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Supporting information for article:

A co-crystal of L-ascorbic acid with picolinic acid: the role of OH···O, NH···O and CH···O bonds and L-ascorbic acid conformation in structure stabilization

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Table S1 Changes in the bond lengths in the L-Asc·Pic co-crystal structure on cooling from 293(2) K to 100(2) K.

Atoms Connected	Bond length (Å)	
	293(2) K	100(2) K
O5-C5	1.425(2)	1.426(1)
O5-H5	0.82(3)	0.80(2)
O1-C1	1.383(2)	1.383(1)
O1-C4	1.439(2)	1.4422(9)
O4-H4	0.91(3)	0.87(3)
O6-C6	1.420(2)	1.420(1)
O6-H6	0.84(2)	0.82(2)
C2-O3	**1.344(2)**	**1.3457(9)**
C3-O4	**1.334(2)**	**1.331(1)**
O3-H3	0.91(3)	0.91(2)
O2-C1	1.201(2)	1.208(1)
C3-C2	1.343(2)	1.3501(9)
C3-C4	1.498(2)	1.496(1)
C2-C1	1.458(2)	1.456(1)
C5-C4	1.530(2)	1.516(1)
C5-C6	1.513(2)	1.531(1)
C5-H5A	0.99(2)	1.00(2)
C4-H4A	0.97(2)	0.95(2)
C6-H6A	0.97(2)	0.94(2)
C6-H6B	0.97(2)	1.02(2)
C12-O7	**1.248(2)**	**1.256(1)**
C12-O8	**1.240(2)**	**1.246(1)**
N1-C7	1.340(2)	1.3437(9)
N1-C11	1.343(2)	1.342(1)
N1-H1	0.87(2)	0.86(2)
C7-C12	1.518(2)	1.514(1)
C7-C8	1.378(2)	1.384(1)
C11-C10	1.377(2)	1.383(1)
C11-H11	0.94(2)	0.95(2)
C8-C9	1.386(3)	1.388(1)
C8-H8	0.95(2)	1.391(1)

Atoms Connected	Bond length (Å)	
	293(2) K	100(2) K
C10-C9	1.377(2)	0.98(2)
C10-H10	0.96(2)	0.95(2)
C9-H9	0.98(3)	0.95(2)
O5-C5	1.425(2)	1.426(1)
O5-H5	0.82(3)	0.80(2)

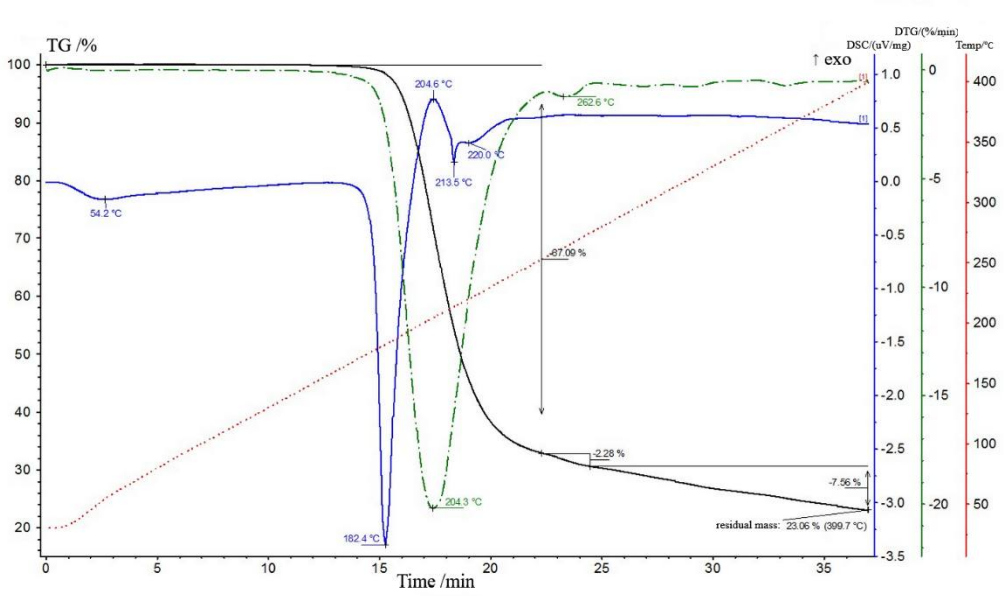

Figure S1 TG/DTG/DSC thermograms of L-Asc·Pic co-crystal powder.

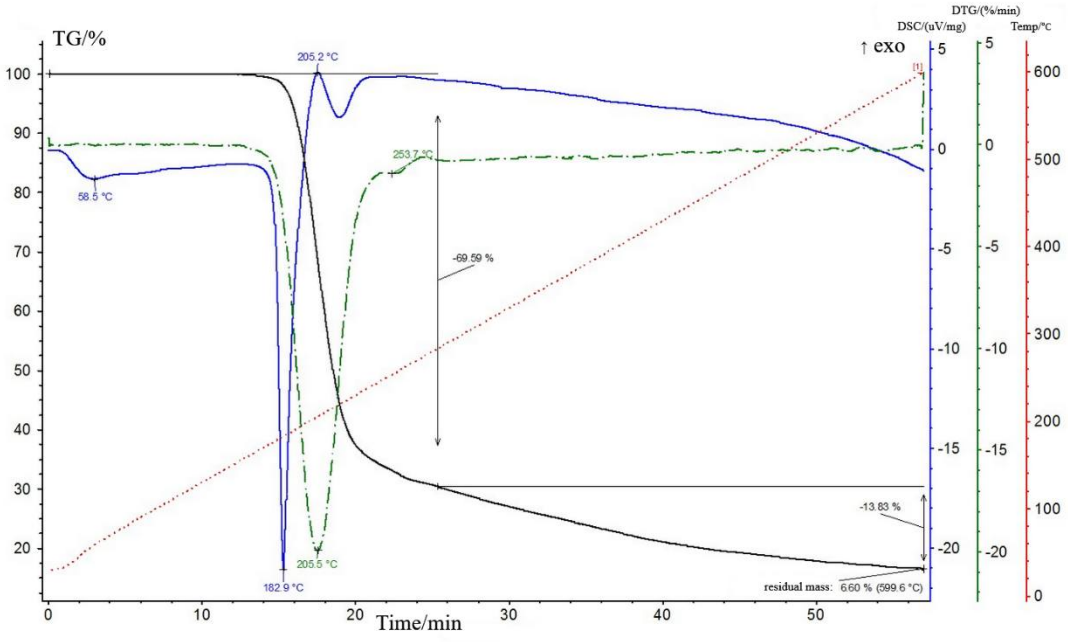

Figure S1 TG/DTG/DSC thermograms of a single crystal of L-Asc·Pic co-crystal.

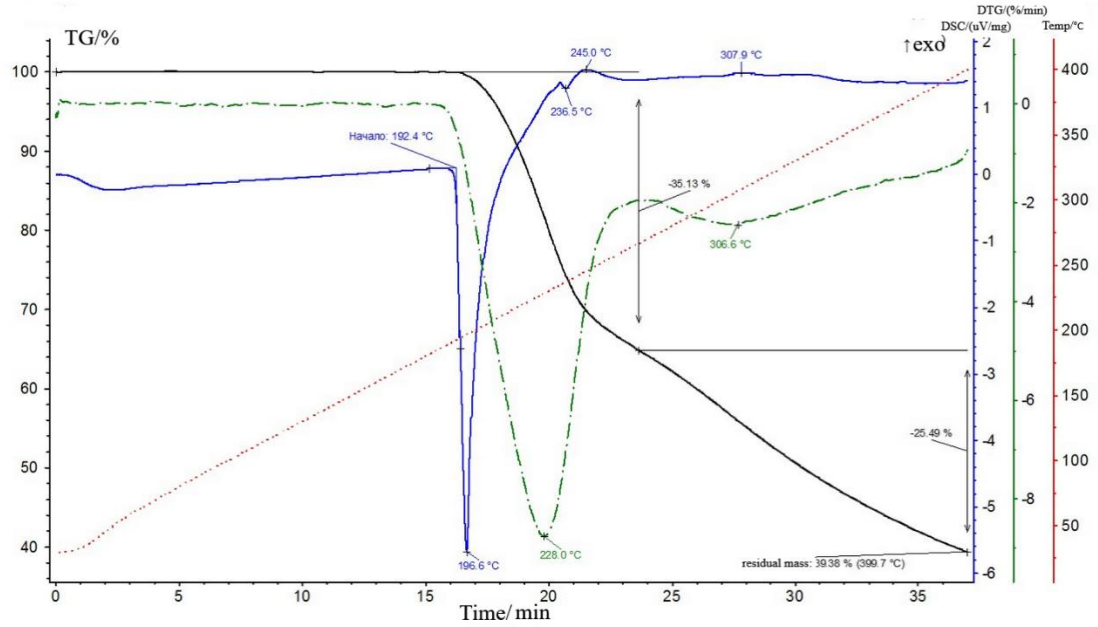

Figure S2 TG/DTG/DSC thermograms of L-ascorbic acid (L-Asc).

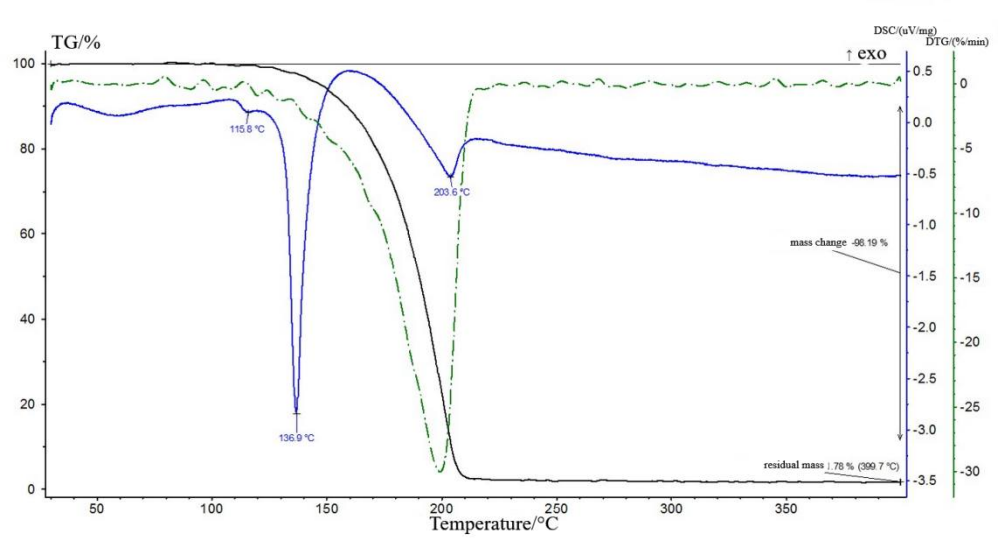

Figure S3 TG/DTG/DSC thermograms of picolinic acid.

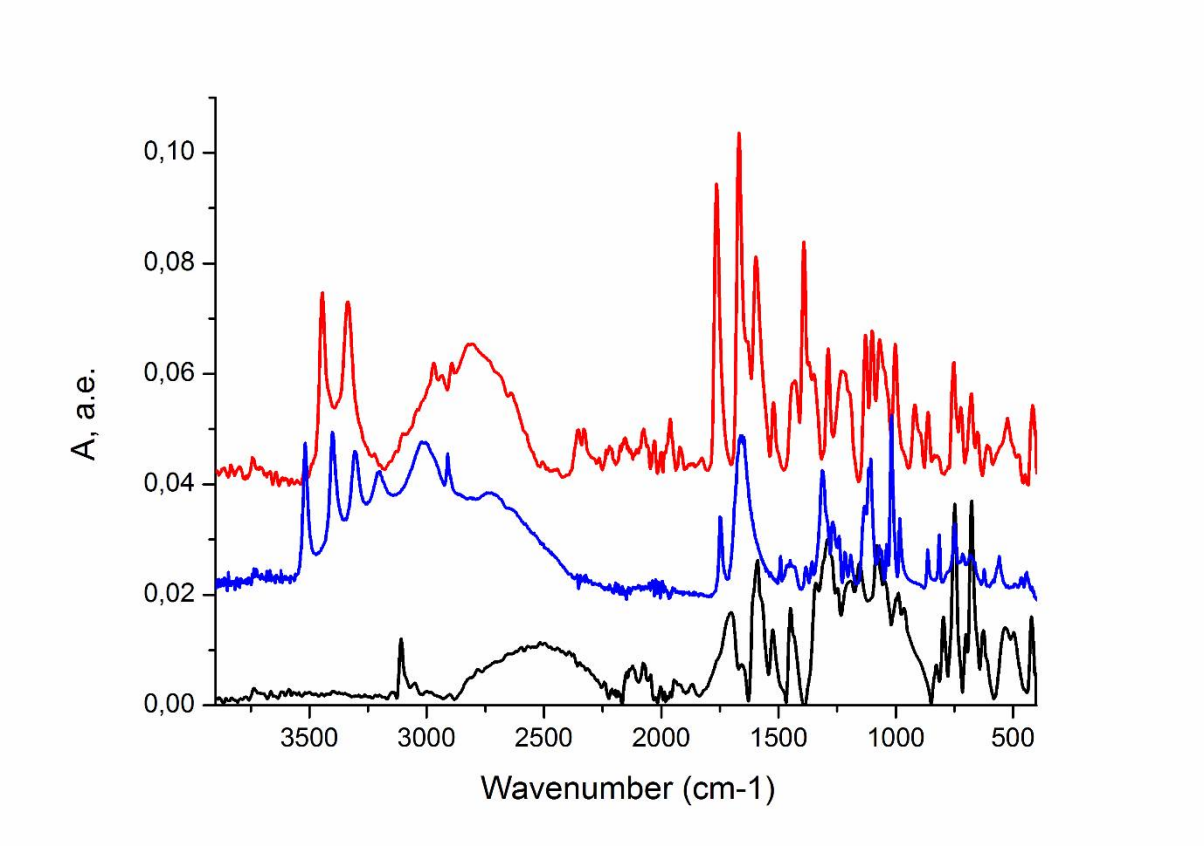

Figure S4 IR spectra of the L-Asc·Pic co-crystal (red), L-ascorbic acid (blue) and picolinic acid (black).

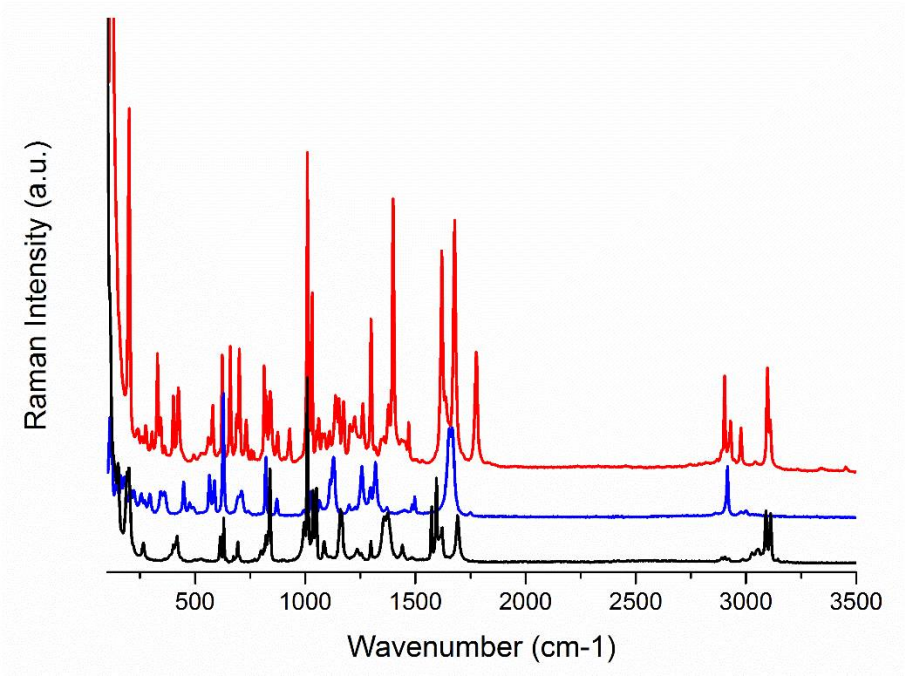

Figure S5 Raman spectra of the L-Asc·Pic co-crystal (red),L-ascorbic acid (blue) and picolinic acid (black).

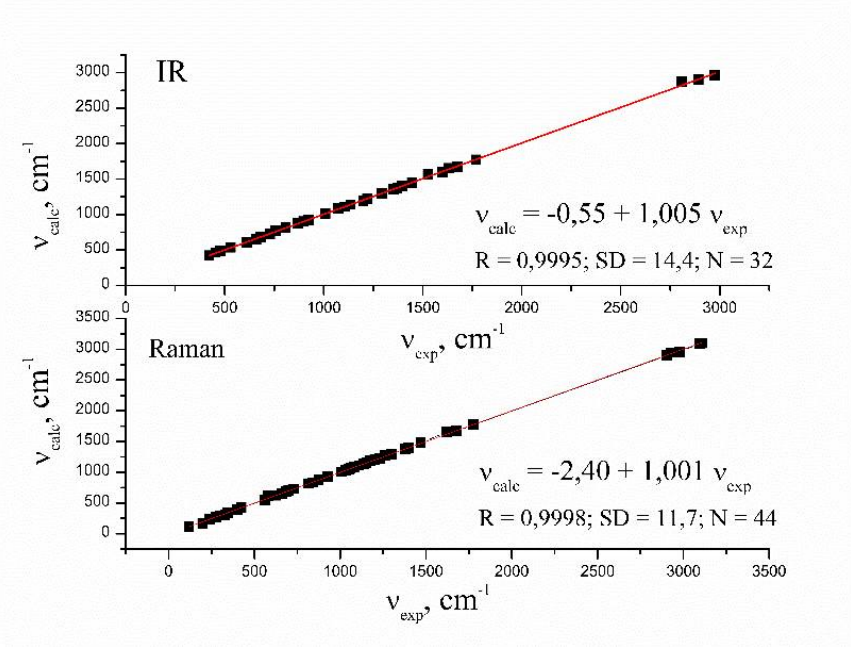

Figure S2 Correlation between the calculated vibrational frequencies and the IR and Raman experimental data for L-Asc·Pic co-crystal. R is the correlation coefficient. SD is the standard deviation, and N is the number of points.

Table S2 Observed and calculated (B3LYP) vibrational frequencies and normal mode assignment of the L-Asc·Pic.

Mode Number	Experimental		B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν Scaled	I ^{IR}	I ^{Raman}	
1			3636,48	39,3976	43,3507	ν C(6)O-H*
2			3620,16	37,5922	39,5516	ν C(5)O-H*
3	3450,9		3359,04	1982,854	971,4486	ν C(5,6)O-H*
4	3340,5		3217,92	797,5125	628,5335	ν C(5,6)O-H* N(1)-H*
5			3195,84	863,8254	108,1797	ν C(5,6)O-H* N(1)-H*
6		3110,3	3099,84	0,2053	208,1926	ν_s C(8,9,10,11)-H
7		3097,3	3093,12	8,1346	43,7508	ν C(8)-H
8			3086,4	0,5715	77,2815	ν_{as} C(8,9,10,11)-H
9			3064,32	1,2563	95,0193	ν_{as}C(8,9,10,11)-H
10	2976,4	2977,1	2958,72	32,9415	88,9536	νC(5,6)-H
11		2930,3	2945,28	10,9456	61,1292	νC(5,6)-H
12	2892,0	2902,7	2898,24	22,8379	135,705	νC(4)-H
13	2807,5		2873,28	34,2102	93,0926	νC(6)-H
14	1769,7	1776,5	1772,16	539,4055	48,7866	νC(1)=O(2), Ring stretch (ASC)
15	1677	1678,3	1673,28	394,0898	104,6555	νO(7)=C(12)=O(8),

Mode Number	Experimental		B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{Scaled}	I^{IR}	I^{Raman}	
						C(2)=C(3)
16	1633,3 плечо	1620,5	1653,12	322,6977	156,8875	νC(2)=C(3), C(1)=O(2), O(7)=C(12)=O(8)
17	1601		1597,44	58,5421	35,8372	νC(7)-C(12) ; Ring stretch(PIC)
18	1527		1562,88	100,6795	65,6637	νO(7)=C(12)=O(8) ; Ring stretch(PIC)
19		1469,7	1481,28	90,6013	0,3635	βC(8,9,10,11)-H ; Ring stretch(PIC)
20	1446,8		1443,84	1,5712	6,5204	βC(6)-HH
21			1427,52	8,2237	2,2531	β C(8,9,10,11)-H ; Ring stretch(PIC)
22	1397,3	1398,9	1399,68	26,4178	5,4025	νC(4)-C(3)-O(4), C(2)-O(3); β O(3,4)-H, C(2)=C(3)
23	1374	1377,9	1373,76	36,214	2,3658	νC(5)-C(6); β C(5,6)-H, O(5,6)-H
24			1365,12	56,4982	11,6855	β CH, β OH (ASC)
25	1353,2		1357,44	112,8552	13,1919	βCH,βOH, Ring stretch(ASC)
26			1332,48	27,5948	3,9906	β CH, β OH (ASC)
27			1320	167,6053	225,8588	βCH, β NH ; ν O(7)=C(12)=O(8), C(7)-C(12) Ring stretch(PIC)
28		1298,3	1296	18,7487	17,8479	βCH, β NH, βC(7)-C(12) ; Ring stretch(PIC)
29	1294,2		1292,16	6,7624	18,1202	β CH, β OH (ASC)
30			1283,52	14,9094	2,2845	βCH,βOH, Ring stretch(ASC)
31		1261,9	1277,76	221,577	131,8355	βCH,βNH;νO(7)=C(12)=O(8) , C(7)-C(12) ; Ring stretch(PIC)
32			1240,32	215,3999	19,4258	βCH,βOH, Ring stretch(ASC)
33	1221,3	1228,4	1225,92	9,5023	7,1194	β CH, β OH (ASC)
34		1202,3	1211,52	10,0066	3,1369	β CH, β OH (ASC)
35	1199,9	1173,9	1187,52	25,7584	7,034	βCH,βNH ; Ring stretch (PIC)
36		1153,1	1154,88	48,212	9,9333	βCH,βOH, Ring stretch(ASC)
37			1144,32	56,6637	3,3927	β CH, β OH (ASC)
38	1135,0	1137,7	1137,6	6,223	2,0604	βCH ; Ring stretch (PIC)
39	1108	1110,0	1109,76	25,8408	87,5842	βCH,βNH;

Mode Number	Experimental		B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{Scaled}	I^{IR}	I^{Raman}	
						νO(7)=C(12)=O(8), C(7)-C(12) ; Ring stretch(PIC)
40	1075,3	1080,0	1083,84	93,8819	4,5089	βCH, βOH, Ring stretch(ASC)
41		1059,9	1062,72	85,5659	4,1777	βCH,βOH, Ring stretch(ASC)
42		1050,9	1053,12	32,6776	1,5244	βCH, βNH ; Ring stretch (PIC)
43			1040,64	95,4891	1,9408	βCH, βOH, Ring stretch(ASC)
44		1030,8	1032	74,9381	5,8032	βCH,βOH, Ring stretch(ASC)
45			1014,72	9,3969	1,5341	Ring stretch (PIC)
46	1007,6	1009,3	1007,04	0,6555	3,33078	βCH,βOH; ν C(1)-O(1)- C(4) ; Ring stretch(ASC)
47			997,44	0,3377	0,087	γ C(8)-C(9)-C(10)
48			983,04	6,9895	70,1901	Ring breathing (PIC)
49			971,52	217,2163	2,3247	γ ASC
50			962,88	12,4636	0,5026	γC-H, N-H + Ring distortion(PIC)
51	924,9	928,5	925,44	24,3507	0,5223	γC-H, N-H + Ring distortion(PIC)
52	898,6		902,4	52,0273	2,8316	γASC
53	868,1	874,3	880,32	1,9144	0,2079	γC-H, N-H ; Ring distortion(PIC)
54		840,6	832,32	48,3086	3,2082	γASC
55	808	825,5 813,8	816,96	28,9357	2,0633	β O(7)=C(12)=O(8), C(7)-C(12);γ C(2)O(3)-H, C(3)O(4)-H
56			795,84	52,989	5,7106	γO(7)=C(12)=O(8), C(7)-C(12);γC(2)O(3)-H,C(3)O(4)-H
57			785,28	30,5128	3,9949	δC(1)-O(1)-C(4),Ring distortion(PIC)
58	763		773,76	78,977	8,3775	γPIC + ASC
59			736,32	63,3134	0,4259	ω C-H, N-H
60	726	729,9	727,68	13,2011	2,0248	ω C(1)-O(1)-C(4)
61		700,1	701,76	9,2691	3,2395	Ring breathing (ASC)
62	683,7	688,1	681,6	15,7657	2,2336	β C(2)O-H ; Ring stretch

Mode Number	Experimental		B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{Scaled}	I^{IR}	I^{Raman}	
						(PIC)
63			669,12	16,8275	10,3889	β C(2)O-H ; Ring stretch (ASC)
64	659,1	659,3	652,8	37,606	0,5018	β C(2)O-H,ωO=C=O
65			635,52	11,0407	5,9103	β C(2)O-H ; Ring stretch (ASC)
66		623,0	623,04	69,9928	4,774	β C(2)O-H
67	613,6	579,2	611,52	6,2056	6,1845	β C(2)O-H ; Ring stretch (PIC)
68		560,9	552	1,6672	10,3384	Ring distortion(ASC)
69	529,3		537,6	20,1928	1,1721	βO(7)- H(4), O(8)-H(3) ; Ring distortion(ASC)
70			509,76	12,6004	0,914	βC(7)-C(12)
71	478,5		489,6	175,9066	5,5977	ρC(5,6)-OH,
72	453,6		463,68	70,6081	1,464	β C(5)-C(6)
73	421,9	423,1	422,4	2,6177	2,5651	Ring distortion(PIC)
74		401,7	390,72	0,9302	0,5128	Ring distortion(PIC)
75			389,76	38,6461	1,4483	τ C(5)-C(6), C(5,6)-OH
76			381,12	73,504	24,6727	δC(2,3)-OH ;βC(7)-C(12); Ring stretch (PIC)
77			376,32	1,7843	1,8348	δC(2,3)-OH ;βC(7)-C(12); Ring stretch (ASC)
78		343,3	337,92	4,4207	8,7732	ω O(3)-C(2)=C(3)-O(4)
79		329,3	310,08	3,6594	3,0943	δC(4)-C(5)-C(6) ; Ring stretch (ASC)
80		302,4	293,76	5,7178	6,9876	δ C(2,3)-OH
81		275,4	273,6	3,3339	0,8345	β O(1)--HOC(5)
82		239,2	237,12	5,323	1,6257	δ C(3)-C(4)-C(5)
83			215,04	6,9146	0,4823	βC(7)-C(12)
84		198,8	162,24	0,8545	1,8523	ω C(7)-C(12)
85			151,68	8,3248	3,928	Ring distortion(PIC) (ASC)
86			136,32	2,2031	2,0877	Ring distortion(ASC)
87			118,08	1,8637	5,5248	δ O(7)=C(12)=O(8)
88		118,5	115,2	16,004	1,3961	τ C(5)-C(6) ; ω C(7)-C(12)
89			91,2	0,3923	1,4124	τ C(7)-C(12)
90			75,84	2,9731	1,5171	τ C(4)-C(5)

Mode Number	Experimental		B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{Scaled}	I^{IR}	I^{Raman}	
91			67,2	1,0946	2,4581	δ C(4)-C(5)
92			52,8	1,0083	0,1556	τ C(4)-C(5)
93			49,92	1,5634	1,2922	
94			35,52	1,0993	1,7526	
95			19,2	0,4383	6,0928	
96			10,56	3,5677	1,713	

*- assignment of bands according to literature data

ν, Stretching; ν_s, sym, stretching; ν_{as}, asym,stretching; β- in-plane stretching; γ- out-of-plane stretching; ω-wagging; τ - twisting; δ - scissoring; ρ -rocking;

Table S3 The L-ascorbic acid amount in the composition of the L-Asc·Pic samples according to the results of titrimetric analysis

No. samples	Composition L-Asc. % (mass.)			
	0 months	6 months	12 months	24 months
I	60.3	60.5	59.8	60.1
II	59.9	58.6	59.8	59.8
III	61.4	60.7	61.0	60.7

Table S4 The charge distribution on atoms of the L-Asc·Pic co-crystal calculated by Mulliken populations, Voronoi and Hirshfeld charge analysis (ADF) bp86/TZ2P+ level of theory.

Atom	Mulliken charge, e	Voronoi charges, e	Hirshfeld charge, e
O5	-0,5858	-0,2138	-0,214
O1	-0,5571	-0,1108	-0,119
O4	-0,541	-0,1773	-0,189
O6	-0,6139	-0,2288	-0,238
O3	-0,5259	-0,183	-0,177
O2	-0,6037	-0,2717	-0,282
C3	0,3655	0,0535	0,005
C2	0,2025	0,0248	-0,023
C1	0,6856	0,1525	0,175
C5	0,571	0,037	0,001
C4	0,4599	0,015	-0,015
C6	0,7554	-0,0183	-0,035
H5A	-0,1958	0,0412	0,072
H6	0,331	0,1442	0,156
H4	-0,1957	0,0506	0,091
H6A	-0,2759	0,0499	0,067
H6B	-0,2486	0,0452	0,066
H3	0,3028	0,1008	0,159
H5	0,3074	0,1463	0,172
H4	0,3206	0,0994	0,162
O8	-0,7212	-0,2538	-0,303
O7	-0,7666	-0,2706	-0,334

N1	0,2385	0,0146	-0,004
C7	0,0998	0,1054	0,079
C12	0,8553	0,1395	0,148
C11	0,4072	0,0693	0,03
C8	0,3012	-0,0006	-0,036
C10	0,336	-0,0144	-0,054
C9	0,4169	0,0147	-0,015
H11	-0,2389	0,079	0,109
H8	-0,2241	0,0698	0,115
H1	-0,0693	0,1468	0,226
H10	-0,2959	0,0701	0,101
H9	-0,2971	0,0732	0,103