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FT-IR, FT-Raman and SERS Spectra of L-Proline

Y. Sheena Mary[a], L. Ushakumari[b], B. Harikumar[c], H. Tresa Varghese[d] and C. Yohannan Panicker[b,]*
[a]*Thushara, Neethinagar-64, Pattathanam, Kollam 691021, Kerala, India*
[b]*Department of Physics, TKM College of Arts and Science, Kollam 691005, Kerala, India*
[c]*Department of Chemistry, TKM College of Arts and Science, Kollam 691005, Kerala, India*
[d]*Department of Physics, Fatima Mata National College, Kollam 691001, Kerala, India*

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IR, Raman and surface-enhanced Raman scattering (SERS) spectra of L-proline were recorded and analyzed. The molecular plane assumes a tilted orientation with respect to the metal surface. The vibrational wavenumbers and corresponding vibrational assignments are examined theoretically using the Gaussian 03 set of quantum chemistry codes.

Keywords: L-Proline, FTIR, FT-Raman, SERS, *Ab initio* HF Calculations

INTRODUCTION

L-Proline, as an imino acid, contains an amino group and a carboxylic acid [1]. Several groups have reported the introduction of chirality into chromophores using L-proline as a donor residue [2]. Proline is the only naturally occurring amino acid with a secondary α-amino group, which explains its more basic character with respect to many other α-amino acids. Marino *et al*. reported the interaction of Li^+, Na^+ and K^+ with proline amino acids [5]. Suh and Moskovits [6] reported the surface-enhanced Raman scattering (SERS) spectra of amino acids (glycine, alanine, 6-aminocaproic acid and aminobenzoic acid) and nucleic acid bases (adenine, cytosine and uracil) adsorbed onto a silver colloid surface. In the present study, the IR, Raman and SERS spectra of L-proline are reported, as are the theoretical calculations of the vibrational wavenumbers.

EXPERIMENTAL

The IR spectra were recorded on Bruker IFS66 V FT-IR spectrometer (KBr and polyethylene pellets). The FT-Raman and SERS spectra were obtained on a Bruker IFS66V NIR-FT instrument equipped with a FRA 106 Raman module. A Nd/YAG laser at 1064 nm with an output of 300 mW was used for excitation. The detector was a Ge-diode cooled to liquid nitrogen temperature. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution was 6 cm^{-1}. The silver colloid for SERS was prepared by the reduction of silver nitrate by sodium citrate, using the Lee-Meisel method [8]. Five milliliters of an aqueous solution of L-proline (2×10^{-4} M) was added to an equal volume of the silver colloid.

RESULTS AND DISCUSSION

Calculation of Wavenumbers

The vibrational wavenumbers of L-proline were calculated using the HF/3-21G* basis set *via* Gaussian 03 software on a personal computer [7]. The vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies. The wavenumber values computed at the HF level contain known systematic

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Corresponding author. E-mail: cyphyp@rediffmail.com errors due to the negligence of electron correlation [9]. Therefore, we have used a scaling factor value of 0.9085 for the HF/3-21G basis set. Parameters corresponding to the optimized geometry of L-proline (Fig. 1) are given in Table 1.

The calculated vibrational spectrum has no imaginary wavenumbers, which helped to confirm that the structure of L-proline deduced following the optimization corresponds to the energy minimum. The optimum geometry was determined by minimizing the energy with respect to all geometric parameters without imposing molecular symmetry constraints. The assignments of the calculated wavenumbers were aided by the animation option of the MOLEKEL program, which gives a visual presentation of the vibrational modes [10,11].

Methylene Vibrations

The FT-IR, FT-Raman and SERS spectra for L-proline are shown in Fig. 2 and the wavenumbers and band assignments for L-proline are summarized in Table 2.

The vibrations of the CH_2 group, the asymmetric stretch $\upsilon_{as}CH_2$, symmetric stretch υ_sCH_2, the scissoring vibrations of the δCH_2, and wagging vibration of the ωCH_2, appear in the regions 3000 ± 50, 2965 ± 30, 1455 ± 55 and 1350 ± 85 cm^{-1}, respectively [12,13]. Methylene asymmetric and symmetric stretching bands of the pyrrolidine are usually observed near 2953 and 2868 cm^{-1}, respectively [14]. The HF calculation gives three bands for the asymmetric and symmetric stretching corresponding to different methylene groups, $C_1H_{2,3}$, $C_4H_{5,6}$ and $C_7H_{8,9}$. Electronic effects including back donation, mainly caused by the presence of the nitrogen atom adjacent to the methylene groups, can shift the position and alter the intensity of CH stretching and bending modes.

The lowering of wavenumbers and the increasing intensity of CH stretching modes of the CH_2 of the ring point to the influence of back donation in the ring owing to the presence of the nitrogen atom. For a molecule containing a methylene group, the electronic charge is back-donated from the lone pair of nitrogen to the σ^* orbital of the CH bonds, causing a weakening of the CH bonds. This is followed by the increase in C-H force constants and can result in the enhancement of IR band intensity of C-H stretching modes [15,16]. The asymmetric CH_2 stretching bands are observed at 3012, 2978 cm^{-1} in the IR spectrum and at 3000, 2983 cm^{-1} in the Raman spectrum. The calculated values are 3005, 2990 and 2980 cm^{-1}. The symmetrical CH_2 stretching bands are observed at

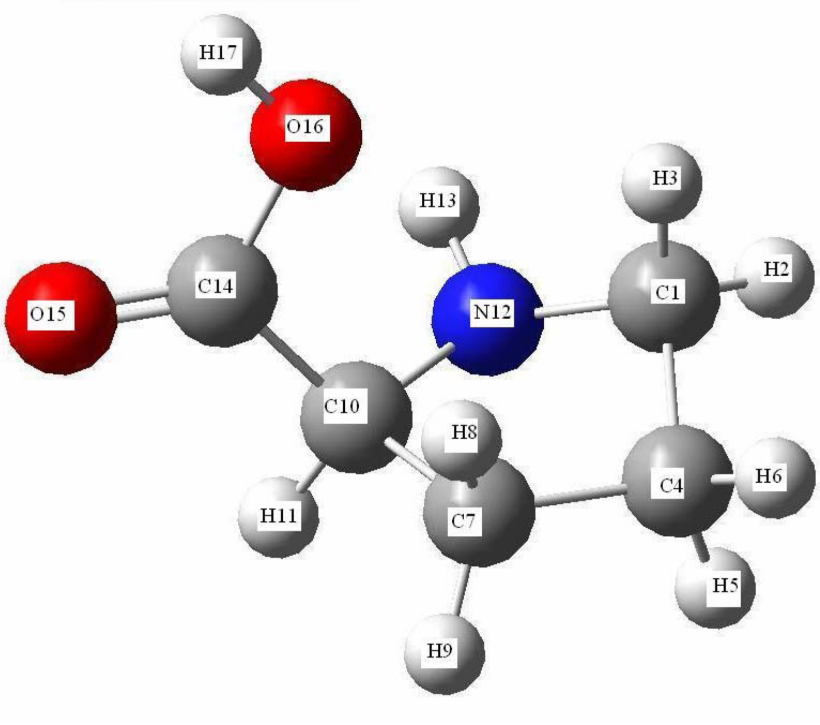

Fig. 1. Optimized geometry of L-proline.

Table 1. Optimized Geometric Parameters of L-Proline[a]

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C_1-H_2	1.0808	A(2,1,3)	109.8	D(2,1,4,5)	80.1
C_1-H_3	1.0849	A(2,1,4)	112.9	D(2,1,4,6)	-42.2
C_1-C_4	1.5353	A(2,1,12)	110.4	D(2,1,4,7)	-159.1
C_1-N_{12}	1.4741	A(3,1,4)	110.4	D(3,1,4,5)	-43.0
C_4-H_5	1.0814	A(3,1,12)	112.5	D(3,1,4,6)	-165.3
C_4-H_6	1.0816	A(4,1,12)	101.0	D(3,1,4,7)	77.8
C_4-C_7	1.5464	A(1,4,5)	113.0	D(12,1,4,5)	-162.2
C_7-H_8	1.0819	A(1,4,6)	109.2	D(12,1,4,6)	75.5
C_7-H_9	1.0798	A(1,4,7)	102.6	D(12,1,4,7)	-41.4
C_7-C_{10}	1.5689	A(5,4,6)	109.6	D(2,1,12,10)	157.0
C_{10}-H_{11}	1.0785	A(5,4,7)	112.0	D(2,1,12,13)	-69.5
C_{10}-N_{12}	1.4673	A(6,4,7)	110.2	D(3,1,12,10)	-80.0
C_{10}-C_{14}	1.5055	A(4,7,8)	109.2	D(3,1,12,13)	53.5
N_{12}-H_{13}	1.0017	A(4,7,9)	113.1	D(4,1,12,10)	37.7
C_{14}-O_{15}	1.2025	A(4,7,10)	104.3	D(4,1,12,13)	171.2
C_{14}-O_{16}	1.3622	A(8,7,9)	109.0	D(1,4,7,8)	-85.9
O_{16}-H_{17}	0.9686	A(8,7,10)	109.7	D(1,4,7,9)	152.6
		A(9,7,10)	111.4	D(1,4,7,10)	31.4
		A(7,10,11)	111.8	D(5,4,7,8)	35.6
		A(7,10,12)	104.2	D(5,4,7,9)	-85.9
		A(7,10,14)	108.7	D(5,4,7,10)	152.9
		A(11,10,12)	111.7	D(6,4,7,8)	157.9
		A(11,10,14)	107.5	D(6,4,7,9)	36.4
		A(12,10,14)	113.0	D(6,4,7,10)	-84.9
		A(1,12,10)	110.1	D(4,7,10,11)	111.5
		A(1,12,13)	116.0	D(4,7,10,12)	-9.3
		A(10,12,13)	115.5	D(4,7,10,14)	-130.1
		A(10,14,15)	127.0	D(8,7,10,11)	-131.7
		A(10,14,16)	111.1	D(8,7,10,12)	107.6
		A(15,14,16)	121.9	D(8,7,10,14)	-13.2
		A(14,16,17)	111.6	D(9,7,10,11)	-10.9
				D(9,7,10,12)	-131.6
				D(9,7,10,14)	107.6
				D(7,10,12,1)	-17.9
				D(7,10,12,13)	-151.6
				D(11,10,12,1)	-138.6
				D(11,10,12,13)	87.6
				D(14,10,12,1)	100.0
				D(14,10,12,13)	-33.7
				D(7,10,14,15)	-104.2
				D(7,10,14,16)	74.2
				D(11,10,14,15)	16.9
				D(11,10,14,16)	-164.7
				D(12,10,14,15)	140.6
				D(12,10,14,16)	-41.0
				D(10,14,16,17)	-178.2
				D(15,14,16,17)	0.3

[a] Atomic labeling is delineated in Fig. 1.

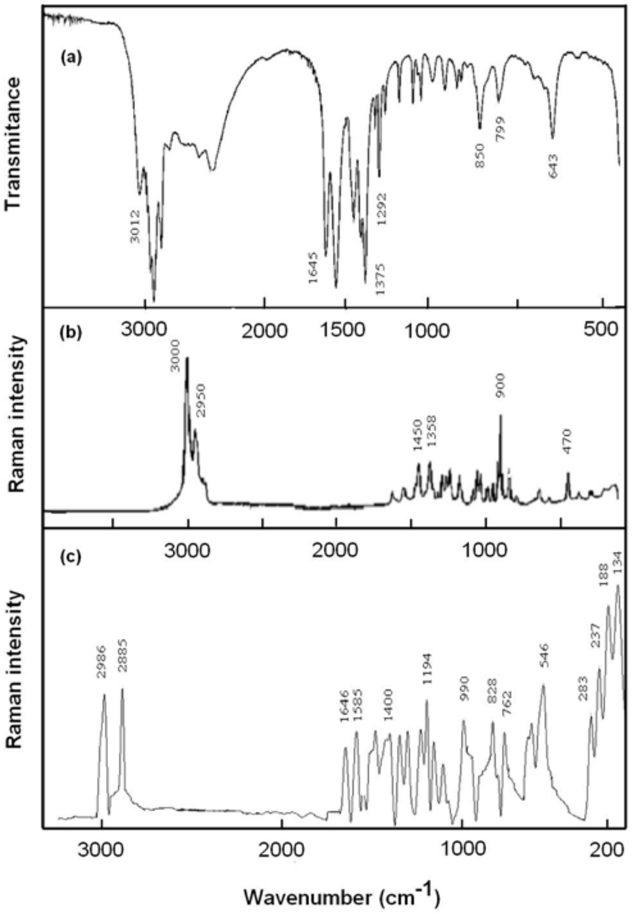

Fig. 2. FT-IR (a), FT-Raman (b) and SERS (c) spectra for L-proline.

Table 2. Wavenumbers and Band Assignments for L-Proline[a]

Wavenumbers (cm^{-1})				Band assignments
Calculated (HF)	IR	Raman	SERS	
3518				υOH
3410				υNH
3005	3012 s	3000 vs		υ$_{as}$CH$_2$
2990		2983 s	2986 s	υ$_{as}$CH$_2$
2980	2978 s			υ$_{as}$CH$_2$
2969				υCH
2951	2956 s	2950 s		υ$_s$CH$_2$
2944	2938 vs	2938 sh		υ$_s$CH$_2$
2908		2900 w	2885 s	υ$_s$CH$_2$
1782	1645 vs	1643 w	1646 m	υC=O
1535	1544 vvs	1540 w	1585 m	δNH
1502				δCH$_2$
1491		1483 sh	1480 m	δCH$_2$
1453	1446 s	1450 m		δCH$_2$
1365	1375 vs	1373 vw	1400 m	δOH
1363		1358 m		ωCH$_2$
1351		1350 vw		ωCH$_2$
1342			1346 m	ωCH$_2$
1317	1320 m	1317 vw		τCH$_2$
1298	1292 s	1293 w	1301 m	δCH
1244	1242 m	1248 w	1229 m	υC-O
1205				τCH$_2$
1191	1189 m	1186 w	1194 s	τCH$_2$
1136			1154 m	τNH
1112			1117 m	υCN
1083	1090 m	1083 vw		υring
1016	1025 m	1023 w	990 s	υring
949	950 wbr	941 m		γOH
908	907 vw	900 s		υring
898				υring
876	866 vw	880 vw		υring
855	850 m	850 w	828 m	ρCH$_2$
796	799 m	789 vw		ρCH$_2$
746			762 m	ρCH$_2$
724	721 vw			δC=O
620	630 m	633 w	612 m	δring
588		583 vw		δring
572			546 s	γC=O
493		470 m		ρC(=O)O
404		383 w		tOH
289		300 w	283 s	γring
252			237 s	γring
204		217 vw		tCOOH
			188 vs	υAg-O
			134 vs	υAg-N
77				tring
44				tring

[a] υ, stretching; δ, in-plane bending; γ, out-of-plane bending; ω, wagging; τ, twisting; ρ, rocking; t, torsional; v, very strog; s, strong; w, weak; m, medium; br, broad; sh, shoulder; as, asymmetric; s, symmetric.

2956, 2938 cm^{-1} in the IR and at 2950, 2938, 2900 cm^{-1} in the Raman spectra. For L-prolinium tartrate, the υCH is reported at 294 cm^{-1} [17].

The bending vibrations of the C-H bonds in the methylene group are identified in their respective positions. The scissoring mode of the CH_2 group gives rise to a characteristic band near 1465 cm^{-1} in IR and Raman spectra [18]. This mode is unambiguously correlated with the strong band at 1483 cm^{-1} in the Raman spectrum. The twisting and rocking vibrations of the CH_2 group appear in the regions 1290 ± 45 and 890 ± 55 cm^{-1}, respectively [12]. The twisting and rocking modes are also identified. For proline oligomers and poly-L-proline [19] the CH_2 deformation bands are reported at 1446, 1261, 1237 (δCH_2), 1198, 1187, 1172 ($\tau/\omega CH_2$), 781, 662 cm^{-1} (ρCH_2). For the title compound, the bands observed at 1446 cm in the IR spectrum, 1483, 1450 cm^{-1} in the Raman spectrum and 1502, 1491, 1453 cm^{-1} calculated values are ascribed to the δCH_2 scissoring modes. The ωCH_2 wagging modes are observed at 1358, 1350 cm^{-1} in the Raman spectrum and at 1363, 1351, 1342 cm^{-1} theoretically. For L-proline, the bands at 1317, 1186 cm^{-1} in the Raman spectrum, 1320, 1189 cm^{-1} in the IR spectrum and 1317, 1205, 1191 cm^{-1} calculated values are assigned to the τCH_2 twisting modes, whereas the bands at 850 and 789 cm^{-1} in the Raman spectrum, 850 and 799 cm^{-1} in the IR spectrum and 855, 796 and 746 cm^{-1} (HF) are assigned to the ρCH_2 modes.

COOH Vibrations

The -C(=O)OH group is best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation as well as the C-O stretch and the OH in-plane deformation. The C=O stretching vibration gives rise to characteristic bands in the IR and Raman spectra and the intensity of these bands can increase due to conjugation or the formation of hydrogen bonds [20]. C=O stretching vibration gives rise to a strong band in the region 1725 ± 65 cm^{-1} [12]. For L-proline, the HF calculation assigns the mode at 1782 cm^{-1} to a C=O stretch. The band at 1645 cm^{-1} in the IR spectrum and 1643 cm^{-1} in the Raman spectrum is assigned to a υC=O band. Rippon *et al.* [19] reported a value of 1647 cm^{-1} for the carbonyl stretching mode. The OH in-plane deformation, coupled to the C-O stretching vibration is expected in the region 1390 ± 55 cm^{-1}. The C(=O)O stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region 1250 ± 80 cm^{-1}. The out-of-plane OH deformation [21] exhibits a moderate band in the region 905 ± 65 cm^{-1}. The C=O in-plane deformation is weakly to moderately active in the region 725 ± 95 cm^{-1}. Most carboxylic acids display γC=O in the region 595 ± 85 cm^{-1}, in the vicinity of that of methyl and ethyl esters. The -C(=O)O deformation or rock has a weak to moderate intensity and appears in the region 445 ± 120 cm^{-1}.

For glutamic acid dipeptides, the intensity of γOH bands [22] is reported at ~940 cm^{-1}. For L-proline, the band at 1242 cm^{-1} in the IR spectrum and 1248 cm^{-1} in the Raman spectrum are assigned to the υC(=O)O mode, with a calculated value of 1244 cm^{-1}. The bands observed at 950 cm^{-1} in the IR spectrum and 941 cm^{-1} in the Raman spectrum are assigned to the γOH mode. The C=O deformation bands are at 721 for IR, and 724 and 572 cm^{-1} for HF.

Ring Modes

The ring stretching modes of the pyrrolidine ring are in the region from 1100 to 800 cm^{-1} and the ring bending modes appear below 800 cm^{-1} [23]. The most prominent ring stretching mode is the symmetrical ring breathing mode, which usually appears as an intense band at 902 cm^{-1} for pyrrolidine [14]. For L-proline, this mode is identified as a strong Raman band at 900 cm^{-1} and as a medium band at 907 cm^{-1} in the IR spectrum. The ring stretching modes of the pyrrolidine ring in the vapor phase generally give rise to a strong IR band at 1095 cm^{-1} along with a reasonably weak Raman band at 980 cm^{-1} at room temperature [23]. Rippon *et al.* [19] reported the proline ring stretching vibrations at 914, 983 and 1000 cm^{-1}. In the present case, the assignments of the proline ring modes, which are in agreement with those reported by Podstawka *et al.* [24], were observed at 1090, 1025, 907, 866 cm^{-1} in the IR spectrum, 1083, 1023, 900, 880 cm^{-1} in the Raman spectrum and 1083, 1016, 908, 898, 876 cm^{-1} (HF), all of which are assigned to the ring stretching modes.

The bond lengths C_4- C_7, C_1- C_4, C_7- C_{10} of the proline ring from the HF calculations are found to be 1.5464, 1.5353 and 1.5689 Å, respectively. Padmaja *et al.* [23] reported the corresponding experimental values as 1.5 Å (HF) and 1.46 to 1.52 Å. The C-N bond length in the proline ring is calculated to be 1.4741 Å (C_1-N_{12}) and 1.4673 Å (C_{10}-N_{12}), whereas the reported experimental values are 1.49, 1.5 Å and 1.4, 1.5 Å by HF calculations [23]. In the present case, the CH bonds lengths are in the range 1.0849-1.0785 Å, which is in agreement with the reported values [23].

SERS Spectrum

Regarded as a highly sensitive method, SERS allows for the detection of individual molecules [25]. The vibrational information contained in the Raman spectrum provides the molecular specificity required to characterize the adsorbate-surface interactions, specifically, the orientation of the adsorbed species on the metal surface. The relative intensities from the SERS spectra are expected to differ significantly from normal Raman spectra owing to specific surface selection rules [26]. These rules suggest that, for a molecule adsorbed flat on the silver surface, its out-of-plane vibrational modes will be enhanced compared to its in-plane vibrational modes and vice versa when its adsorbed position is perpendicular to the surface [26,27]. It is further seen that vibrations involving atoms that are close to the silver surface will be enhanced. When the wavenumber difference between Raman bands in the normal and SERS spectra is not more than 5 cm^{-1}, the molecular plane is perpendicular to the silver surface [28].

In the SERS spectrum of L-proline, prominent bands are observed at 2986, 2885, 1585, 1480, 1346, 1301, 1229, 1194, 990, 828, 762, 283, 237, 188 and 134 cm^{-1}. In the case of the SERS spectra of thymine molecules on silver [29], the deformation bands of the methyl group are present at 1355 cm^{-1}, with the position of the methyl group close to the metallic surface. For 2-methylpyridine, Bunding *et al*. [30] noticed significant shift and broadening of the CH modes in the SERS spectrum. They explained this in terms of the interaction of the methyl group with the metal surface. In the present case, the asymmetric CH stretching of the methylene group appears at 2986 cm^{-1} in the SERS spectrum. Also, the symmetric CH stretching of the methylene group, a weak band in the Raman spectrum at 2900 cm^{-1}, is shifted to 2885 cm^{-1} as a strong band in the SERS spectrum. This is related to the closeness of the CH_2 group to the silver surface, which is justifiable because the modes in the groups directly interacting with the metal surface are prominent in the SERS spectrum and undergo a wavenumber shift [31]. Furthermore, the presence of the deformation bands of the CH_2 group in the SERS spectrum also supports the above argument.

The C=O and C-O stretching bands are also present in the SERS spectrum at 1646 and 1229 cm^{-1}. In the SERS spectrum, the presence of strong band at 188 cm^{-1} is due to the υAg-O vibration, giving evidence of an interaction of the silver surface with the carbonyl group [32]. The interaction between the carboxylate group and the metal surface is supported by the presence of a strong band at 546 cm^{-1} in the SERS spectrum due to the C=O deformation band, which is absent in the normal Raman spectrum.

According to surface selection rules [33,34], the presence of in-plane and out-of-plane modes of the proline ring at 612, 283, 237 cm^{-1} in the SERS spectrum of L-proline suggest that there is a certain angle between the ring and the metal surface. Also, L-proline interacts with the silver surface through the NH group. This is supported by the SERS bands at 1585 cm^{-1} (δNH), 1154 cm^{-1} (τNH) and 1117 cm^{-1} (υCN). The presence of a strong band υAg-N at 134 cm^{-1} in the SERS spectrum also supports this argument [24].

CONCLUSIONS

A useful technique for studying the adsorption of molecules on metal surfaces, SERS spectroscopy aided in determining the tilted orientation of L-proline on a silver surface due to the presence of the in-plane and out-of-plane modes of the proline ring. The presence of significant metal-molecule interaction is confirmed by the appearance of intense Ag-O and Ag-N modes in the SERS spectrum, indicative of the nearness of carboxylate and NH groups to the silver surface. The presence of methylene group modes in the SERS spectrum verifies the proximity of the methylene group to the metal surface, affecting the orientation and the interaction of the metal with the L-proline molecules. The calculated vibrational wavenumbers obtained by HF are in good agreement with the experimental values obtained for the investigated molecule.

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