SUPPORTING INFORMATION

Theoretical benchmark

A set of 12 candidate structures bellow an energy window of 1400 cm^{-1} were identified by subsequent geometry optimizations of the MMFFs predicted structures. The density functional theory B3LYP method with the Becke's three-parameter exchange functional and the Lee-Yang-Parr correlation functional (Becke, 1988; Lee et al. 1988) was used. Also, Grimme´s D3 dispersion correction factors were included (Grimme et al. 2010).

Table S1. Theoretical spectroscopic parameters for the low energy L-DOPA conformers.

Parameter [a]	GIa	GIIa	GIb	GIIb	AIb	AIa	AIIb	AIIIb
A /MHz [b]	1195	1323	1203	1343	1743	1750	1800	1793
B /MHz	433	395	428	389	306	305	303	299
C /MHz	373	355	369	351	279	280	277	277
$\|\mu_a\|$/D [c]	0.3	2.6	2.6	2.1	3.6	5.7	5.7	5.6
$\|\mu_b\|$/D	3.0	2.1	6.4	6.5	0.2	4.1	0.4	0.1
$\|\mu_c\|$/D	0.3	0.5	1.3	0.0	2.1	1.9	2.7	2.5
ΔE / cm^{-1} [d]	0	276	495	582	508	537	546	635
Parameter [a]	AIVb	AIVa	AIIa	AIIIa	AVb	AVIb	AVIIb	
A /MHz [b]	1720	1730	1804	1808	1790	1410	1427	
B /MHz	301	300	302	295	303	387	356	
C /MHz	279	282	277	278	276	330	300	
$\|\mu_a\|$/D [c]	3.3	5.6	4.0	3.9	0.4	2.8	1.6	
$\|\mu_b\|$/D	0.6	4.3	3.3	3.6	0.2	2.7	3.0	
$\|\mu_c\|$/D	1.7	1.6	1.3	0.8	0.4	1.6	0.1	
ΔE / cm^{-1} [d]	652	661	657	795	1044	1347	1364	

[a] Calculated at the B3LYP/aug-cc-pVTZ level of the theory with Grimme D3 dispersion. [b] *A*, *B*, and *C* are the rotational constants; [c] $|\mu_a|$, $|\mu_b|$ and $|\mu_c|$ are the absolute values of the electric dipole moment components along the inertial axis *a*, *b*, *c*; [d] ΔE represents the relative energy, with respect to the global minimum (the zero-point energy corrections are taken into account).

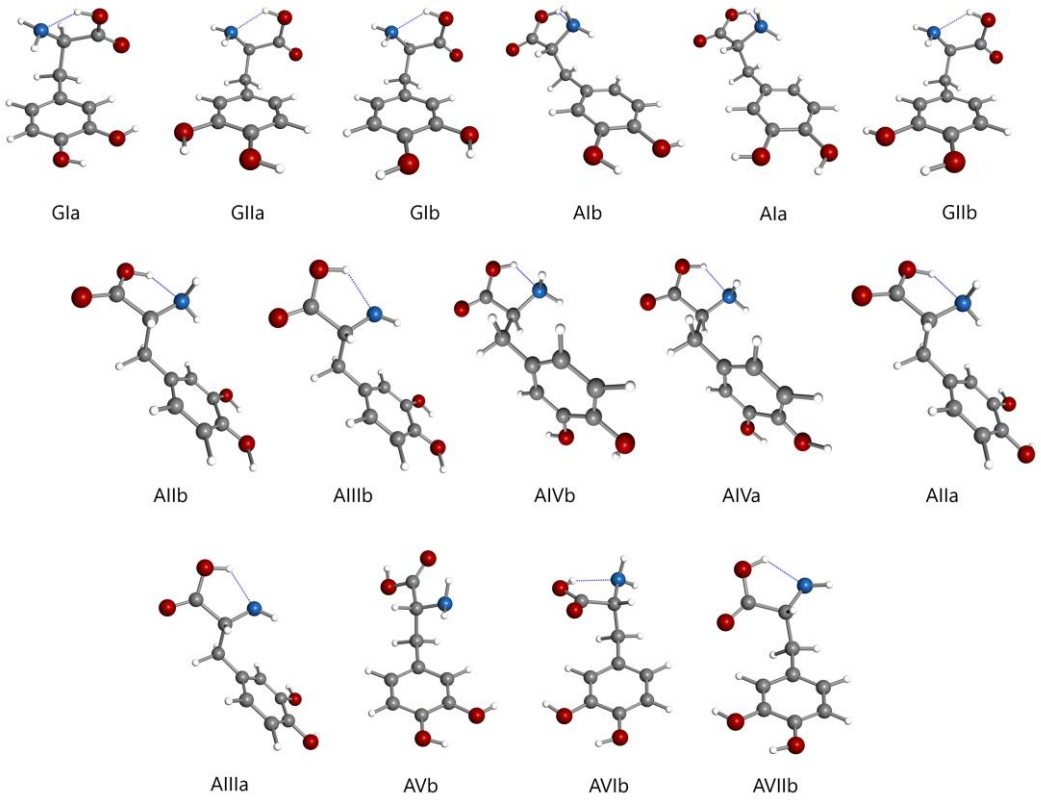

Figure S1. Chemical structure of the lowest-energy conformers of L-DOPA (< 1400 cm^{-1}) predicted by theoretical calculations.

Measured transitions for L-DOPA

In Tables S2–S5 a list containing all measured lines for GIa, GIIa, AIb and AIa L-DOPA, is provided.

Table S2. List of the measured rotational transitions (frequencies and residuals, in MHz) of GIa *L-DOPA.*

J'	K_a'	K_c'	J''	K_a''	K_c''	υ_{obs} (MHz)[a]	υ_{calc} (MHz)[b]	$\upsilon_{obs} - \upsilon_{calc}$ (MHz)[c]	weight
6	2	4	6	1	5	1981.217	1981.220	-0.003	
5	2	3	5	1	4	2034.990	2034.984	0.006	
3	1	3	2	0	2	3043.679	3043.683	-0.004	
5	0	5	4	1	4	3476.403	3476.372	0.031	
7	3	4	7	2	5	3664.242	3664.258	-0.016	
4	1	4	3	0	3	3741.790	3741.821	-0.031	
6	3	3	6	2	4	3768.218	3768.219	-0.001	
5	3	2	5	2	3	3842.695	3842.655	0.040	
4	3	1	4	2	2	3889.402	3889.373	0.029	
2	2	1	1	1	0	3954.316	3954.292	0.024	
6	3	4	6	2	5	3993.164	3993.147	0.017	
9	2	7	8	3	6	4080.072	4080.079	-0.008	

7	1	6	6	2	5	4108.932	4108.929	0.003	
8	3	6	8	2	7	4114.892	4114.911	-0.019	
9	3	7	9	2	8	4212.022	4212.038	-0.017	
5	1	5	4	0	4	4422.569	4422.583	-0.014	
11	3	9	11	2	10	4494.511	4494.548	-0.037	
3	2	2	2	1	1	4706.349	4706.392	-0.043	
6	1	6	5	0	5	5094.968	5094.992	-0.023	
11	4	7	11	3	8	5182.565	5182.593	-0.028	
7	0	7	6	1	6	5196.266	5196.265	0.001	
10	4	6	10	3	7	5292.090	5292.120	-0.030	
7	4	3	7	3	4	5457.506	5457.492	0.013	
6	4	2	6	3	3	5477.627	5477.634	-0.007	
9	4	6	9	3	7	5480.170	5480.231	-0.061	
8	4	5	8	3	6	5480.505	5480.488	0.017	
7	4	4	7	3	5	5483.948	5483.941	0.008	
10	4	7	10	3	8	5486.092	5486.119	-0.027	
6	4	3	6	3	4	5488.393	5488.413	-0.021	
7	1	7	6	0	6	5768.158	5768.188	-0.030	
8	0	8	7	1	7	6030.426	6030.432	-0.006	
9	1	8	8	2	7	6107.632	6107.635	-0.003	
5	2	4	4	1	3	6117.528	6117.527	0.002	
10	1	10	9	0	9	7849.698	7849.729	-0.031	
5	3	3	4	2	2	7967.294	7967.281	0.013	
5	3	2	4	2	3	8024.162	8024.153	0.009	
11	0	11	10	1	10	8430.105	8430.104	0.001	
11	1	11	10	0	10	8568.445	8568.446	-0.001	
6	3	4	5	2	3	8736.614	8736.611	0.003	
6	3	3	5	2	4	8869.262	8869.279	-0.017	
12	0	12	11	1	11	9205.201	9205.193	0.008	
12	1	12	11	0	11	9296.898	9296.908	-0.010	
7	3	5	6	2	4	9474.335	9474.351	-0.015	
5	4	2	4	3	1	9570.488	9570.424	0.064	
5	4	1	4	3	2	9571.444	9571.383	0.061	
7	3	4	6	2	5	9737.330	9737.345	-0.015	
13	0	13	12	1	12	9972.817	9972.810	0.007	
13	1	13	12	0	12	10032.750	10032.740	0.010	
6	4	3	5	3	2	10382.428	10382.369	0.059	
8	3	5	7	2	6	10638.501	10638.489	0.012	
14	0	14	13	1	13	10735.188	10735.176	0.012	
5	5	0	4	4	1	11142.063	11142.066	-0.003	
7	4	4	6	3	3	11190.091	11190.072	0.018	
7	4	3	6	3	4	11201.729	11201.690	0.040	
9	3	6	8	2	7	11584.923	11584.968	-0.045	
8	4	5	7	3	4	11989.969	11990.007	-0.038	
4	4	1	3	3	0	8756.546	8756.552	-0.006	0.50
4	4	0	3	3	1	8756.546	8756.552	-0.006	0.50

Note. Upper and lower state quantum numbers are indicated by' and", respectively. [a] Observed frequency. [b] Calculated frequency. [c] Observed minus calculated frequency.

Table S3. List of the measured rotational transitions (frequencies and residuals, in MHz) of GIIa *L-DOPA.*

J'	K_a'	K_c'	J''	K_a''	K_c''	υ_{obs} (MHz) [a]	υ_{calc} (MHz) [b]	$\upsilon_{obs} - \upsilon_{calc}$ (MHz) [c]
5	1	4	4	1	3	3866.784	3866.764	0.020
6	1	6	5	1	5	4402.949	4402.910	0.039
6	2	5	5	2	4	4523.947	4523.925	0.024
6	2	4	5	2	3	4565.138	4565.132	0.004
6	1	5	5	1	4	4636.399	4636.412	-0.013
3	2	2	2	1	1	5046.165	5046.163	0.002
7	1	7	6	1	6	5132.830	5132.810	0.021
7	2	5	6	2	4	5339.232	5339.220	0.012
7	1	6	6	1	5	5403.804	5403.820	-0.016
8	1	8	7	1	7	5861.184	5861.192	-0.008
8	0	8	7	0	7	5945.755	5945.805	-0.050
8	2	7	7	2	6	6024.405	6024.395	0.009
8	3	6	7	3	5	6050.902	6050.903	-0.001
8	3	5	7	3	4	6056.741	6056.743	-0.002
8	1	7	7	1	6	6168.421	6168.435	-0.014

Note. Upper and lower state quantum numbers are indicated by' and", respectively. [a] Observed frequency. [b] Calculated frequency. [c] Observed minus calculated frequency.

Table S4. List of the measured rotational transitions (frequencies and residuals, in MHz) of AIb *L-DOPA.*

J'	K_a'	K_c'	J''	K_a''	K_c''	υ_{obs} (MHz) [a]	υ_{calc} (MHz) [b]	$\upsilon_{obs} - \upsilon_{calc}$ (MHz) [c]
6	1	6	5	1	5	3440.950	3440.936	0.014
7	1	7	6	1	6	4013.018	4013.016	0.002
7	0	7	6	0	6	4092.584	4092.639	-0.055
7	2	5	6	2	4	4133.744	4133.770	-0.026
7	1	6	6	1	5	4206.023	4206.001	0.022
8	1	8	7	1	7	4584.512	4584.496	0.017
8	2	7	7	2	6	4697.721	4697.699	0.022
8	2	6	7	2	5	4730.569	4730.596	-0.027
8	1	7	7	1	6	4804.654	4804.661	-0.007
9	1	9	8	1	8	5155.334	5155.320	0.014
9	0	9	8	0	8	5243.947	5243.954	-0.007
9	2	8	8	2	7	5283.224	5283.217	0.007
9	1	8	8	1	7	5402.369	5402.365	0.004
10	1	10	9	1	9	5725.457	5725.449	0.008
10	0	10	9	0	9	5815.356	5815.376	-0.020
10	2	8	9	2	7	5930.942	5930.947	-0.005
10	1	9	9	1	8	5998.977	5998.948	0.029

Note. Upper and lower state quantum numbers are indicated by' and", respectively. [a] Observed frequency. [b] Calculated frequency. [c] Observed minus calculated frequency.

Table S5. List of the measured rotational transitions (frequencies and residuals, in MHz) of AIa *L-DOPA.*

J'	K_a'	K_c'	J''	K_a''	K_c''	υ_{obs} (MHz) [a]	υ_{calc} (MHz) [b]	$\upsilon_{obs} - \upsilon_{calc}$ (MHz) [c]	weight
3	3	1	2	2	0	9045.121	9045.197	-0.076	0.50
3	3	0	2	2	1	9045.121	9045.197	-0.076	0.50
16	1	16	15	1	15	9145.543	9145.578	-0.035	
15	1	15	14	1	14	8578.190	8578.141	0.049	
4	3	2	3	2	1	9631.300	9631.255	0.045	
4	3	1	3	2	2	9632.932	9632.887	0.044	
5	3	3	4	2	2	10216.261	10216.238	0.023	
5	3	2	4	2	3	10221.172	10221.149	0.022	
6	3	4	5	2	3	10799.043	10799.092	-0.049	
6	3	3	5	2	4	10810.579	10810.580	-0.011	
11	0	11	10	0	10	6388.454	6388.445	0.009	
11	1	11	10	1	10	6302.151	6302.174	-0.023	
9	1	8	8	1	7	5384.632	5384.627	0.005	
9	2	7	8	2	6	5313.780	5313.795	-0.015	
8	1	8	7	1	7	4588.695	4588.681	0.014	
7	1	6	6	1	5	4191.373	4191.365	0.008	
7	1	7	6	1	6	4016.376	4016.389	-0.013	

Note. Upper and lower state quantum numbers are indicated by' and", respectively. [a] Observed frequency. [b] Calculated frequency. [c] Observed minus calculated frequency.

Table S6. List of the measured hyperfine components (frequencies and residuals, in MHz) of GIa *L-DOPA using the LA-MB-FTMW technique.*

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	υ_{obs} (MHz) [a]	υ_{calc} (MHz) [b]	$\upsilon_{obs} - \upsilon_{calc}$ (MHz) [c]
6	1	6	7	5	0	5	6	5094.947	5094.952	-0.005
6	1	6	6	5	0	5	5	5095.059	5095.059	0.000
3	2	2	3	2	1	1	2	4706.437	4706.442	-0.005
3	2	2	4	2	1	1	3	4706.384	4706.383	0.001
5	1	5	6	4	0	4	5	4422.539	4422.537	0.002
5	1	5	5	4	0	4	4	4422.662	4422.658	0.004
4	1	4	5	3	0	3	4	3741.780	3741.782	-0.002
4	1	4	4	3	0	3	3	3741.913	3741.909	0.004
2	2	1	3	1	1	0	2	3954.291	3954.291	-0.000
2	2	1	2	1	1	0	2	3954.071	3954.069	0.002
2	2	1	1	1	1	0	0	3954.022	3954.021	0.001

Note. Upper and lower state quantum numbers are indicated by' and", respectively. [a] Observed frequency. [b] Calculated frequency. [c] Observed minus calculated frequency.

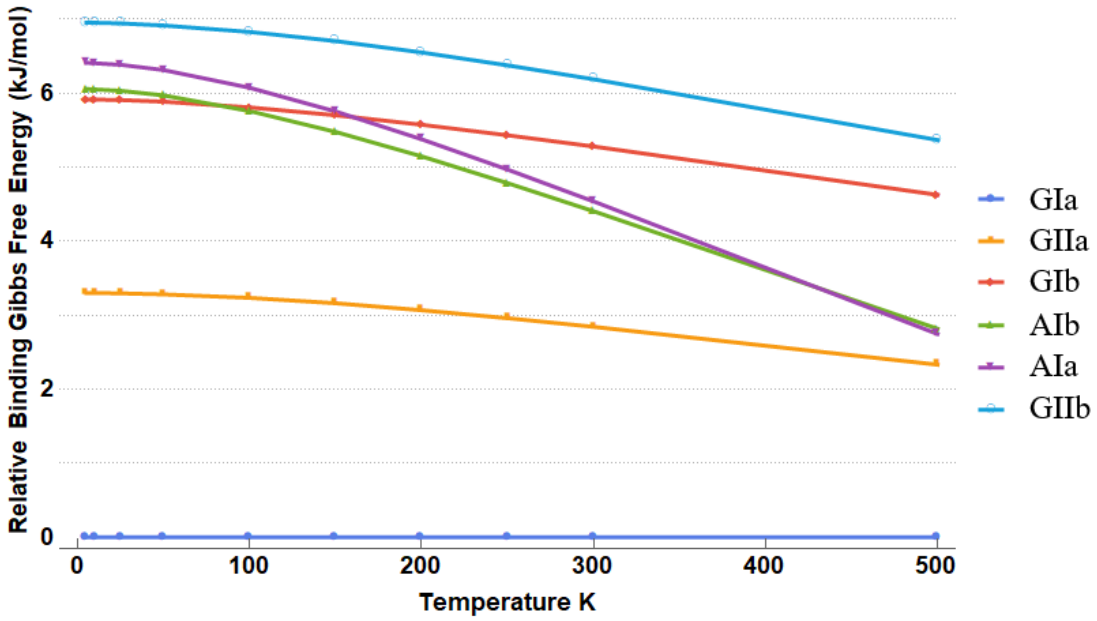

Figure S2. Diagram including the free energies computed at different temperatures. As can be seen conformers AIb and AIa suffer from a significant stabilization, which may be attributed to the contribution of the corresponding entropic terms.

Tentative fits of conformers GIb and GIIb

Rotamer V (conformer GIb)

EXP.FREQ. - CALC.FREQ. - DIFF. - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. - DIFF. - WT.

1:	4 1 4 3 0 3	3728.67935	3728.63205	0.04731	0.05000	0.00000
2:	5 1 5 4 0 4	4406.26179	4406.35698	-0.09519	0.05000	0.00000
3:	6 0 6 5 1 5	4268.85021	4268.85082	-0.00061	0.05000	0.00000
4:	6 1 6 5 0 5	5074.90766	5074.85925	0.04841	0.05000	0.00000

NORMALIZED DIAGONAL:

1 1.00000E+000 2 3.47915E-001 3 6.67032E-001

MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00

NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION

1	10000	A /	1196.757(115)	0.000
2	20000	B /	430.2260(166)	0.0000
3	30000	C /	372.8900(70)	-0.0000

MICROWAVE AVG = -0.000018 MHz, IR AVG = 0.00000

MICROWAVE RMS = 0.058401 MHz, IR RMS = 0.00000

END OF ITERATION 1 OLD, NEW RMS ERROR= 1.16802

Rotamer VI (conformer GIIb)

	EXP.FREQ.	- CALC.FREQ.	- DIFF.	- EXP.ERR.	- EST.ERR.	- AVG. CALC.FREQ.	- DIFF.	- WT.
1: 6 4 3 5 3 2		11271.46022	11271.49202	-0.03181	0.05000	0.00000		
2: 6 4 2 5 3 3		11272.05932	11272.14690	-0.08758	0.05000	0.00000		
3: 7 4 4 6 3 3		12009.83019	12009.80068	0.02951	0.05000	0.00000		
4: 7 4 3 6 3 4		12011.86178	12011.77271	0.08907	0.05000	0.00000		
5: 10 1 10 9 0 9		7528.21711	7528.21358	0.00353	0.05000	0.00000		
6: 14 0 14 13 1 13		9878.36053	9878.37118	-0.01065	0.05000	0.00000		

NORMALIZED DIAGONAL:

1 1.00000E+000 2 8.98270E-001 3 9.76685E-001

MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00

NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION

1	10000	A /	1346.0583(40)	-0.0000
2	20000	B /	389.5842(45)	0.0000
3	30000	C /	350.01893(156)	-0.00000

MICROWAVE AVG = -0.001320 MHz, IR AVG = 0.00000

MICROWAVE RMS = 0.054178 MHz, IR RMS = 0.00000

END OF ITERATION 1 OLD, NEW RMS ERROR= 1.08356 1.08356