

Decoding the Structure of Non-Proteinogenic Amino Acids: The Rotational Spectrum of Jet-Cooled Laser-Ablated Thioproline

Complete Reference [62]

Figure S1. Predicted conformers of thiazolidine. Relative energies in cm^{-1} calculated at B3LYP-GD3/6-311++G(2d,p). Illustration of conformer labelling.

Figure S2. Predicted conformers of SPro showed in 3 different perspectives. See text for labelling. Relative energies in cm^{-1} calculated at B3LYP-GD3/6-311++G(2d,p). The green highlighting remarks the alignment of the COOH group with the S atom.

Figure S3. Predicted MP2/6-311++G(2d,p) potential energy function for the internal rotation of COOH group interconverting III-ax-ce and I-ax-ce conformers.

Figure S4. QTAIM analysis results for the predicted conformers of SPro in three different perspectives. Bond critical points (yellow) and bond paths (orange) are also shown in the same perspectives as Figures S1 and S2. The green highlighting remarks the alignment of the COOH group with the S atom.

Figure S5. Results of the NCI analysis for the predicted conformers of SPro in three different perspectives. The colour code of the energy surfaces is the same as described in Figure 3. The green highlighting remarks the alignment of the COOH group with the S atom.

Figure S6. Atom labelling for the I-ax-ce and II-ax-ta detected conformers of SPro.

Figure S7: 500 MHz ^1H NMR spectra of thioproline (SPro) obtained in D_2O solution at pH 7.0. The spectrum is formed by an ABX system and an AB system.

Table S1. Rotational parameters for the SPro conformers predicted at B3LYP-D3/(6-311++G(2d,p)) level.

Table S2. Rotational parameters for the most stable conformers of SPro predicted at MP2/(6-311++G(2d,p)) level.

Table S3. r_e geometry for I-ax-ce and II-ax-ta detected conformers of TPro (DFT: B3LYP-D3/(6-311++G(2d,p)); MP2: MP2/(6-311++G(2d,p))).

Table S4. Observed rotational transitions and residuals (all the values in MHz) for the I-ax-ce SPro conformer in the ground vibrational state.

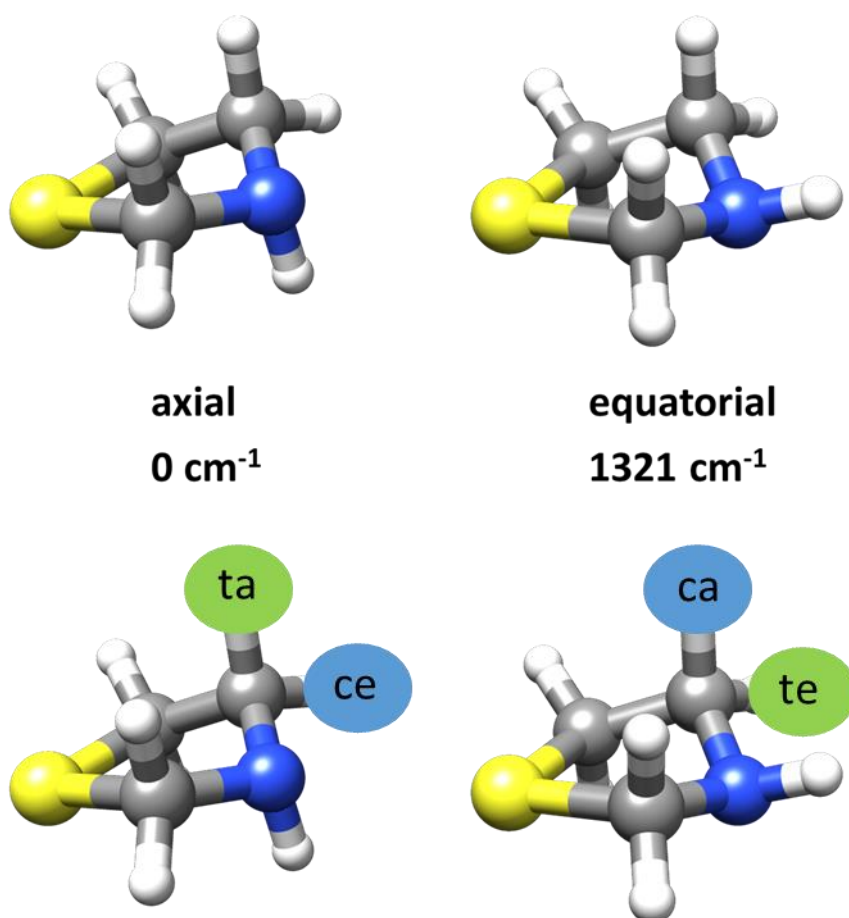
Table S5. Observed rotational transitions and residuals (all the values in MHz) for the II-ax-ta SPro conformer in the ground vibrational state.

Complete Reference [62]

Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, M. J.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.;

Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

Figure S1. Predicted axial and equatorial conformers of thiazolidine. Relative energies in cm^{-1} calculated at B3LYP-GD3/6-311++G(2d,p). Illustration of conformer labelling.



The COOH group will be in the alpha position, that it is remarked with a sphere in the lower part of the figure in order to indicate the possible positions of this group and how it is labelled in the SPro.

"... The third feature is the orientation of the acid group. It can be classified as axial or equatorial but to avoid confusion with the orientation of the N-H group we have chosen to use also the possible arrangements as a function of the *cis* or *trans* orientation of the COOH group relative to the side of the ring of the N-H group. In this way, we can have *trans*-axial (Z=ta), *trans*-equatorial (Z=te), *cis*-axial (ca), or *cis*-equatorial (Z=ce) orientations of the COOH group."

Figure S2. Predicted conformers of SPro showed in 3 different perspectives. See text for labelling. Relative energies in cm^{-1} calculated at B3LYP-GD3/6-311++G(2d,p). The green highlighting remarks the alignment of the COOH group with the S atom.

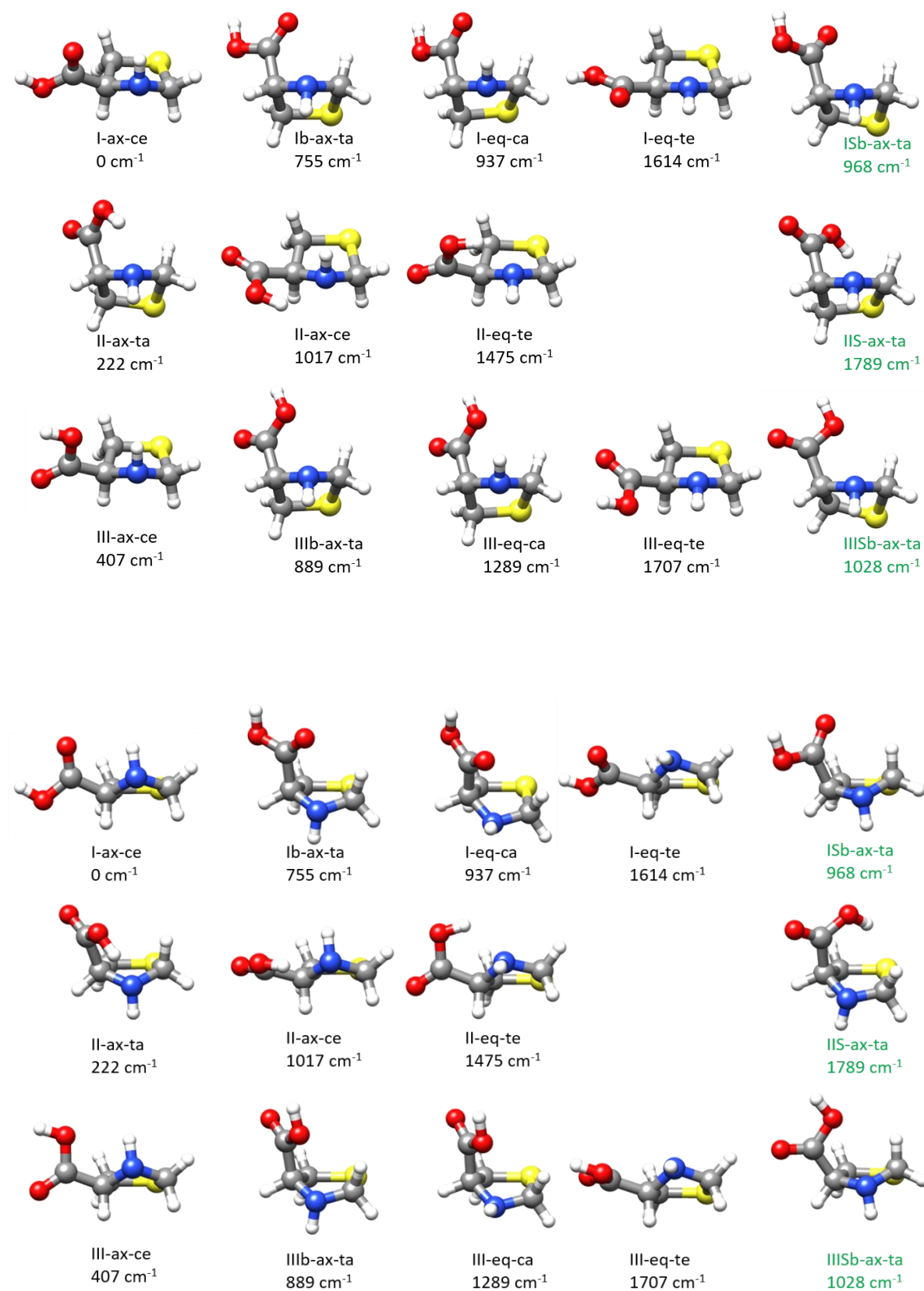


Figure S2. Continuation.

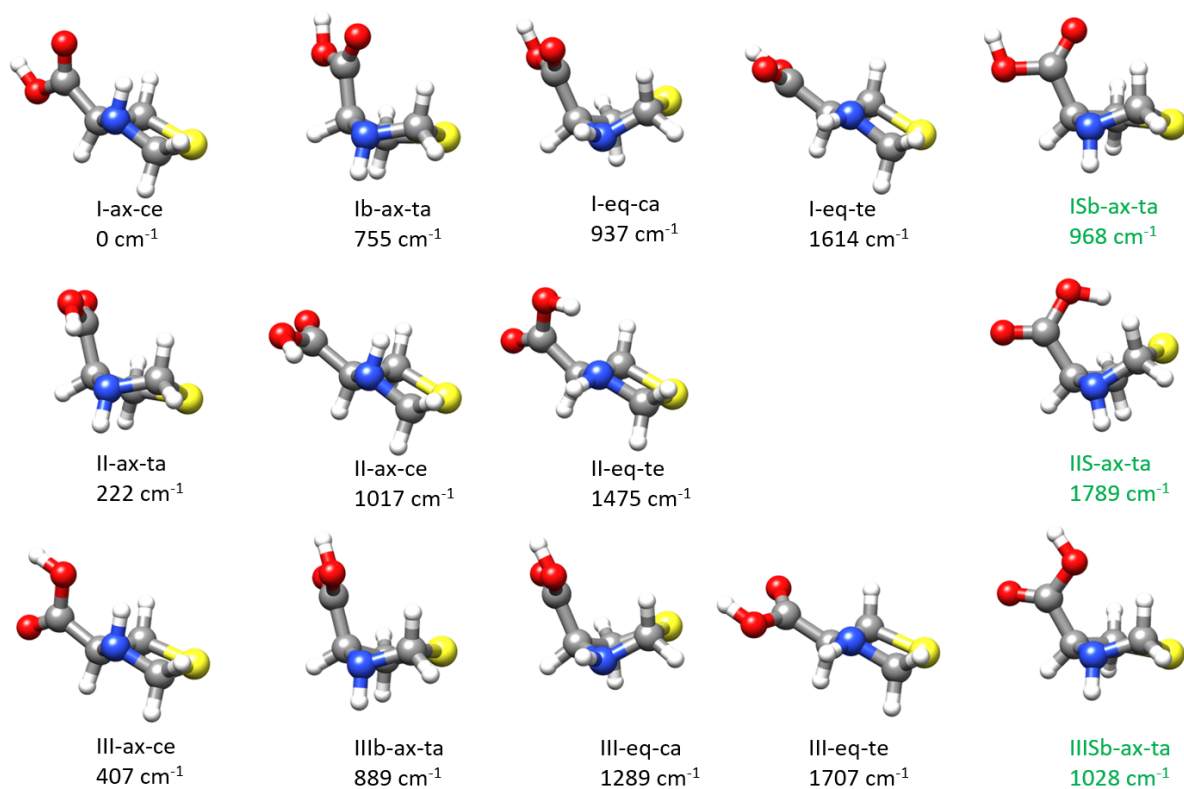


Figure S3. Predicted MP2/6-311++G(2d,p) potential energy function for the internal rotation of COOH group interconverting III-ax-ce and I-ax-ce conformers (see Figure S6 for atom labelling).

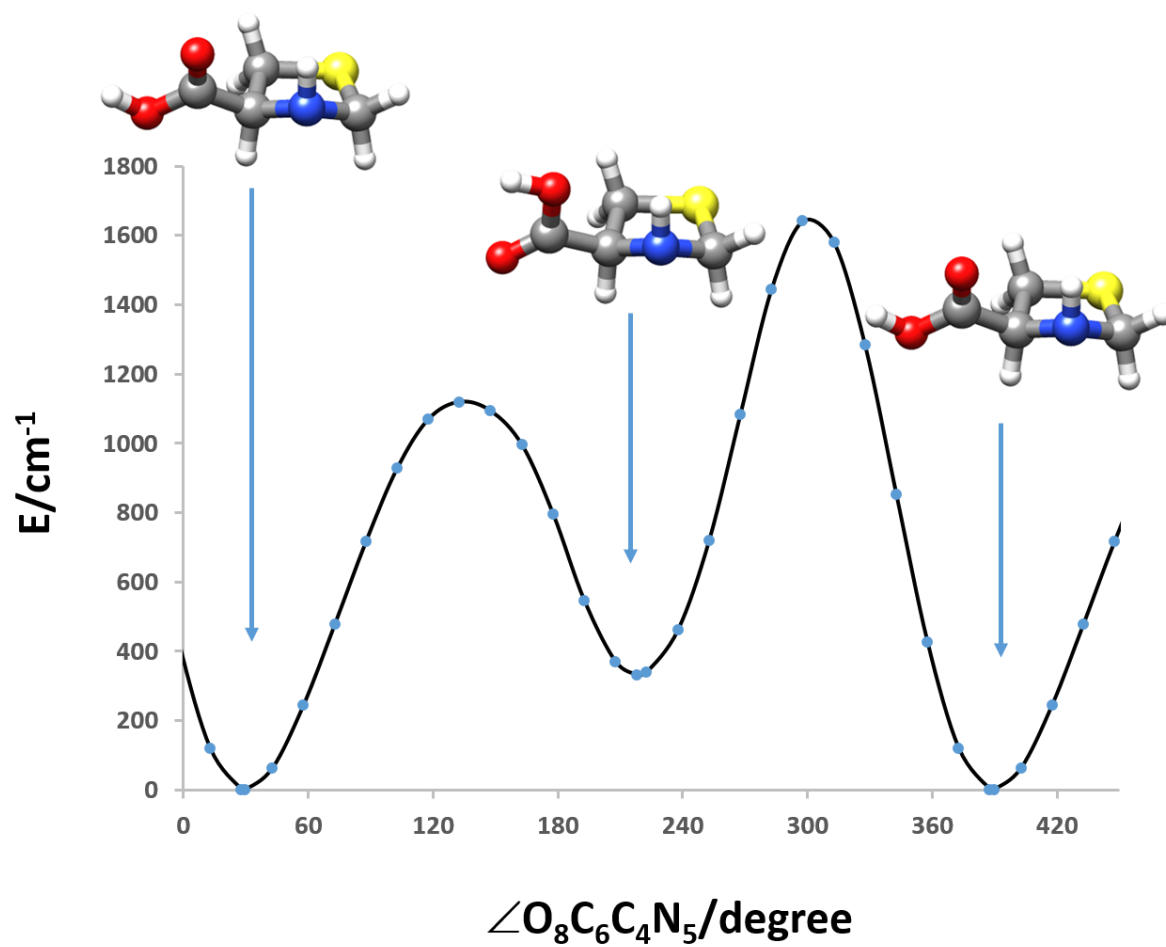


Figure S4. QTAIM analysis results for the predicted conformers of SPro in three different perspectives. Bond critical points (yellow) and bond paths (orange) are also shown in the same perspectives as Figures S1 and S2. The green highlighting remarks the alignment of the COOH group with the S atom.

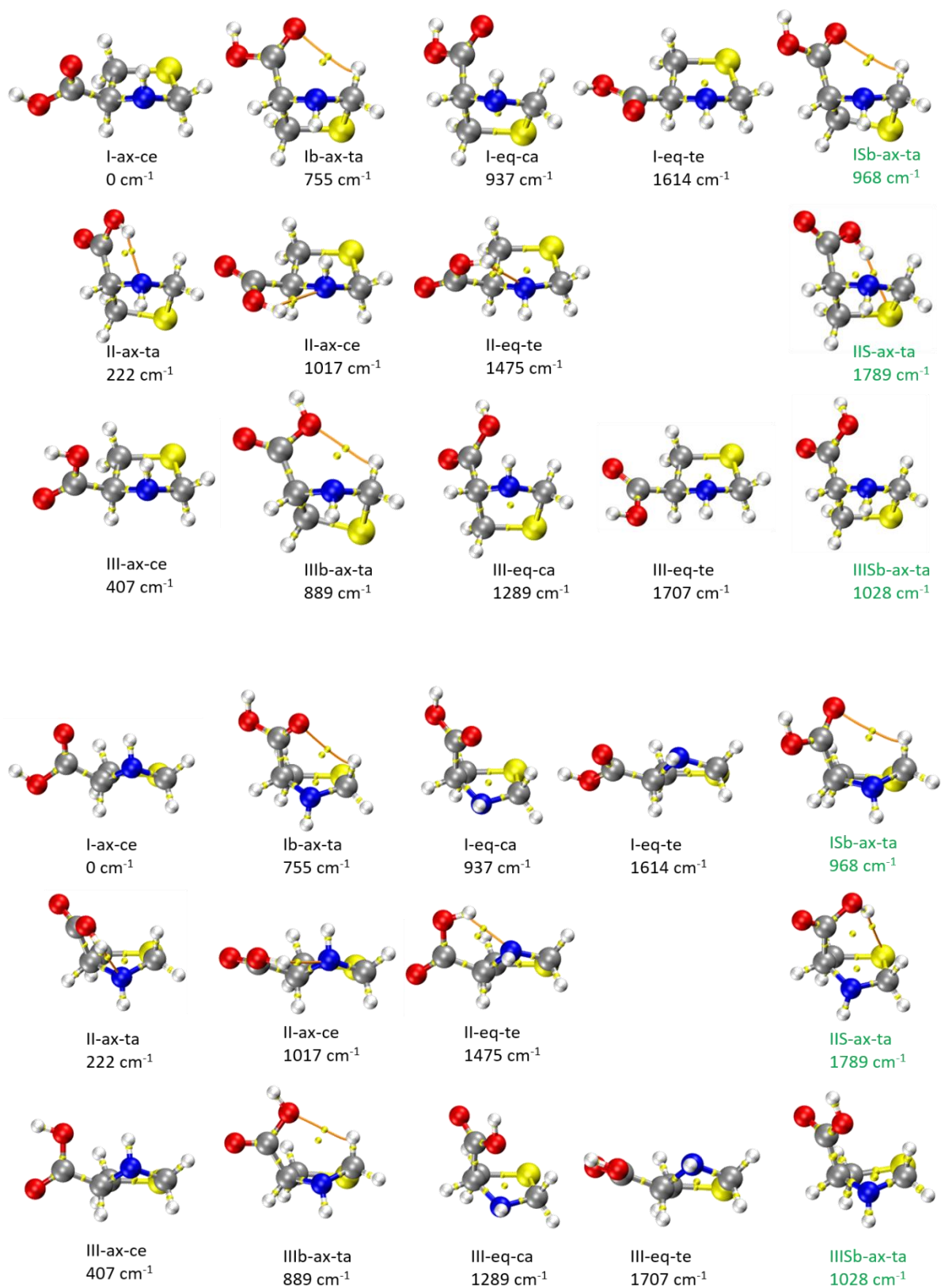


Figure S4. Continuation.

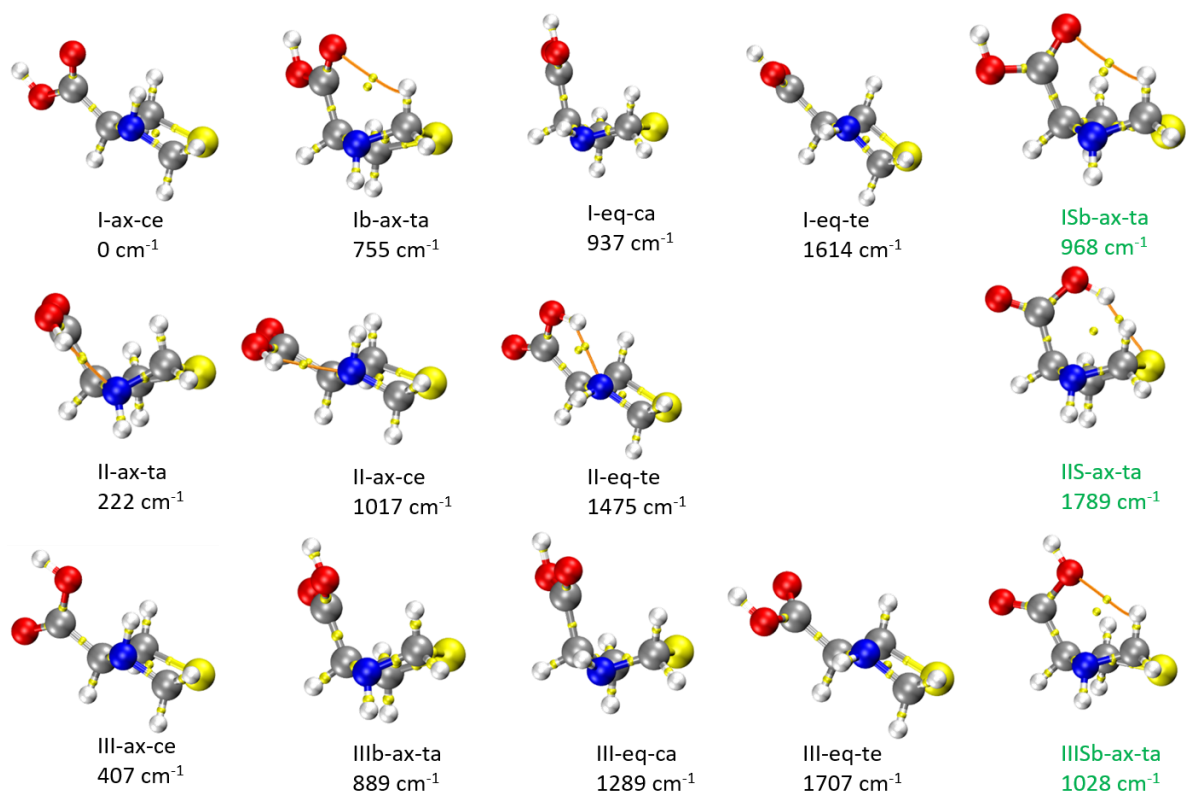


Figure S5. Results of the NCI analysis for the predicted conformers of SPro in three different perspectives. The colour code of the energy surfaces is the same as described in Figure 3. The green highlighting remarks the alignment of the COOH group with the S atom.

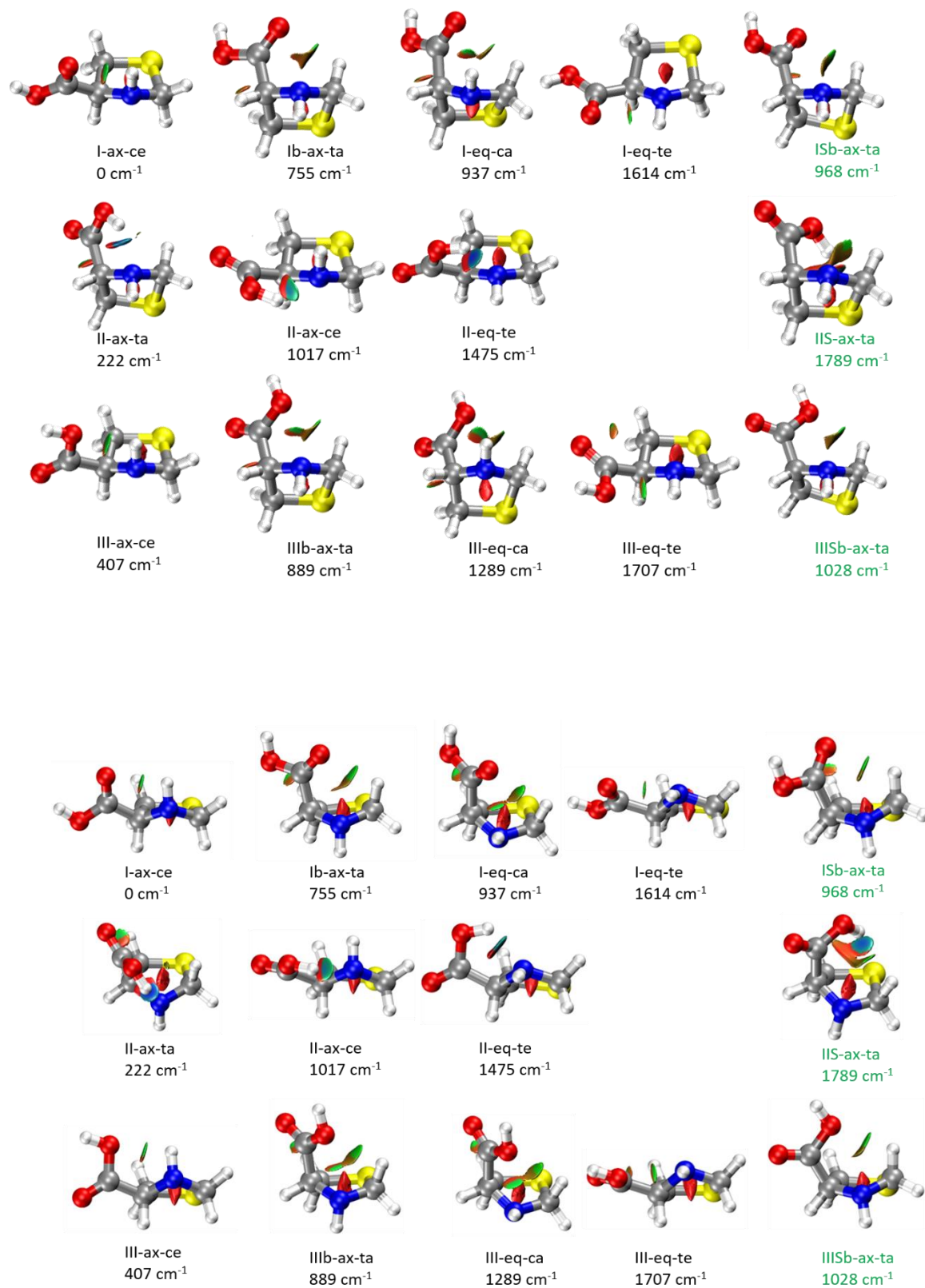


Figure S5. Continuation.

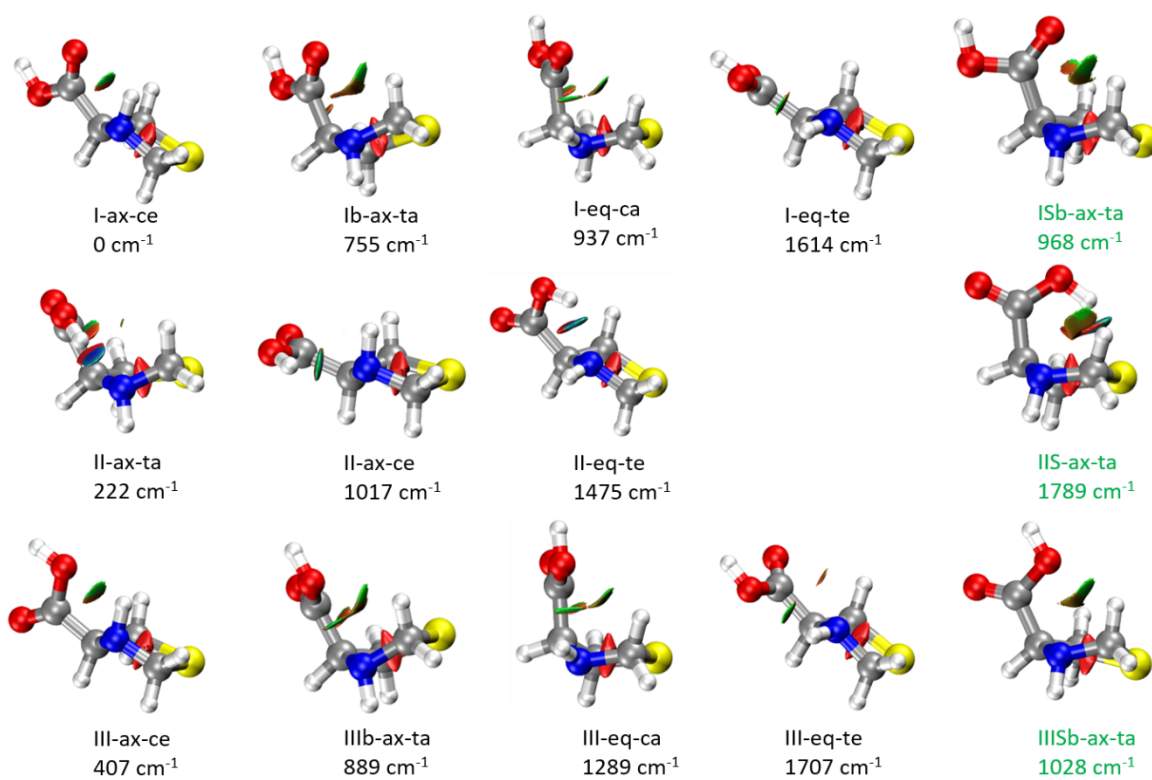


Figure S6. Atom labelling for the I-ax-ce and II-ax-ta detected conformers of SPro.

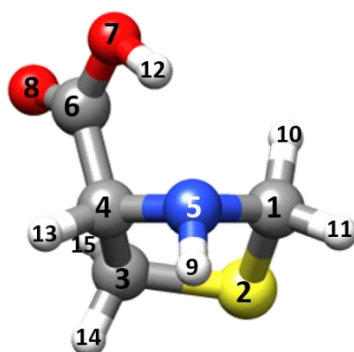
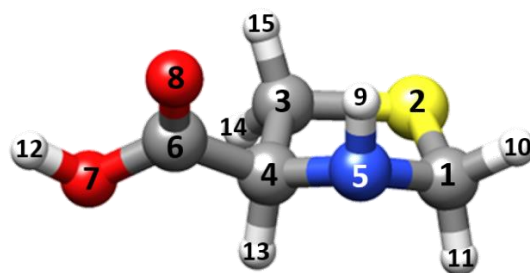
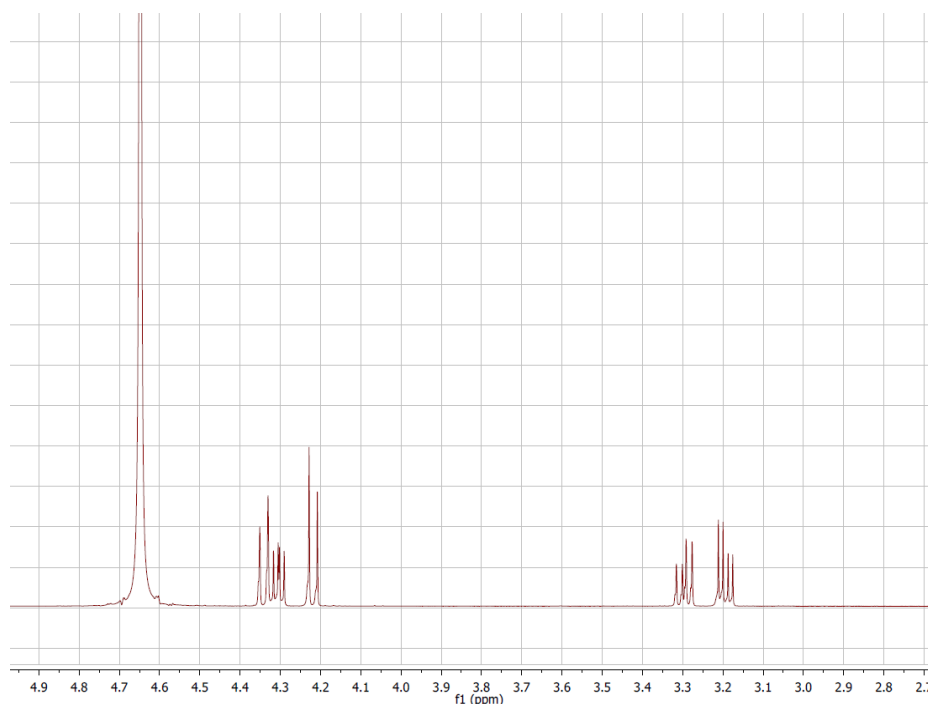
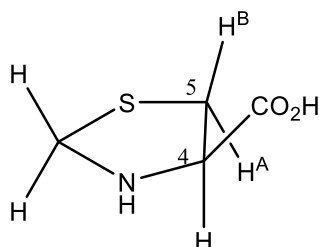


Figure S7: 500 MHz ^1H NMR spectra of thioproline(SPro) obtained in D_2O solution at pH 7.0. The spectrum is formed by an ABX system and an AB system.



In order to study the possible conformations existing in solution for thioproline (SPro), we examined by ^1H NMR and ^{13}C NMR in 0,1 M solution in D_2O . The H^{A}_5 , H^{B}_5 protons form the AB part of an ABX system ($\text{X} = \text{H}_4$). The coupling constants of $^3\text{J } \text{H}_4\text{-H}^{\text{A}}_5$ and $^3\text{J } \text{H}_4\text{-H}^{\text{B}}_5$ are parameters that can be utilized in structure determination. They lead to conformationally reasonable values of the dihedral angles in thioproline. The coupling constants of the hydrogens attached to carbons 4 and 5 ($^3\text{J } \text{H}_4\text{-H}^{\text{A}}_5 = 5.8 \text{ Hz}$ and $^3\text{J } \text{H}_4\text{-H}^{\text{B}}_5 = 7.4 \text{ Hz}$) allowed us to assume dihedral angles $\text{H}_4\text{-C}_4\text{-C}_5\text{-H}^{\text{A}}_5$ and $\text{H}_4\text{-C}_4\text{-C}_5\text{-H}^{\text{B}}_5$ approximately 30° and 130° , respectively, according to the curve by Kopple [1]. The observed conformation is not planar, the probable conformation in solution correspond to S_{exo} form, relative to the orientation *anti* of the S atom in respect of the carboxyl group.



Thioproline (SPro)

Table S1. Rotational parameters for the SPro conformers predicted at B3LYP-D3/(6-311++G(2d,p)) level.

Param. ^a	I-ax-ce	II-ax-ta	III-ax-ce	Ib-ax-ta	III-ax-ta	I-eq-ca	ISb-ax-ta
<i>A</i> /MHz	3775.74	3125.48	3798.10	2970.97	2874.27	2850.97	3608.40
<i>B</i> /MHz	1079.47	1322.18	1065.84	1339.11	1390.92	1413.94	1157.11
<i>C</i> /MHz	950.35	1094.73	968.17	1180.32	1190.65	1211.60	1111.71
κ	-0.91	-0.78	-0.93	-0.82	-0.76	-0.75	-0.96
$P_{aa}/\text{u}\text{\AA}^2$	433.05	341.09	431.55	317.73	305.98	298.64	375.65
$P_{bb}/\text{u}\text{\AA}^2$	98.73	120.56	90.45	110.44	118.47	118.48	78.95
$P_{cc}/\text{u}\text{\AA}^2$	35.12	41.14	42.61	59.67	57.36	58.79	61.11
$3/2(\chi_{aa})/\text{MHz}$	3.16	-2.19	2.88	-0.09	-1.04	0.02	-1.93
$1/4(\chi_{bb}-\chi_{cc})/\text{MHz}$	0.22	-0.65	0.07	-1.18	-1.04	1.29	-0.25
χ_{aa}/MHz	2.11	-1.46	1.92	-0.06	-0.69	0.01	-1.29
χ_{bb}/MHz	-0.62	-0.57	-0.82	-2.33	-1.73	2.58	0.15
χ_{cc}/MHz	-1.49	2.03	-1.11	2.39	2.42	-2.59	1.13
μ_a/D	-1.06	2.38	-0.33	-0.67	0.06	-1.50	1.25
μ_b/D	-0.69	2.73	1.12	-1.11	1.62	-0.48	0.89
μ_c/D	0.76	2.82	-1.34	2.09	1.45	0.94	1.92
μ_T/D	1.48	4.59	1.78	2.46	2.18	0.94	2.46
<i>E</i> / h	-760.1966725	-760.1956576	-760.1948158	-760.1932292	-760.1926191	-760.1923991	-760.1922594
$\Delta E / \text{cm}^{-1}$	0.0	222.74	407.50	755.72	889.62	937.92	968.56
$\Delta E / \text{kJ mol}^{-1}$	0.0	2.66	4.87	9.04	10.64	11.22	11.59

^a *A*, *B* and *C* are the rotational constants. κ is the Ray asymmetry parameter $\kappa=(2B-A-C)/(A-C)$. $P_{\alpha\alpha}$ ($\alpha = a, b, c$) are the planar moments of inertia, derived from the inertial moments $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa} , χ_{bb} and χ_{cc} are the ^{14}N quadrupole coupling constants. μ_a, μ_b, μ_c are the electric dipole moment components. *n* is the number of quadrupole coupling components fitted. *E* is the electronic energy in Hartree. ΔE is the relative energy to the most stable conformer.

Table S1. Continuation

Param. ^a	II-ax-ce	IIISb-ax-ta	III-eq-ca	II-eq-te	I-eq-te	III-eq-te	IIS-ax-ta
<i>A</i> /MHz	3810.53	3525.85	2843.06	3799.96	3862.29	3906.56	3085.68
<i>B</i> /MHz	1123.98	1168.05	1419.97	1098.51	1116.52	1112.45	1345.21
<i>C</i> /MHz	897.57	1106.51	1210.41	963.92	897.43	897.72	1242.01
κ	-0.84	-0.95	-0.74	-0.91	-0.85	-0.86	-0.89
$P_{aa}/\text{u}\text{\AA}^2$	440.03	373.03	297.84	425.68	442.47	443.94	309.41
$P_{bb}/\text{u}\text{\AA}^2$	123.02	83.70	119.69	98.62	120.68	119.01	97.50
$P_{cc}/\text{u}\text{\AA}^2$	9.60	59.64	58.07	34.38	10.17	10.35	66.28
$3/2(\chi_{aa})/\text{MHz}$	1.65	-1.09	-0.39	3.99	4.77	4.55	-1.23
$1/4(\chi_{bb}-\chi_{cc})/\text{MHz}$	-0.78	-0.92	1.28	1.68	2.11	1.87	0.44
χ_{aa}/MHz	1.10	-0.73	-0.26	2.66	3.18	3.03	-0.82
χ_{bb}/MHz	-2.12	-1.47	2.69	2.03	2.62	2.22	1.29
χ_{cc}/MHz	1.02	2.19	-2.43	-4.69	-5.80	-5.25	-0.47
μ_a/D	2.21	0.55	-1.15	3.12	-0.92	-1.15	-4.30
μ_b/D	2.72	0.62	2.22	2.47	-0.37	2.45	-1.61
μ_c/D	0.23	0.04	0.46	0.90	1.38	1.23	1.63
μ_T/D	3.52	0.83	2.55	4.08	1.70	2.97	4.87
<i>E</i> / h	-760.192038	-760.191988	-760.1907986	-760.1899494	-760.1893161	-760.1888934	-760.1885202
$\Delta E / \text{cm}^{-1}$	1017.16	1028.15	1289.17	1475.55	1614.54	1707.32	1789.22
$\Delta E / \text{kJ mol}^{-1}$	12.17	12.30	15.42	17.65	19.31	20.42	21.40

Table S2. Rotational parameters for the most stable conformers of SPro predicted at MP2/(6-311++G(2d,p)) level.

Param. ^a	I-ax-ce	II-ax-ta	III-ax-ce
A/MHz	3806.75	3076.88	3835.54
B/MHz	1084.75	1365.99	1071.96
C/MHz	960.86	1136.06	980.62
κ	-0.91	-0.76	-0.94
$P_{aa}/\text{u}\text{\AA}^2$	429.6	325.3	427.5
$P_{bb}/\text{u}\text{\AA}^2$	96.4	119.6	87.8
$P_{cc}/\text{u}\text{\AA}^2$	36.3	44.7	43.9
D_J/kHz	0.085	0.828	0.080
D_{JK}/kHz	0.193	-5.017	0.306
D_K/kHz	0.788	10.195	0.509
d_1/kHz	-0.020	-0.021	-0.008
d_2/kHz	-0.008	-0.001	-0.002
$3/2(\chi_{aa})/\text{MHz}$	2.93	-2.14	2.67
$1/4(\chi_{bb}-\chi_{cc})/\text{MHz}$	0.17	-0.61	0.01
χ_{aa}/MHz	1.95	-1.43	1.78
χ_{bb}/MHz	-0.63	-0.51	-0.87
χ_{cc}/MHz	-1.32	1.93	-0.91
μ_a/D	1.03	2.30	0.32
μ_b/D	0.72	2.62	0.86
μ_c/D	0.61	2.87	1.33
μ_T/D	1.40	4.52	1.62
E/E_h	-758.7399655	-758.739426	-758.7384506
$\Delta E / \text{cm}^{-1}$	0.00	118.41	332.48
$\Delta E / \text{kJ mol}^{-1}$	0.00	1.42	3.98
$E_{\text{Gibbs}} / \text{h}$	-758.655017	-758.653584	-758.65333
$\Delta E_{\text{Gibbs}} / \text{cm}^{-1}$	0.00	314.51	370.25
$\Delta E_{\text{Gibbs}} / \text{kJ mol}^{-1}$	0.00	3.76	4.43

^a A , B and C are the rotational constants. κ is the Ray asymmetry parameter $\kappa=(2B-A-C)/(A-C)$. $P_{\alpha\alpha}$ ($\alpha = a, b, c$) are the planar moments of inertia, derived from the inertial moments $P_{\alpha\alpha}=(I_a+I_b-I_c)/2$. D_J , D_{JK} , D_K , d_1 , and d_2 , are the quartic centrifugal distortion constants. χ_{aa} , χ_{bb} and χ_{cc} are the ^{14}N quadrupole coupling constants. μ is the dipole moment in Debay. E is the electronic energy in Hatrees, ΔE is the relative energy to the global minimum. E_{Gibbs} is the Gibbs energy in Hatrees calculated at 298.15 K, ΔE_{Gibbs} is the relative Gibbs energy to the global minimum.

Table S3. r_e geometry for I-ax-ce and II-ax-ta detected conformers of SPro (DFT: B3LYP-D3/(6-311++G(2d,p); MP2: MP2/(6-311++G(2d,p)

I-ax-ce	DFT			MP2		
atom ^a	a^b	b	c	a	b	c
C1	1.706346	1.135542	0.444810	-1.700381	1.117842	-0.455048
O2	2.197678	-0.562844	-0.232949	-2.188466	-0.558669	0.225158
C3	0.442070	-1.104036	-0.257636	-0.440188	-1.085679	0.286861
C4	-0.352574	0.019912	0.477511	0.347204	0.012216	-0.471956
N5	0.292984	1.300649	0.250652	-0.287036	1.297953	-0.248714
C6	-1.777125	0.047681	-0.030627	1.767423	0.044486	0.028502
O7	-2.550116	-0.857918	0.606235	2.547551	-0.843307	-0.630587
O8	-2.173811	0.745884	-0.926995	2.158289	0.732505	0.944114
H9	0.077231	1.621002	-0.689279	-0.091232	1.590598	0.707962
H10	2.272657	1.908652	-0.069484	-2.273886	1.895582	0.046143
H11	1.952608	1.142721	1.506028	-1.925420	1.121671	-1.521242
H12	-3.429429	-0.828736	0.196158	3.424686	-0.802306	-0.210842
H13	-0.354722	-0.197877	1.547547	0.333977	-0.214663	-1.540884
H14	0.332666	-2.061352	0.248864	-0.320464	-2.059711	-0.187158
H15	0.108703	-1.202409	-1.291359	-0.109141	-1.141855	1.325636

II-ax-ta	DFT			MP2		
atom ^a	a^b	b	c	a	b	c
C1	1.119172	1.224949	-0.445523	1.056786	1.208612	-0.483343
O2	2.045276	-0.386547	-0.366017	1.998374	-0.377676	-0.386849
C3	0.674857	-1.177396	0.582179	0.699625	-1.136189	0.661966
C4	-0.374718	-0.073196	0.853190	-0.367748	-0.052649	0.886829
N5	0.208455	1.264908	0.687518	0.193695	1.286889	0.685433
C6	-1.617141	-0.218457	-0.050449	-1.572024	-0.235280	-0.049517
O7	-2.178179	0.951678	-0.393254	-2.170192	0.921763	-0.390117
O8	-2.073167	-1.278331	-0.377279	-1.980678	-1.312906	-0.404960
H9	0.710841	1.530347	1.527475	0.745810	1.550271	1.498419
H10	0.551459	1.262714	-1.375535	0.443617	1.210100	-1.385447
H11	1.822301	2.054425	-0.417140	1.751491	2.046424	-0.513874
H12	-1.593604	1.651090	-0.033453	-1.604839	1.627631	-0.006628
H13	-0.758966	-0.160508	1.872865	-0.771563	-0.116086	1.902042
H14	1.085288	-1.567098	1.511871	1.150982	-1.442068	1.605053
H15	0.229790	-1.992625	0.016422	0.257729	-2.001688	0.170990

^a Atom labelling, see Figure S6. ^b a , b , and c are the coordinates in the principal axis system of the conformer in Å.

Table S4. Observed rotational transitions and residuals (all the values in MHz) for the I-ax-ce SPro conformer in the ground vibrational state.

J'	K ₋₁ '	K ₊₁ '	J''	K ₋₁ ''	K ₊₁ ''	F'	F''	Obs.	Obs.-Cal.
1	1	1	0	0	0	1	1	4760.6866	-0.0037
						2	1	4760.8748	0.0029
						0	1	4761.1295	-0.0148
1	1	0	0	0	0	2	1	4894.9575	0.0024
2	0	2	1	0	1	1	1	4092.5225	-0.0040
						3	2	4093.4930	0.0018
						1	0	4094.0363	0.0029
2	1	1	1	1	0	2	2	4094.1467	0.0041
						3	1	4232.3078	-0.0037
						2	2	4232.5207	0.0146
2	1	2	1	0	1	1	0	4232.6281	0.0032
						2	2	4232.9226	-0.0047
						1	1	6675.1353	0.0002
2	1	1	1	0	1	2	1	6675.8315	-0.0053
						3	2	6675.9901	0.0017
						2	2	6676.4354	-0.0041
2	1	1	1	0	1	1	0	6676.6507	0.0088
						1	1	7077.4645	0.0013
						2	1	7077.7674	0.0017
3	1	3	2	1	2	3	2	7078.1724	-0.0014
						2	2	7078.3543	-0.0141
						1	0	7078.9753	0.0053
3	0	3	2	0	2	4	3	5943.4620	-0.0044
						3	2	5943.6561	0.0037
						2	2	6127.3020	0.0012
3	1	2	2	1	1	4	3	6128.1983	-0.0066
						3	2	6128.1983	-0.0066
						2	1	6128.3124	-0.0014
3	2	2	2	2	1	2	2	6127.3020	0.0012
						3	3	6128.8802	0.0044
						4	3	6345.4948	0.0033
3	2	1	2	2	0	3	2	6345.6656	-0.0023
						3	3	6345.8653	0.0028
						2	1	6147.0567	-0.0040
3	2	1	3	1	2	3	3	6147.4197	0.0003
						4	3	6147.4197	0.0003
						3	2	6148.0635	-0.0018
3	2	1	3	1	2	2	2	6148.0635	-0.0018
						2	1	6166.4110	-0.0002
						3	3	6166.7654	-0.0014
3	2	1	3	1	2	4	3	6166.7654	-0.0014
						3	2	6167.4022	-0.0027
						4	4	7961.2590	0.0030
						2	2	7961.3885	-0.0024

Table S4. Continuation.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	F'	F''	Obs.	Obs.-Cal.
4	0	4	3	0	3	5	4	8148.6286	0.0056
4	1	4	3	1	3	5	4	7919.2541	0.0059
						4	3	7919.3310	-0.0028
4	0	4	3	1	3	5	4	5750.8520	0.0011
						4	3	5750.9191	-0.0059
4	0	4	3	1	2	5	4	4946.6458	0.0054
						4	3	4946.9804	-0.0003
4	2	2	4	1	3	4	4	7747.2800	0.0013
						5	5	7747.4888	0.0079
						3	3	7747.5388	0.0059
4	2	3	4	1	3	4	4	7675.0160	0.0009
						5	5	7675.2060	-0.0020
						3	3	7675.2060	-0.0020
5	0	5	4	1	4	6	5	7982.4025	0.0028
						5	4	7982.4025	-0.0111
5	2	3	5	1	4	5	5	7518.9196	0.0042
						6	6	7519.0255	-0.0070
5	2	4	5	1	4	5	5	7351.6069	0.0039
						6	6	7351.6836	-0.0015
						4	4	7351.6836	-0.0015
						5	6	7352.0874	-0.0123
6	1	5	6	0	6	6	6	4438.9496	0.0056
						7	7	4439.1981	0.0037
						5	5	4439.1981	0.0037
6	2	4	6	1	5	6	6	7299.9332	0.0014
						7	7	7300.0159	0.0017
						5	5	7300.0159	0.0017
7	1	6	7	0	7	7	7	5090.2479	0.0064
						8	8	5090.4692	-0.0068
						6	6	5090.5057	-0.0041
7	2	6	7	1	6	6	6	6533.6060	-0.0010
						8	8	6533.6060	-0.0010
						7	7	6533.6060	-0.0010
7	2	5	7	1	6	7	7	7116.4568	-0.0025
						8	8	7116.5241	0.0044
						6	6	7116.5241	-0.0042
8	2	6	8	1	7	7	7	6049.5121	0.0055
						9	9	6049.5121	0.0055
8	2	6	8	1	7	8	8	6994.5214	-0.0013
						9	9	6994.5794	-0.0036
						7	7	6994.5794	-0.0036
9	2	8	9	1	8	8	8	5525.3848	-0.0015
						10	10	5525.3848	-0.0015
9	2	7	9	1	8	9	9	6958.1350	-0.0013
						10	10	6958.2025	0.0016
						8	8	6958.2025	0.0016

Table S4. Continuation.

J'	K₋₁'	K₊₁'	J''	K₋₁''	K₊₁''	F'	F''	Obs.	Obs.-Cal.
10	2	8	10	1	9	10	10	7028.2098	0.0039
						11	11	7028.2774	-0.0021
						9	9	7028.2774	-0.0021

Table S5. Observed rotational transitions and residuals (all the values in MHz) for the II-ax-ta SPro conformer in the ground vibrational state.

J'	K ₋₁ '	K ₊₁ '	J''	K ₋₁ ''	K ₊₁ ''	F'	F''	Obs.	Obs.-Cal.
1	1	1	0	0	0	1	1	4305.3583	-0.0033
						2	1	4305.5233	-0.0001
						0	1	4305.7641	-0.0018
1	1	0	0	0	0	0	1	4532.4988	0.0000
						2	1	4533.3356	0.0003
						1	1	4533.8895	-0.0033
2	1	2	1	1	1	2	2	4586.1557	-0.0011
						2	1	4586.3182	-0.0004
						3	2	4586.7551	0.0007
						1	0	4586.8429	-0.0007
						1	1	4587.2511	0.0031
2	0	2	1	0	1	2	2	4794.7937	0.0004
						1	0	4794.9276	0.0039
						2	1	4795.1875	-0.0016
						3	2	4795.2597	0.0008
						1	1	4795.9154	0.0019
2	1	1	1	1	0	1	1	5041.9130	0.0016
						2	1	5042.1827	0.0020
						3	2	5042.5649	-0.0001
						2	2	5042.7389	0.0006
						1	0	5043.3080	0.0026
2	2	1	2	1	1	1	2	5694.0095	0.0019
						1	1	5694.2771	0.0002
						3	3	5694.4180	0.0015
						2	2	5694.6682	0.0008
						2	3	5694.8404	-0.0002
2	0	2	2	1	1	2	1	5694.9311	-0.0056
						1	2	5713.3041	0.0106
						3	2	5713.5667	0.0067
						1	1	5713.5667	0.0067
						3	3	5713.7283	0.0029
2	2	1	2	1	2	2	2	5714.0189	0.0012
						2	3	5714.1923	0.0013
						2	1	5714.2920	0.0049
						1	1	6377.4665	-0.0049
						3	3	6378.0384	-0.0005
2	2	0	2	1	2	2	2	6379.0608	0.0001
						1	1	6396.7537	-0.0036
						3	3	6397.3485	0.0005
2	1	2	1	0	1	2	2	6398.4124	0.0014
						2	2	6484.3298	0.0023
						1	0	6484.6614	-0.0016
						2	1	6484.7209	-0.0024
						3	2	6484.9235	-0.0014
						1	1	6485.6499	-0.0028

Table S5. Continuation.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	F'	F''	Obs.	Obs.-Cal.
2	1	1	1	0	1	1	0	7167.8534	-0.0041
						3	2	7168.5448	-0.0027
						2	2	7168.7206	-0.0001
						1	1	7168.8455	-0.0018
						2	1	7169.1146	-0.0021
3	1	3	2	1	2	3	3	6867.5935	-0.0045
						3	2	6868.1954	-0.0001
						2	1	6868.2682	0.0000
						4	3	6868.3401	-0.0001
						2	2	6869.2007	0.0032
3	0	3	2	0	2	3	3	7144.8502	0.0019
						3	2	7145.3155	-0.0031
						2	1	7145.3155	-0.0031
						4	3	7145.3934	-0.0001
						2	2	7146.0415	-0.0085
3	2	2	2	2	1	3	2	7221.6346	0.0001
						2	2	7221.6346	0.0001
						3	3	7222.0594	0.0007
						4	3	7222.0594	0.0007
						2	3	7222.0594	0.0007
3	2	1	2	2	0	2	1	7222.2952	0.0008
						2	2	7297.9002	-0.0024
						3	2	7298.0445	-0.0003
						4	3	7298.4049	-0.0001
						3	3	7298.5042	-0.0063
3	1	2	2	1	1	2	1	7298.6245	-0.0023
						2	2	7550.8821	0.0002
						3	2	7550.9585	0.0020
						4	3	7551.0741	-0.0002
						2	1	7551.1547	0.0035
3	0	3	2	1	1	3	2	4771.3864	0.0001
						4	3	4772.1081	0.0032
						2	1	4772.3930	0.0011
3	0	3	2	1	2	3	3	5455.1828	0.0007
						2	1	5455.5878	0.0014
						4	3	5455.7343	-0.0144
						3	2	5455.7343	-0.0144
						2	2	5456.5165	0.0007
3	2	1	3	1	2	2	2	5461.0810	0.0134
						4	4	5461.0810	0.0134
						3	3	5461.0810	0.0134
3	1	3	2	0	2	4	3	8558.0086	0.0018
						2	1	8558.0086	0.0018
3	2	2	3	1	2	3	3	5365.3516	0.0061
						3	4	5365.3869	-0.0138
						4	4	5365.3869	-0.0138

Table S5. Continuation.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	F'	F''	Obs.	Obs.-Cal.
3	2	2	3	1	3	3	2	6731.4922	-0.0055
						2	2	6731.4922	-0.0055
						3	4	6731.7582	0.0009
						4	4	6731.7582	0.0009
						3	3	6732.4983	-0.0013
						4	3	6732.4983	-0.0013
						2	3	6732.4983	-0.0013
3	2	1	3	1	3	2	2	6827.1129	-0.0031
						4	4	6827.4151	0.0024
						3	3	6828.2572	-0.0031
4	2	2	4	1	3	3	3	5217.5684	-0.0014
						5	5	5217.5684	-0.0014
						4	4	5217.5684	-0.0014
4	1	3	3	2	2	4	3	4677.4858	0.0034
						4	4	4677.4858	0.0034
						5	4	4677.4858	0.0034
						3	2	4677.4858	0.0034
						3	3	4677.4858	0.0034
4	1	3	3	2	1	4	3	4581.7114	-0.0013
						5	4	4581.8371	0.0066
4	2	3	4	1	3	4	4	4936.4642	0.0025
						5	5	4936.6485	0.0087
						3	3	4936.6832	-0.0022
4	2	3	4	1	4	4	3	7208.1638	0.0087
						3	3	7208.3902	-0.0040
						5	5	7208.5557	-0.0010
						4	4	7209.1886	-0.0003
4	0	4	3	1	2	4	3	6663.8379	0.0003
						5	4	6664.5323	0.0030
						3	2	6664.7120	-0.0001
4	2	2	4	1	4	4	3	7489.2684	-0.0056
						3	3	7489.2684	-0.0056
						4	5	7489.4817	-0.0029
						5	5	7489.4817	-0.0029
						4	4	7490.3049	0.0012
						5	4	7490.3049	0.0012
						3	4	7490.3049	0.0012
						4	4	7490.3049	0.0012
5	1	4	5	0	5	4	4	4202.8698	-0.0041
						6	6	4203.0106	0.0017
						5	5	4203.6690	-0.0023
5	2	3	5	1	4	4	4	5050.9388	-0.0043
						6	6	5050.9388	-0.0043
						5	5	5050.9388	-0.0043
5	2	4	5	1	5	4	4	7810.0995	0.0014
						6	6	7810.2131	-0.0028
						5	5	7810.7957	0.0009

Table S5. Continuation.

J'	K₋₁'	K₊₁'	J''	K₋₁''	K₊₁''	F'	F''	Obs.	Obs.-Cal.
5	1	4	4	2	3	6	5	7573.3518	0.0054
						5	4	7573.4716	0.0039
5	1	5	4	2	3	5	4	4182.3736	-0.0069
						6	5	4183.0705	0.0006
5	2	4	5	1	4	5	5	4419.7061	-0.0014
						6	6	4419.9467	0.0072
						4	4	4419.9869	0.0002
5	1	4	4	2	2	5	5	7292.3556	0.0023
						5	4	7292.3556	0.0023
						6	5	7292.4266	0.0030
						4	3	7292.4266	0.0030
6	2	4	6	1	5	7	7	5025.6173	0.0056
						6	6	5025.7164	-0.0025
6	1	6	5	2	3	7	6	5189.4462	0.0052
						5	4	5189.5749	-0.0170
6	1	5	6	0	6	5	5	5265.1572	-0.0026
						7	7	5265.2776	0.0008
						6	6	5265.9709	0.0010
6	2	4	5	3	3	6	5	5325.8356	0.0052
						7	6	5325.8356	0.0052
						5	4	5325.8356	0.0052
						5	5	5325.8356	0.0052
6	1	6	5	2	4	6	5	5819.8114	0.0034
						7	6	5820.4402	0.0070
						5	4	5820.5323	0.0040
7	2	5	7	1	6	8	8	5194.6485	0.0057
						7	7	5194.8235	-0.0023
7	2	6	6	3	3	8	7	6227.9873	-0.0009
						6	5	6228.0374	-0.0025
7	1	6	7	0	7	6	6	6547.6590	0.0014
						8	8	6547.7545	-0.0044
						7	7	6548.4631	0.0009
7	2	6	6	3	4	7	6	6311.7203	-0.0007
						8	7	6312.0516	0.0007
7	1	7	6	2	5	8	7	7319.0498	0.0018
						6	5	7319.1165	-0.0069
8	2	6	8	1	7	7	7	5598.9190	0.0120
						9	9	5598.9190	0.0120
						8	8	5599.1795	-0.0018
8	3	6	8	2	6	9	9	7967.9561	-0.0060
9	2	7	9	1	8	8	8	6268.2780	-0.0087
						10	10	6268.2780	-0.0087
9	3	6	9	2	7	9	9	6268.6380	0.0021
						9	9	7993.3695	0.0052
						10	10	7993.4425	0.0047
						8	8	7993.4425	0.0047

Table S5. Continuation.

J'	K₋₁'	K₊₁'	J''	K₋₁''	K₊₁''	F'	F''	Obs.	Obs.-Cal.
9	3	7	9	2	7	9	9	7166.1897	0.0025
						10	10	7166.4322	-0.0013
10	2	8	10	1	9	9	9	7217.3855	0.0028
						11	11	7217.3855	0.0028
						10	10	7217.7946	-0.0012
10	3	7	10	2	8	10	10	7707.9686	-0.0020
						11	11	7707.9686	-0.0020
						9	9	7707.9686	-0.0020
10	3	7	10	2	8	10	10	7707.9686	-0.0020
						11	11	7707.9686	-0.0020
						9	9	7707.9686	-0.0020
11	3	8	11	2	9	10	10	7620.0436	0.0012
						12	12	7620.0436	0.0012
12	3	9	12	2	10	11	11	7786.6612	-0.0028
						13	13	7786.6612	-0.0028
						12	12	7786.7822	-0.0018