)	65 m	–	69	68	64	3.15	50.35

$\nu\alpha$: Unscaled wavenumbers. ν^β: scaled with 0.955 above 1800 cm−1, 0.977 under 1800 cm−1. ν^φ: scaled by SQM methodology. I_{IR} and I_R: Calculated infrared and Raman intensities. PED data are taken from VEDA4. Freq: frequency, v: very, s: strong, m: medium, w: weak, sh: shoulder.
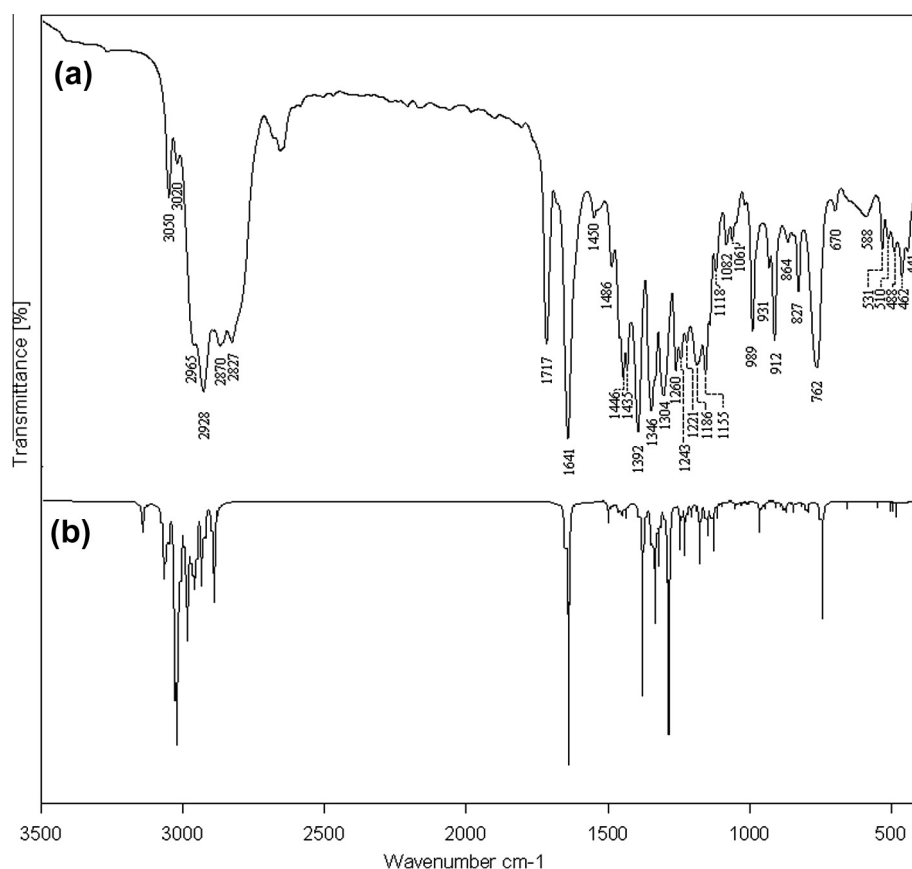
Fig. 3. Experimental (a) and calculated (b) FT-MIR spectra of 1pych.

pyrrolidine. The biggest difference between the experimental and calculated bond angles is 6.93°. All the other bond angles are reasonably close to the experimental data. The MAD value of calculated bond angles is 1.73°.

Dihedral angles of cyclohexene part C3—C2—C1—C6, C5—C6—C1—C2 and C2—C3—C5—C6 are found as −2.47°, −13.04°, −14.02° nearly indicate a planar system. Angles of C2—C3—C4—C5 and C3—C4—C5—C6 are calculated as 45.250° and −61.470° which are 44.90° free cyclohexene [28]. In the case of the mixture of envelope and twist forms, the dihedral angle of C10—C11—C9—C8 and C8—C11—C9—C10 are calculated as 34.88° and this indicates that C10—C8—C11 on the pyrrolidine ring is on the same plane. The calculated dihedral angle C9—C8—C11—C1, 7.65°, shows that cyclohexene ring is almost equatorial preference regarding to the plane constructed by C9—C8—C11 atoms. In case of twist form, the N-atom with the attached carbons 8 and 11 were considered to lie horizontally and the other carbons (9 and 10) are

twisted about the horizontal axis passing through the nitrogen atom and the mid point of the C9—C10 bond as seen in Fig. 1 [23]. This twist angle is referred to dihedral angle of C8—C9—C10—C11, in the present study related angle is calculated as 35.45° whereas 10.2° in literature. Normally, in the case of the envelope structure, the molecule may be regarded as if it is composed of two groups of atoms, each constitutes a planar moiety in the structure. The first planar moiety is that involving the carbons 8, 9, 10, and 11. The second one is formed from nitrogen atom and the two attached carbons 8 and 11. But, in the present study, carbon 10 shifted below from C9—C8—C11 plane. Due to this situation, we have used C9—C8—C11 and C11—N7 planes for angle of envelope. The dihedral angle of between the planes is C9—C8—C11—N7 which is calculated as 6.4° whereas 36.4° and 39.4° in literature [23]. According to the literature, the obtained structure in the present study can be called the mixture of envelope and twist forms.
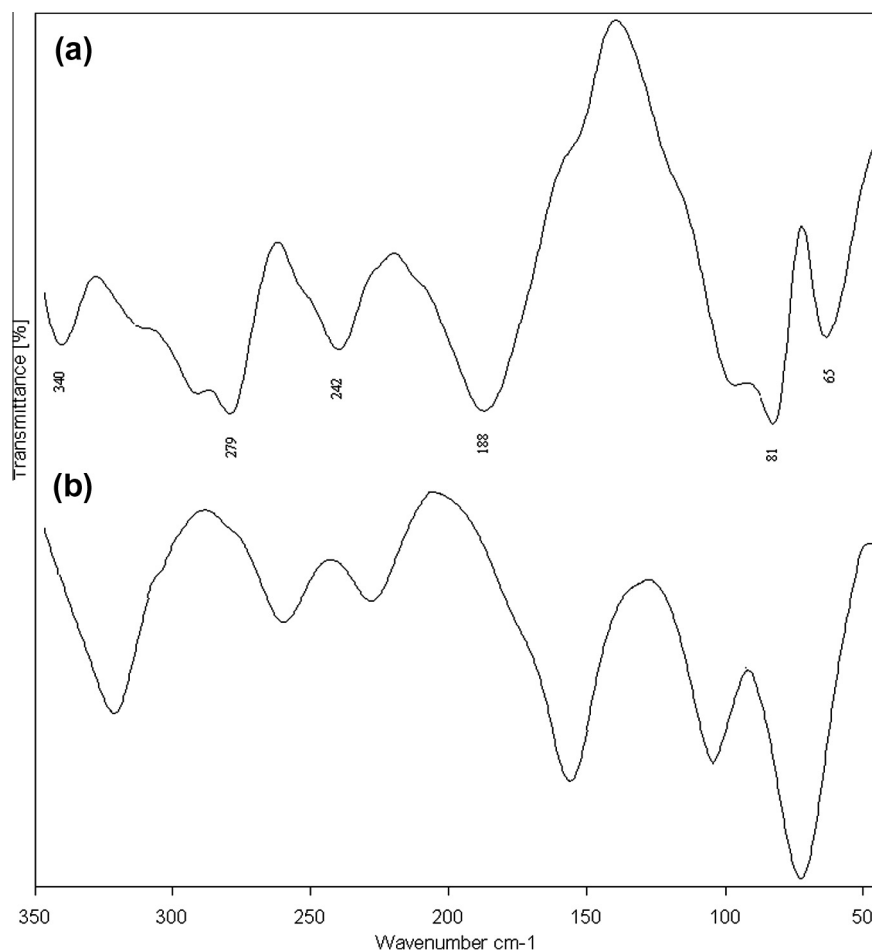
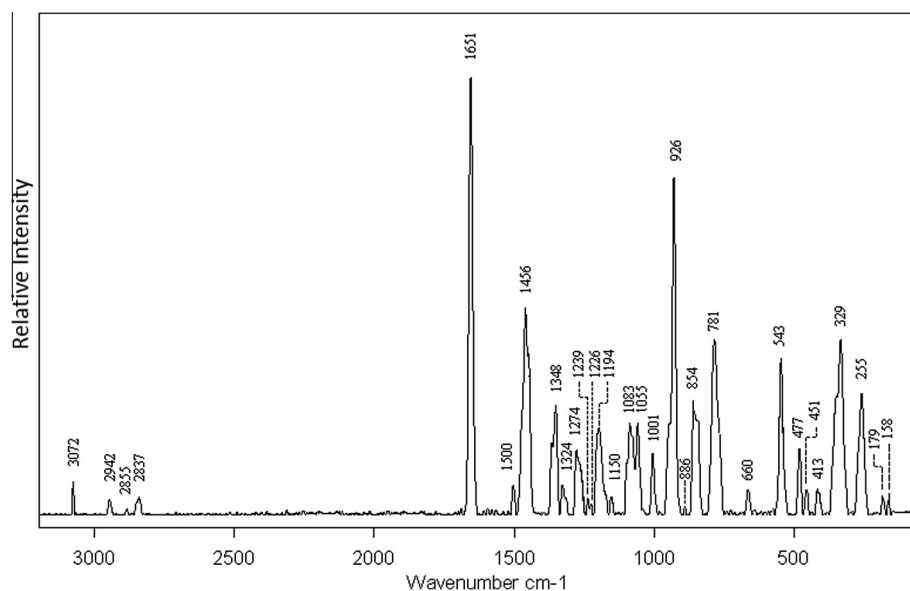**Fig. 4.** Experimental (a) and calculated (b) FT-FIR spectra of 1pych.

Fig. 5. Experimental Raman spectrum of 1pych.

Vibrational studies of 1pych

To the best of our knowledge, the vibrational frequencies and assignments for 1pych have not been reported in the literature. The measured and calculated vibrational frequencies for 1pych along with corresponding vibrational assignments and intensities are given in Table 2 and the theoretical and experimental vibrational spectra of 1pych are shown in Figs. 3–5. All calculated frequency values presented in this paper are obtained within the harmonic approximation which allows us to describe the

vibrational motion in terms of independent vibrational modes each of which is governed by a simple one dimensional harmonic potential. The 1pych molecule consists of 28 atoms, so it has 78 normal vibrational modes and it belongs to the point group C_1 with only identity (E) symmetry element or operation. It is difficult to determine the 1pych's vibrational assignments in the observed spectrum due to its low symmetry. Therefore, the assignments of vibrational modes of the most stable form for 1pych determined by VEDA 4 given in Table 2. According to the calculations, nine normal vibrational modes of 1pych are below 400 cm^{-1} while 69 modes are between 4000 cm^{-1} and 400 cm^{-1}.

The high frequency region contains characteristic frequencies of CH stretching that are observed at 3050 cm^{-1} and 3020 cm^{-1} as medium and weak bands in the IR spectrum and at 3072 cm^{-1} as medium in the Raman spectrum. The CH vibrational frequencies are consistent with previously reported for free cyclohexene which has two CH bands at 3067 cm^{-1} and 3026 cm^{-1} in the IR spectrum as weak and medium [28]. The corresponding scaled theoretical values of these modes are 3041 cm^{-1} (or 3048 cm^{-1}) and 2971 cm^{-1} (or 2978 cm^{-1}). CH$_2$ antisymmetric and symmetric stretchings of 1pych are experimentally observed between 2965 and 2827 cm^{-1}. According to PED results all the contributions between 2961 and 2801 cm^{-1} (2968–2807 cm^{-1}) are due to CH$_2$ antisymmetric and symmetric stretchings. Similar vibrational modes are also observed for other pyrrolidine derivatives [15].

The C—C stretching vibrations of 1pych have been observed at 1717 cm^{-1}/1641 cm^{-1} (IR) and 1651 cm^{-1} (R). The corresponding scaled theoretical value of this mode is 1648 cm^{-1} (or 1676 cm^{-1}). The free cyclohexene has a CC stretching band at 1656 cm^{-1} [29] while free pyrrolidine has no band for this region in the both IR and Raman spectra [23]. The CN stretching of 1pych are observed at 1392 cm^{-1} (IR), 1304 cm^{-1} (IR), 1186 cm^{-1} (IR) and 1194 cm^{-1} (R) as very strong, strong, weak and strong, respectively, while the present theoretical values are 1389 cm^{-1} (1399 cm^{-1}), 1300 cm^{-1} (1302 cm^{-1}) and 1192 cm^{-1} (1202 cm^{-1}). The CC or CN stretching, CCC, CCN or CCH bending, some torsion and out modes dominate the regions of 1000–500 cm^{-1} while CCC or CCN bending and CCCN, HCNC, HCCC or CCCC torsion modes are seen in the low frequency region. Vibrational modes in the low frequency region of the spectrum contain contributions of several internal coordinates and their assignment is a reduction approximation to one of two of the internal coordinates. As it can be seen from Table 2, Figs. 3–5 and S1, there is a good agreement between the experimental and theoretical vibrational frequencies.

To make a comparison between the experimental and theoretical frequencies, we have calculated root mean square deviation (RMSD) frequently used to measure of the differences between values predicted by a model and actually observed from the thing being modeled. In this study, RMSD values have been obtained as 17 cm^{-1} (IR)/12 cm^{-1} (R) with dual scaling factors and 15 cm^{-1} (IR)/13 cm^{-1} (R) for SQM methodology. It can be seen that the B3LYP calculation is reliable for both IR and Raman spectra for both scaling methods. Furthermore, the correlation values between the experimental and calculated vibrational frequencies are found to be as 0.99962 (IR) and 0.99978 (R) with dual scaling and 0.99968 (IR) and 0.99974 (R) with SQM.

Regarding the calculated fundamentals, in general, the computed vibrational intensities are in agreement with the experimental results. Although, the vibrational intensities of the some mode are about zero, these bands can be seen in the vibrational spectra (Figs. 3–5). The opposite situation has also been observed. Similarly, the ν_{18}, ν_{67} and ν_{68} modes are observed as doublets in the infrared spectrum which can be attributed to molecular interactions (Figs. 3 and 4). It is also important to note that calculations have been performed for a single molecule in the gaseous state

contrary to the experimental values recorded for the presence of interactions in the liquid phase. Additionally, the anharmonicity can explain substantial differences between the experimental and calculated values and the differences can be due to the intra- and intermolecular interactions or laser used for Raman [30].

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 act as an electron donor, since it is the outermost orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since 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 located over all carbon atoms in 1pych whereas the LUMO is dominated for N7 atom. The atomic compositions of frontier molecular orbital and their orbital energies are given in Fig. S2 together with the energy difference between these orbitals termed the HOMO–LUMO gap.

Conclusions

The experimental and theoretical vibrational investigations of 1pych are performed, for the first time, by using infrared, Raman and quantum chemical calculations. In conclusion, following results can be summarized:

1. Results of energy calculations indicate that the mixture of envelope and twist forms is the most stable conformer of 1pych.
2. Standard scaling factors and SQM method could be proposed as scaling methods for the calculated vibrational frequencies and SQM methodology performs slightly better than other for 1pych.
3. The results obtained in this study also indicate that the B3-LYP/6-31++G(d,p) method is reliable and makes the understanding of vibrational spectrum and structural parameters of 1-pych easier.
4. Any differences observed between the experimental and calculated frequencies, intensities or structural parameters could be due to the fact that the calculations have been performed for single molecule in the gaseous state contrary to the experimental values have been recorded in the liquid phase.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.04.100.

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