

Structural, vibrational and electronic properties of *cis* and *trans* conformers of 4-hydroxy-*l*-proline: a density functional approach

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Abstract. 4-hydroxy-*l*-proline is formed by hydroxylation of proline, an amino acid found in protein, whose inhibition results in hair problems in human, causing scurvy disease. We report a theoretical study on *cis* and *trans* conformers of 4-hydroxy-*l*-proline using first principle density functional approach at B3LYP/6-31+G(d,p) level. The equilibrium structures of both conformers are obtained to analyze their vibrational properties. The calculated vibrational modes are assigned and interpreted on the basis of potential energy distribution analysis. A good correlation has been obtained between calculated frequencies and corresponding experimental values from FTIR spectra. The electronic properties of both conformers are also calculated and discussed.

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Key words: 4-hydroxy-*l*-proline, *cis-trans* conformers, vibrational analysis, density functional theory

1 Introduction

4-hydroxyproline or 4-hydroxy-*l*-proline (4HLP) is a non native amino acid which differs from proline, a proteinogenic amino acid, by the presence of a hydroxyl (–OH) group attached to the gamma carbon. It was isolated from hydrolyzed gelatin by Hermann Emil in the beginning of 20th century. Although, it is not directly incorporated into proteins, it comprises about 4% of all amino acids found in animal tissue, an amount greater than

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many other translationally incorporated amino acids [1]. Furthermore, hydroxyproline is a major component of the protein collagen [2] which plays key roles in collagen stability [3], permitting the sharp twisting of the collagen helix [4]. For this reason, its content has been used as an indicator to determine collagen and/or gelatin amount. Moreover, hydroxyproline rich glycoproteins are also found in plant cell walls [5].

The pharmacological impact of this non-proteinogenic amino acid can never be ignored. Since, the hydroxylation of proline requires ascorbic acid i.e. vitamin C, the absence of vitamin C in humans inhibits the hydroxylation, consequently reducing the stability of collagen molecule and causing the hair problems i.e. scurvy. Apart from this, the increased serum and urine levels of hydroxyproline have also been demonstrated in Paget's disease [6]. Quantum chemical methods provide a lot of information about the system of biological interests that often complements with the experiment findings. Many chemical and/or biological properties are closely associated to the molecular structures or geometries. Different conformations of the same molecule may lead to different chemical properties. The aim of the present study includes detailed structural and vibrational analyses of two potential conformers of 4HLP, namely, *cis*-4HLP and *trans*-4HLP. Our literature survey reveals a recent study performed on *trans*-4HLP [7], however, there is no corresponding study on *cis*-4HLP to the best of our knowledge. Thus, the present study provides a comparative analysis of *cis* and *trans* conformers of 4HLP for the first time.

2 Computational methods

Our quantum chemical calculations are based density functional scheme as implemented in Gaussian 09 package [8]. Initial geometries of *cis*- and *trans*-4HLYP are fully optimized without any symmetry constraint in the potential energy surfaces (PESs) using gradient corrected hybrid functional B3LYP [9, 10] and 6-31+G(d,p) basis set. B3LYP is one of the most widely used functionals in case of medium size biomolecules and hence, employed successfully in a number of previous studies [7, 11-14]. Vibrational frequency calculations are repeated using optimized geometries at the same level of theory. All calculated frequencies are found to be real which ensure that the optimized geometries belong to true minima on respective PESs.

Normal modes of both conformers of 4HLP are interpreted and assigned in terms of potential energy distribution (PED) using Gar2ped program [15]. The calculated frequencies are uniformly scaled by a factor of 0.9648 [16] in order to compensate for anharmonicity of vibrations as well as electron correlations. The scaled frequencies are compared with corresponding experimental FTIR values. The FTIR spectra of *cis*-4HLP and *trans*-4HLP are adopted from literature, which are available from SDBS website [17].

3 Results and discussion

3.1 Structural properties

The optimized geometries of *cis*- and *trans*-4HLP are displayed in Fig. 1 and corresponding structural parameters (bond-lengths and bond-angles) are listed in Table 1. 4HLP is composed of one hetero-pentagonal ring with one carbon replaced by nitrogen. Pentagonal ring deviates from planarity due to repulsion created by non-bonding electrons of nitrogen. The covalent bond between the side-chain and nitrogen backbone has relevant structural consequences on the properties of both conformers. However, there is a strict dependence between main- and side-chain proline conformations. This is reflected in the non-bonding distances between backbone atoms, R(1-4) which is 2.12 Å for *cis* and 2.118 Å for *trans* and R(1-5), 2.128 Å (*cis*) and 2.12 Å (*trans*) (not given in Table 1). The observed correlation between proline puckering and peptide bond conformation suggests a new mechanism to explain the reported shift of the *cis-trans* equilibrium in proline derivatives.

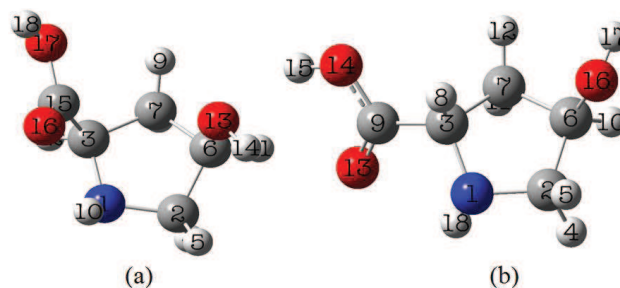


Figure 1: Optimized geometries of 4-hydroxy-*L*-proline at B3LYP/6-31+G(d,p) level (a) *cis* conformer (b) *trans* conformer. Dark, light, red and blue spheres represent C, H, O and N atoms, respectively.

In *cis* and *trans* conformers the same group ($-\text{OH}$ and $-\text{COOH}$) are present at different angular positions of hetero-pentagonal ring. This results in the change in ring geometries which have also been proven to be a sensitive indicator of the interaction between the substituent and the ring. Consequently, a re-adjustment takes place in the ring due to presence of these groups in both *cis* and *trans* conformations. The average bond-length of C–C in ring for *cis* (1.52 Å) takes slightly lower value than that in *trans*-4HLP (1.53 Å). However C–N bond-length in *cis* (1.47 Å) becomes slightly higher than that in *trans* conformer, 1.46 Å (see Table 1). In general, calculated bond-lengths are consistent with the observed values for 4HLP [18] by X-ray and neutron diffraction. For instance, observed C–C bond-lengths in 4HLP are found to be in between 1.52 Å and 1.53 Å.

3.2 Vibrational properties

In this section, we discuss the vibrational properties of *cis*- and *trans*-4HLP. The calculated frequencies are scaled as mentioned earlier and compared with corresponding FTIR

Table 1: Bond-length (R in Å) and bond-angle (A in °) of *cis*- and *trans*-4-hydroxy-*l*-proline calculated at B3LYP/6-31+G(d,p) level. Refer to Fig. 1 for atomic labeling.

cis-4-hydroxy- <i>l</i> -proline		trans-4-hydroxy- <i>l</i> -proline	
Parameter	Value	Parameter	Value
R(1-2)	1.475	R(1-2)	1.475
R(1-3)	1.469	R(1-3)	1.462
R(1-10)	1.016	R(1-18)	1.017
R(2-4)	1.099	R(2-4)	1.094
R(2-5)	1.096	R(2-5)	1.095
R(2-6)	1.537	R(2-6)	1.553
R(3-7)	1.555	R(3-7)	1.555
R(3-12)	1.099	R(3-8)	1.096
R(3-15)	1.525	R(3-9)	1.512
R(6-7)	1.528	R(6-7)	1.539
R(6-11)	1.099	R(6-10)	1.098
R(6-13)	1.432	R(6-16)	1.434
R(7-8)	1.094	R(7-11)	1.097
R(7-9)	1.091	R(7-12)	1.094
R(13-14)	0.966	R(9-13)	1.214
R(15-16)	1.213	R(9-14)	1.354
R(15-17)	1.354	R(14-15)	0.973
R(17-18)	0.972	R(16-17)	0.966
A(2-1-3)	108.7	A(2-1-3)	107.0
A(2-1-10)	111.5	A(2-1-18)	111.5
A(1-2-4)	110.3	A(1-2-4)	110.2
A(1-2-5)	110.9	A(1-2-5)	110.7
A(1-2-6)	106.5	A(1-2-6)	108.1
A(3-1-10)	108.8	A(3-1-18)	108.6
A(1-3-7)	106.0	A(1-3-7)	105.3
A(1-3-12)	111.2	A(1-3-8)	110.4
A(1-3-15)	111.2	A(1-3-9)	111.0
A(4-2-5)	107.2	A(4-2-5)	108.0
A(4-2-6)	109.2	A(4-2-6)	112.3
A(5-2-6)	112.8	A(5-2-6)	107.6
A(2-6-7)	101.8	A(2-6-7)	104.1
A(2-6-11)	112.5	A(2-6-10)	112.1
A(2-6-13)	112.7	A(2-6-16)	106.9
A(7-3-12)	109.5	A(7-3-8)	109.3
A(7-3-15)	113.9	A(7-3-9)	111.9
A(3-7-6)	103.3	A(3-7-6)	102.4
A(3-7-8)	109.5	A(3-7-11)	109.3
A(3-7-9)	113.2	A(3-7-12)	113.7
A(12-3-15)	105.2	A(8-3-9)	108.9
A(3-15-16)	125.2	A(3-9-13)	125.0
A(3-15-17)	112.1	A(3-9-14)	112.2
A(7-6-11)	112.6	A(7-6-10)	111.6
A(7-6-13)	106.4	A(7-6-16)	112.4
A(6-7-8)	109.8	A(6-7-11)	109.9
A(6-7-9)	112.4	A(6-7-12)	112.7
A(11-6-13)	110.3	A(10-6-16)	109.6
A(6-13-14)	109.5	A(6-16-17)	109.1
A(8-7-9)	108.5	A(11-7-12)	108.6
A(16-15-17)	122.6	A(13-9-14)	122.7
A(15-17-18)	107.2	A(9-14-15)	107.3

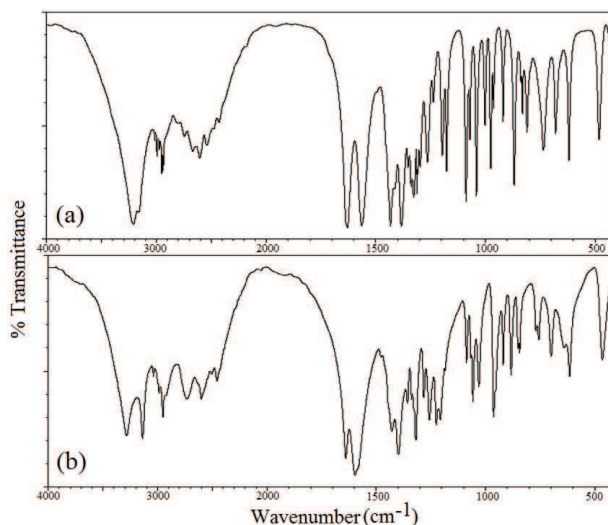


Figure 2: FTIR spectra of 4-hydroxy-*l*-proline (a) *cis* conformer (b) *trans* conformer.

values. The FTIR spectra of both conformers are displayed in Fig. 2. In Fig. 3, we have shown a correlation between calculated and experimental frequencies. In both cases, the correlation coefficients (R^2) are close enough to unity, ensuring the reliability of our computations. Furthermore, R^2 value for *trans*-4HLP (0.99886) is higher than that for *cis*-4HLP (0.99608), showing a better correlation in case of *trans* conformer.

Table 2 and 3 list vibrational frequencies, IR intensity and corresponding assignments including PED for *cis*-4HLP and *trans*-4HLP, respectively. Note that PED less than 10% are not included in the assignment. We divide the whole spectra into three regions for the sake of simplicity of discussion.

3.2.1 Spectral region above 1800 cm^{-1}

In this region, nearly all modes correspond to the stretching vibrations. The highest frequency corresponds to OH stretching with PED 100%, polarized perpendicular to the ring are obtained at 3691 cm^{-1} and 3690 cm^{-1} in *cis*- and *trans*-4HLP, respectively which is associated to $-\text{OH}$ group, whereas, at 3624 cm^{-1} in *cis* and 3618 cm^{-1} in *trans* conformer associated to $-\text{COOH}$ group. This difference may due to intra-molecular hydrogen bond which is stronger in case of *trans*-4HLP, $13\text{O} \cdots 15\text{H}$ (2.23 \AA) than *cis* conformer $16\text{O} \cdots 18\text{H}$ (2.29 \AA). At 3421 cm^{-1} , pure NH stretching mode polarized along 3C-15C in *cis* form and corresponding mode in *trans* conformer lies at 3409 cm^{-1} . Furthermore, in *cis*-4HLP, CH stretching vibrations polarized along a plane contain 7C making 45° with plane of ring is calculated at 2973 cm^{-1} with PED of 82%, agreeing well with the experimental value of 2976 cm^{-1} . Similarly, corresponding mode of vibration polarized along 3C-8H in *trans*-4HLP lies at 2997 cm^{-1} having FTIR value of 2986 cm^{-1} . Other CH modes lying at 2966 cm^{-1} (90% PED) and 2925 cm^{-1} (84% PED) in *cis* conformer match well with the experimental values, 2976 cm^{-1} and 2938 cm^{-1} , respectively. Moreover,

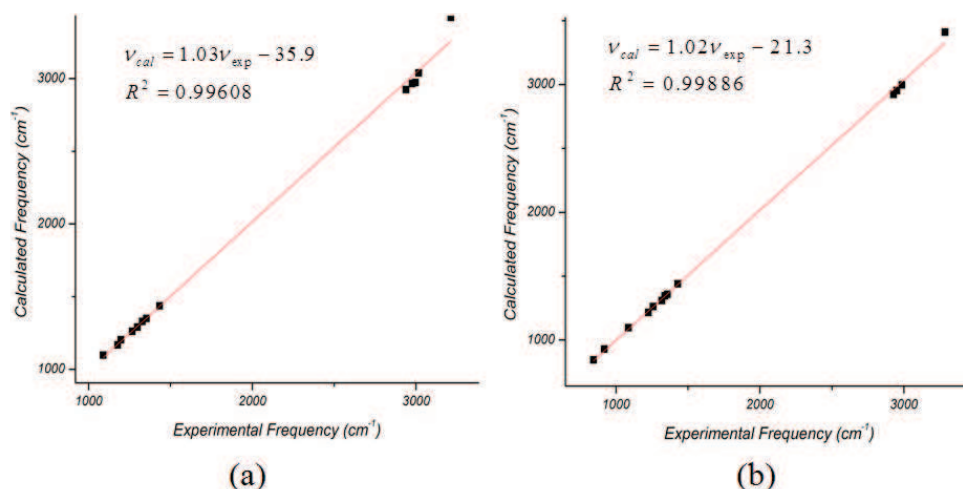


Figure 3: Correlation between calculated (scaled) frequency (ν_{cal}) and experimental frequency (ν_{exp}) for *cis* (a) and *trans* (b) conformers of 4-hydroxy-*l*-proline.

corresponding modes in *trans* form, scaled at 2953 cm^{-1} (65% PED) and 2922 cm^{-1} (85% PED) are seen at 2951 cm^{-1} and 2928 cm^{-1} in FTIR spectrum.

3.2.2 Spectral region $1800\text{-}1000\text{ cm}^{-1}$

Carbonyl absorptions are very sensitive as both the carbon and oxygen atoms of $-\text{COOH}$ group move during the vibration, having nearly equal amplitude. In *cis*-4HLP, a very intense band due to CO stretching polarized along 1N-10H direction is calculated at 1746 cm^{-1} with PED of 78%. A mixing of vibrational modes obtained at 1322 cm^{-1} , polarized along the plane of ring, corresponds to out of plane CNH bending (21%) and CH₂ rocking (12%) which is in agreement with the experimental one (see Table 2). At 1291 cm^{-1} , a moderately intense mode corresponding to the mixing of CHC wagging (29%), CC stretching (12%) and CHO out of plane bending (10%) matches well with experimental value of 1298 cm^{-1} . Furthermore, the mixing of $-\text{COOH}$ group deformation with CH₂ rocking mode and CN stretching mode are calculated at 1262 cm^{-1} and 1098 cm^{-1} against the experimental bands at 1266 cm^{-1} and 1089 cm^{-1} , respectively.

In *trans*-4HLP, like its *cis* form, a very intense band due to CO stretching polarized along 1N-18H direction is calculated at 1747 cm^{-1} with a PED of 79%. At 1345 cm^{-1} , a mixing of out of plane deformation of $-\text{COOH}$ group (20%), CC stretching (16%) and CN stretching (10%) corresponds to the experimental band at 1339 cm^{-1} . Other significant modes calculated at 1262 cm^{-1} and 1096 cm^{-1} correspond to the mixing of $-\text{COOH}$ group deformation with in plane NH bending and CCN deformation with CN stretching agree well with the experiment values of 1258 cm^{-1} and 1087 cm^{-1} .

Table 2: Proposed assignments and potential energy distribution (PED) for vibrational modes of *cis*-4-hydroxy-*l*-proline calculated at B3LYP/6-31+G(d,p) level.

Calc. Freq. (cm ⁻¹)	Scaled Freq. (cm ⁻¹)	Int. (a.u.)	FTIR Freq. (cm ⁻¹)	Assignments (PED ≥ 10%)
3826	3691	26.3		$\nu(\text{O13H14})(100)$
3757	3624	67.5		$\nu(\text{O17H18})(100)$
3546	3421	31.8	3212	$\nu(\text{N1H10})(100)$
3150	3039	5.0	3016	$\nu(\text{C7H9})(84)+\nu(\text{C7H8})(16)$
3082	2973	32.7	2996	$\nu(\text{C7H8})(82)+\nu(\text{C7H9})(15)$
3075	2966	31.6	2976	$\nu(\text{C2H5})(90)$
3032	2925	88.7	2938	$\nu(\text{C6H11})(84)+\nu(\text{C2H4})(12)$
3018	2911	27.8		$\nu(\text{C3H12})(97)$
3010	2904	35.8		$\nu(\text{C2H4})(77)+\nu(\text{C6H11})(13)$
1810	1746	296		$\nu(\text{C15O16})(78)$
1509	1455	0.5		$\rho(\text{CH2})(85)+\rho(\text{CH2})(11)$
1489	1436	7.1	1434	$\rho(\text{CH2})(84)+\rho(\text{CH2})(12)$
1481	1428	12.0		$\delta(\text{C2H10N1})(71)$
1400	1350	4.3	1353	$\delta(\text{H11O13C6})(36)+\delta(\text{C6H14O13})(12)+\nu(\text{C6C7})(10)$
1378	1329	22.5	1328	$\omega(\text{N1H4C2})(23)+\delta(\text{H11O13C6})(12)+\omega(\text{C6H8C7})(10)$
1371	1322	38.5		$\omega(\text{N1H4C2})(21)+\rho(\text{CH2})(12)$
1339	1291	25.8	1298	$\omega(\text{C2H11C6})(29)+\nu(\text{C2C6})(12)$ $+\delta(\text{H11O13C6})(10)+\delta(\text{C6H14O13})(10)$
1327	1280	0.4		$\omega(\text{C6H8C7})(42)+\omega(\text{N1H4C2})(20)$
1309	1262	20.4	1266	$\rho(\text{CH2})(34)+\delta(\text{C15H18O17})(22)+\rho(\text{CH2})(15)$
1281	1235	24.3		$\omega(\text{CH2})(29)+\tau(\text{N1H4C2})(15)+\tau(\text{N1H12C3})(13)$
1247	1203	0.6	1198	$\tau(\text{N1H4C2})(24)+\omega(\text{CH2})(20)$ $+\tau(\text{N1H12C3})(14)+\tau(\text{C6H8C7})(11)$
1210	1167	6.1	1178	$\tau(\text{C6H8C7})(32)+\tau(\text{N1H4C2})(12)$
1177	1135	75.4		$\nu(\text{C15O17})(21)+\delta(\text{C15H18O17})(18)+\nu(\text{N1C2})(12)$
1173	1131	46.3		$\delta(\text{C6H14O13})(25)+\omega(\text{C2H11C6})(15)+\tau(\text{C2H11C6})(13)$
1139	1098	227.5	1089	$\nu(\text{N1C2})(27)+\nu(\text{N1C2})(14)+\delta(\text{C15H18O17})(12)$
1098	1059	29.8		$\nu(\text{C6O13})(20)+\tau(\text{C6H8C7})(14)$ $+\nu(\text{N1C2})(14)+\delta\text{inp}(\text{R})(13)$
1060	1022	2.2		$\tau(\text{N1H4C2})(15)+\nu(\text{C3C7})(11)+\nu(\text{C6O13})(11)$
983	948	7.2		$\nu(\text{C3C7})(24)+\nu(\text{N1C2})(13)$
977	942	28.7		$\delta\text{inp}(\text{R})(20)+\nu(\text{C6O13})(13)+\nu(\text{C6C7})(12)+\nu(\text{C3C7})(11)$
961	927	14.8		$\delta\text{inp}(\text{R})(30)+\nu(\text{N1C2})(17)+\nu(\text{C6O13})(14)+\nu(\text{C2C6})(13)$
932	899	5.7		$\nu(\text{C6C7})(24)+\nu(\text{C3C15})(16)+\nu(\text{C2C6})(10)$
870	839	15.1		$\nu(\text{C2C6})(28)+\nu(\text{C6O13})(17)+\delta\text{inp}(\text{R})(14)$
825	795	30.2		$\delta\text{inp}(\text{R})(37)+\delta\text{oop}(\text{C15O16})(18)+\rho(\text{CH2})(12)$
798	769	26.3		$\delta\text{oop}(\text{H10C2C3})(29)+\nu(\text{C3C7})(17)$
777	749	4.0		$\nu(\text{C3C15})(13)+\delta\text{inp}(\text{R})(22)+\nu(\text{C6C7})(11)+\nu(\text{C6O13})(10)$
722	696	71.8		$\delta\text{oop}(\text{H10C2C3})(33)+\nu(\text{N1C2})(12)$
681	657	84.2		$\delta\text{inp}(\text{R})(31)+\delta\text{oop}(\text{C15O16})(20)$ $+\tau(\text{C3C15})(13)+\delta\text{oop}(\text{H10C2C3})(10)$
608	586	33.9		$\delta(\text{O16O17C3})(40)+\tau(\text{C3C15})(28)$
549	529	41.5		$\tau(\text{C3C15})(40)+\delta\text{oop}(\text{C15O16})(15)$
454	438	17.1		$\delta(\text{O16O17C3})(29)+\delta(\text{O16C15C3})(16)$

3.2.3 Spectral region below 1000 cm⁻¹

As expected, the ring torsions along with wagging modes appear in this low frequency region. For *cis*-4HLP, a mixing of modes appears at 696 cm⁻¹, corresponding to out of plane CCH bending (33%) and CN stretching (12%). A polarized mode of vibration with polarization vector along CN bond occurs at 657 cm⁻¹, corresponding to deformations of ring and out of plane -COOH with the PED of 31% and 16%, respectively. For *trans*

Table 3: Proposed assignments and potential energy distribution (PED) for vibrational modes of *trans*-4-hydroxy-*l*-proline calculated at B3LYP/6-31+G(d,p) level.

Calc. Freq. (cm ⁻¹)	Scaled Freq. (cm ⁻¹)	Int. (a.u.)	FTIR Freq. (cm ⁻¹)	Assignments (PED ≥ 10%)
3825	3690	29.0		$\nu(\text{O16H17})(100)$
3750	3618	73.0		$\nu(\text{O14H15})(100)$
3534	3409	15.7	3286	$\nu(\text{N1H18})(99)$
3112	3009	26.3		$\nu(\text{C7H12})(74)+\nu(\text{C7H11})(23)$
3107	2997	21.0	2986	$\nu(\text{C2H4})(65)+\nu(\text{C2H5})(33)$
3070	2961	12.6		$\nu(\text{C3H8})(91)$
3061	2953	40.1	2951	$\nu(\text{C2H5})(65)+\nu(\text{C2H4})(30)$
3049	2941	33.3		$\nu(\text{C7H11})(63)+\nu(\text{C7H12})(16)+\nu(\text{C6H10})(11)$
3029	2922	29.3	2928	$\nu(\text{C6H10})(85)+\nu(\text{C7H11})(11)$
1811	1747	300.7		$\nu(\text{C9O13})(79)$
1505	1452	3.6		$\delta(\text{H4H5C2})(81)+\tau(\text{H18C2})(14)$
1493	1440	1.6	1430	$\nu(\text{N1C2})(38)+\delta(\text{H11H12C7})(17)+\delta\text{inp}(\text{R})(10)$
1439	1388	9.0		$\delta(\text{H11H12C7})(56)+\nu(\text{N1C2})(17)$
1409	1359	12.0	1358	$\delta(\text{H10O61C6})(41)+\omega(\text{NH})(11)$
1395	1345	92.6	1339	$\delta(\text{C12C6O11})(20)+\nu(\text{N1C2})(16)$ $+\nu(\text{C3C9})(10)+\delta\text{inp}(\text{R})(10)$
1357	1309	3.9	1319	$\omega(\text{NH})(46)$
1345	1297	16		$\omega(\text{CH2})(29)+\omega(\text{N1H8C3})(12)+\tau(\text{C3H8N1})(11)$
1324	1277	9.6		$\omega(\text{N1H8C3})(25)+\tau(\text{C3H8N1})(18)+s(\text{C6C2H10})(15)$
1309	1262	27.4	1258	$\delta\text{inp}(\text{R})(18)+\delta(\text{C12C6O11})(17)$ $+\delta(\text{C12C6O11})(11)+\delta\text{inp}(\text{H18N1})(11)$
1262	1217	15.3	1226	$\tau(\text{C2N1H4})(42)$
1260	1215	33.4	1216	$\omega(\text{CH2})(22)+\delta(\text{C12C6O11})(20)$
1226	1182	43.6		$\delta\text{inp}(\text{H18N1})(35)+\delta\text{oop}(\text{N1H18})(15)+\nu(\text{N1C2})(13)$
1195	1152	5.0		$\omega(\text{C6C2H10})(20)+\tau(\text{C6C2H10})(15)$ $+\tau(\text{C7C3H11})(14)+\delta(\text{C6H17O16})(11)$
1163	1122	211.4		$\nu(\text{C9O14})(32)+\delta(\text{C12C6O11})(24)+\delta(\text{C12C6O11})(10)$
1137	1096	100.7	1087	$\nu(\text{N1C3})(40)+\delta(\text{N1C3C7})(31)+\nu(\text{N1C2})(15)$
1085	1046	15.0		$\delta\text{inp}(\text{H18N1})(17)+\delta\text{inp}(\text{R})(13)$ $+\nu(\text{C3C7})(11)+\nu(\text{N1C3})(11)$
1044	1007	43.2		$\delta\text{inp}(\text{H18N1})(35)+\delta\text{oop}(\text{N1H18})(15)+\nu(\text{N1C2})(13)$
1039	1002	5.7		$\nu(\text{C6C7})(31)+\delta\text{inp}(\text{H18N1})(10)$
984	949	4.0		$\nu(\text{C3C9})(24)+\delta\text{inp}(\text{H18N1})(12)$ $+\nu(\text{N1C2})(12)+\nu(\text{C3C7})(10)$
964	930	48.1	920	$\nu(\text{C2C6})(21)+\delta\text{inp}(\text{R})(19)+\nu(\text{C6O16})(14)$ $+\nu(\text{N1C3})(10)+\tau(\text{H18C2})(10)$
930	897	10.8		$\nu(\text{C3C7})(16)+\delta\text{inp}(\text{R})(12)$
875	844	2.4	844	$\delta\text{inp}(\text{R})(20)+\delta\text{inp}(\text{H18N1})(16)$ $+\nu(\text{C3C7})(11)+\nu(\text{N1C3})(11)$
841	811	5.6		$\nu(\text{C2C6})(22)+\delta\text{inp}(\text{H18N1})(17)$ $+\nu(\text{C6C7})(12)+\nu(\text{C6O16})(10)$
787	759	134.2		$\delta\text{oop}(\text{N1H18})(59)+\delta\text{inp}(\text{H18N1})(23)$
738	712	31.7		$\omega(\text{C9C3})(34)+\delta\text{inp}(\text{H18N1})(13)+\delta\text{oop}(\text{N1H18})(10)$
715	689	13.8		$\delta\text{oop}(\text{N1H18})(26)+\tau(\text{H18C2})(19)$
658	634	28.3		$\delta(\text{N1C3C7})(34)+\rho(\text{O13C3C9})(28)+\delta\text{inp}(\text{H18N1})(12)$
613	591	49.5		$\tau(\text{O14C9})(26)+\delta(\text{N1C3C7})(24)$ $+\delta\text{inp}(\text{R})(16)+\delta\text{inp}(\text{H18N1})(10)$
593	572	30.0		$\tau(\text{O14C9})(24)+\delta\text{inp}(\text{H18N1})(19)+\delta\text{inp}(\text{R})(12)+\delta(\text{N1C3C7})(10)$
450	434	25.4		$\delta\text{inp}(\text{R})(26)+\rho(\text{O13C3C9})(13)+\delta\text{inp}(\text{R})(12)$
425	410	10.1		$\tau(\text{C6C2H10})(33)+\tau(\text{H18C2})(16)$ $+\omega(\text{C6C2H10})(13)+\delta\text{inp}(\text{R})(10)$

Types of vibrations: ν -stretching, ρ -rocking, ω -wagging, τ -twisting, δ -deformation, δinp -in plane ring bending, δoop -out of plane ring bending, τ -ring torsion.

conformer, a mixing of modes appears at 689 cm^{-1} which is corresponding to out of plane NH bending (26%) and CH torsion (19%). The deformation of $-\text{COOH}$ group mixed with in plane NH bending is obtained at 634 cm^{-1} .

3.3 Electronic properties

Total electronic energies (including zero point energy), energy related parameters and dipole moments of *cis* and *trans* conformers of 4HLP are collected in Table 4. *Trans* conformer is merely 0.027 eV higher in energy than *cis*-4HLP. Ionization potential (*I*) and electron affinity (*A*) of molecules are calculated within the framework of Koopmans' theorem, which describes *I* and *A* as the negative of energy eigen-values of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The energy difference between HOMO and LUMO results in an energy gap (E_{gap}) which is an important factor for analyzing the chemical stability of molecular species.

Table 4: Electronic parameters of *cis*- and *trans*-4-hydroxy-*l*-proline calculated at B3LYP/6-31+G(d,p). Refer to the text for symbols.

Parameters ^a	<i>cis</i> -4-hydroxy- <i>l</i> -proline	<i>trans</i> -4-hydroxy- <i>l</i> -proline
Total energy (a.u.)	-476.2604	-476.2594
<i>I</i> (eV)	6.35	6.50
<i>A</i> (eV)	0.38	0.47
E_{gap} (eV)	5.97	6.03
μ (Debye)	2.06	3.17

^a defined as: $I = -E[\text{HOMO}]$, $A = -E[\text{LUMO}]$, $E_{gap} = E[\text{LUMO}] - E[\text{HOMO}]$.

I and *A* values of *trans*-4HLP are slightly larger than those for its *cis* counterpart (see Table 4). This may suggest that *trans* conformer is relatively more stable against addition or removal of an electron. This fact is further supported by its higher E_{gap} as compared to *cis*-4HLP. More interestingly, the dipole-moment (μ) of *trans*-4HLP exceeds to that of *cis*-4HLP by 1.11 Debye. The higher dipole-moment of *trans* conformer results due to the fact that the groups attached to the ring lie in different planes which increase the polarity, unlike *cis*-4HLP in which both groups lie in the same plane.

4 Conclusions

Using density functional theory calculations, we have discussed the structural, vibrational and electronic properties of 4-hydroxy-*l*-proline in *cis* and *trans* conformations. Detailed assignments to the all normal modes up to 450 cm^{-1} has been offered and potential energy distribution along with direction of polarization has also been discussed. The calculated vibrational frequencies have been found in better agreement with corresponding FTIR spectra. Furthermore, we have noticed that *trans* conformer is relatively more stable and polar as compared to its *cis* counterpart.

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