Supplementary Materials

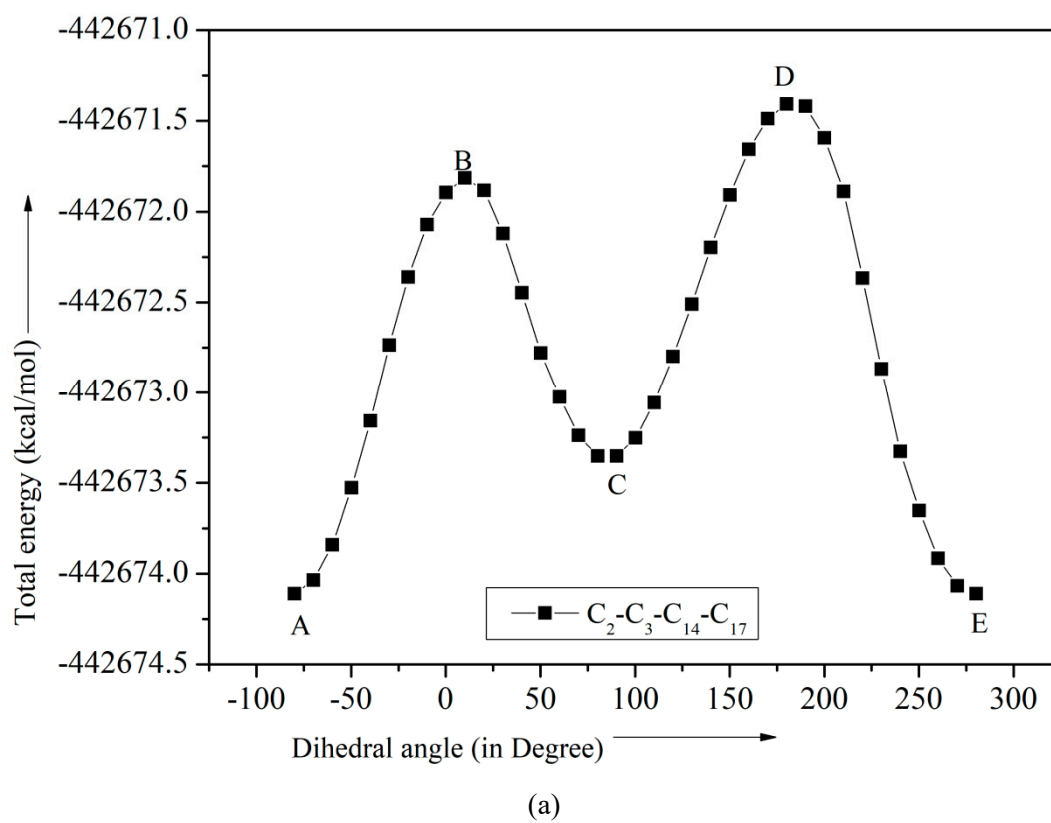## SM-Figures:

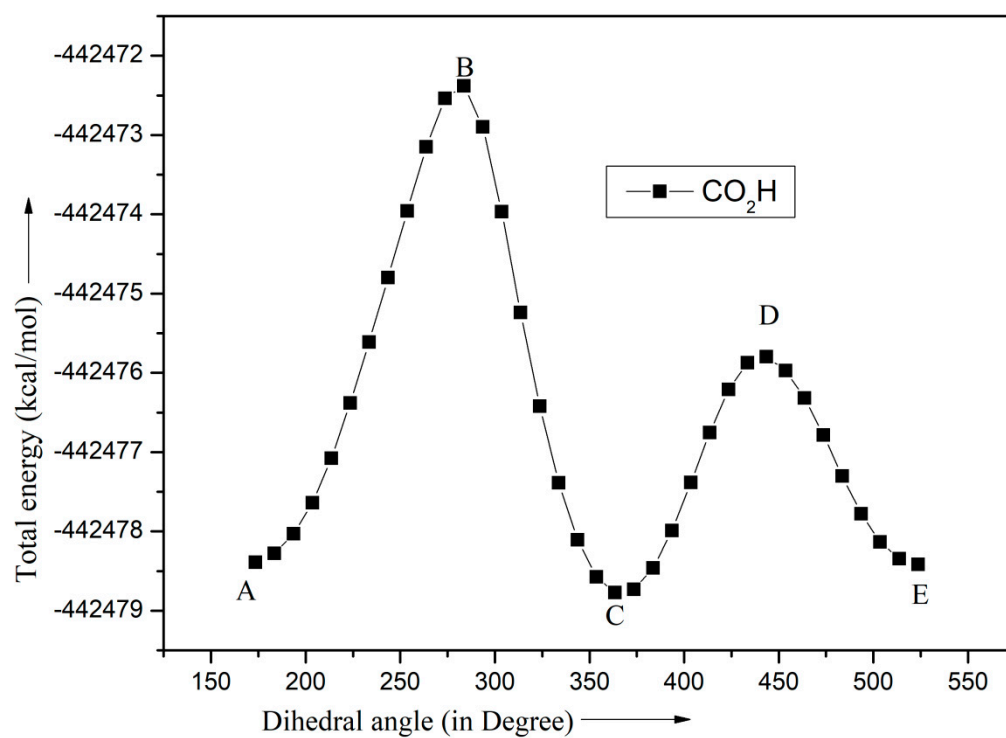Captions

Figure S1: Total energy vs dihedral angle plots for different tops of 2-aminopropenoic acid group.
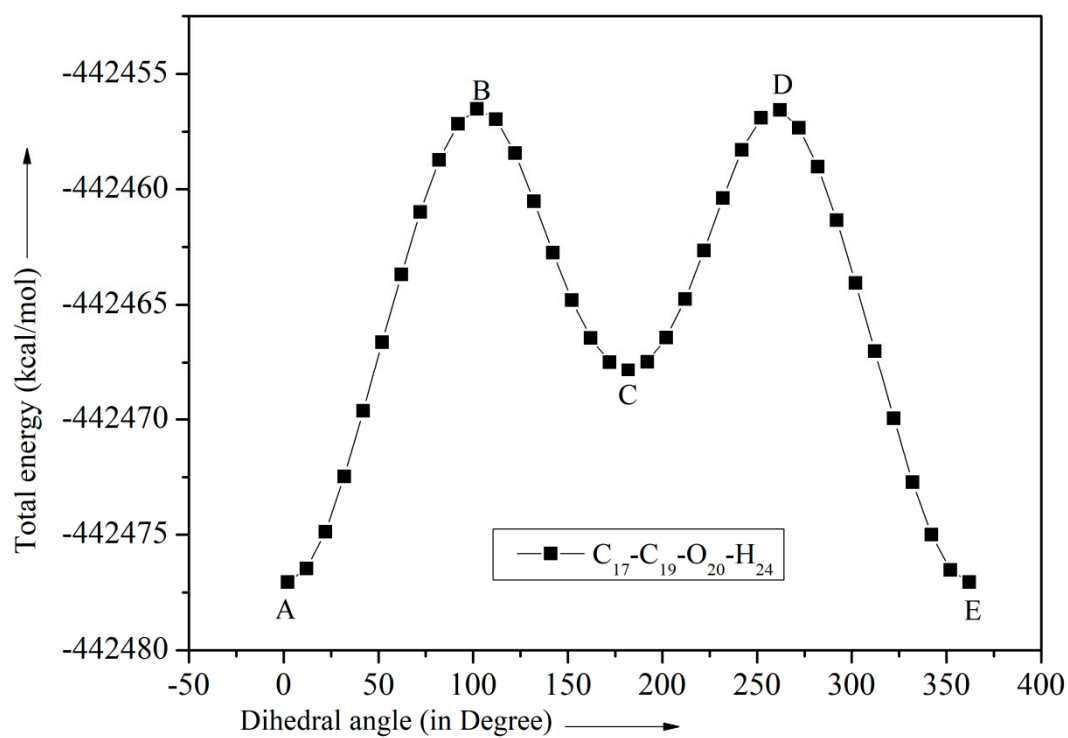
Figure S2: The optimized structures of the six lower energy conformers of L-dopa.

Figure S3: Computed and observed UV-vis spectra of L-dopa.

(a)

(b)

(c)

(d)

(e)

Figure S1. Total energy *vs* dihedral angle plots for different tops of 2-aminopropenoic acid group.

C-I

C-II

C-III

C-IV

C-V

C-VI

Figure S2. The optimized structures of the six lower energy conformers of L-dopa.

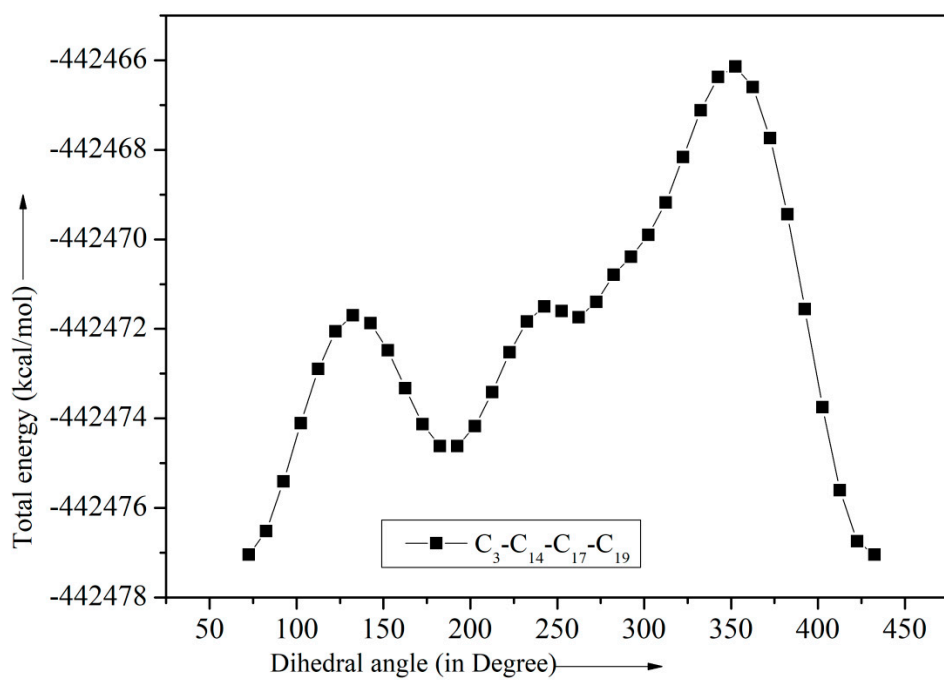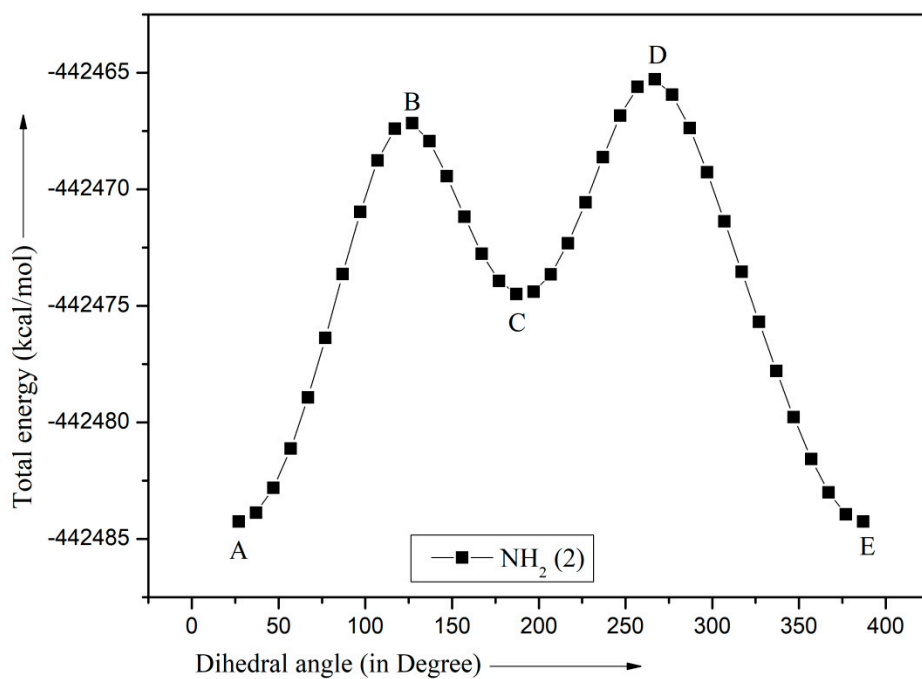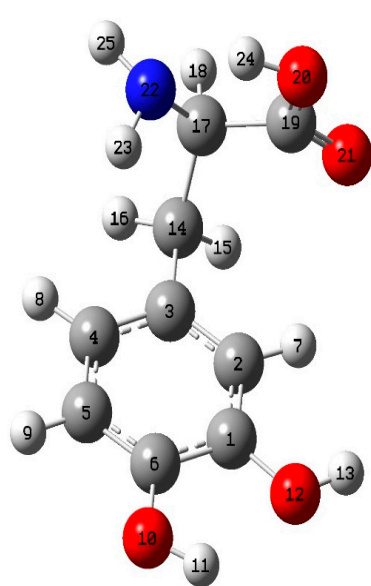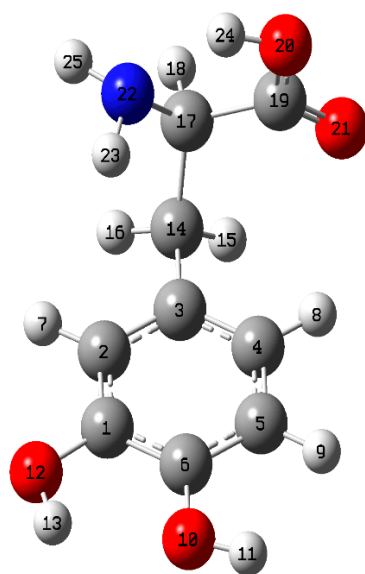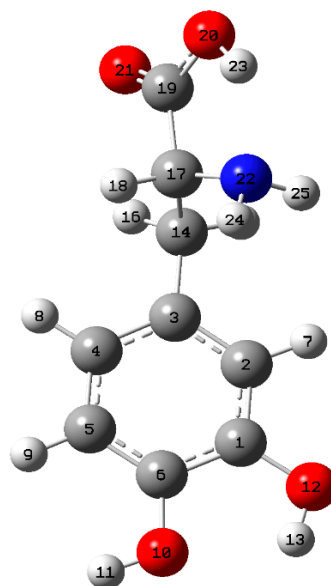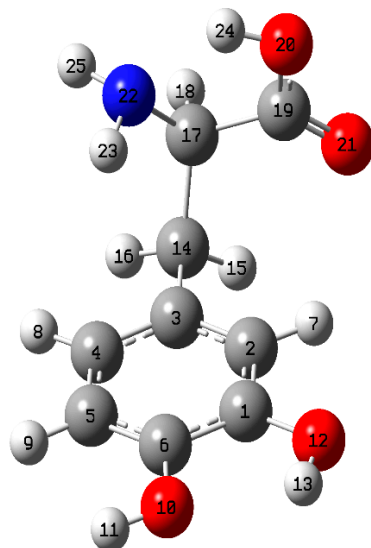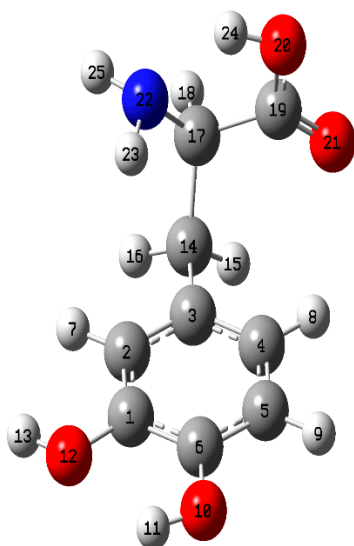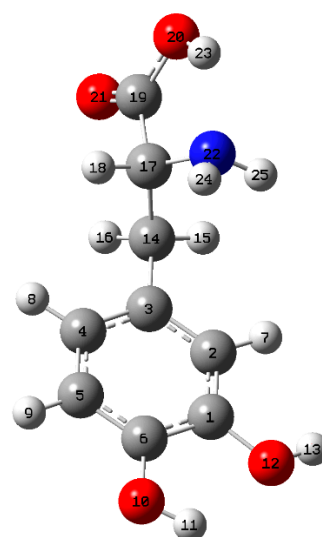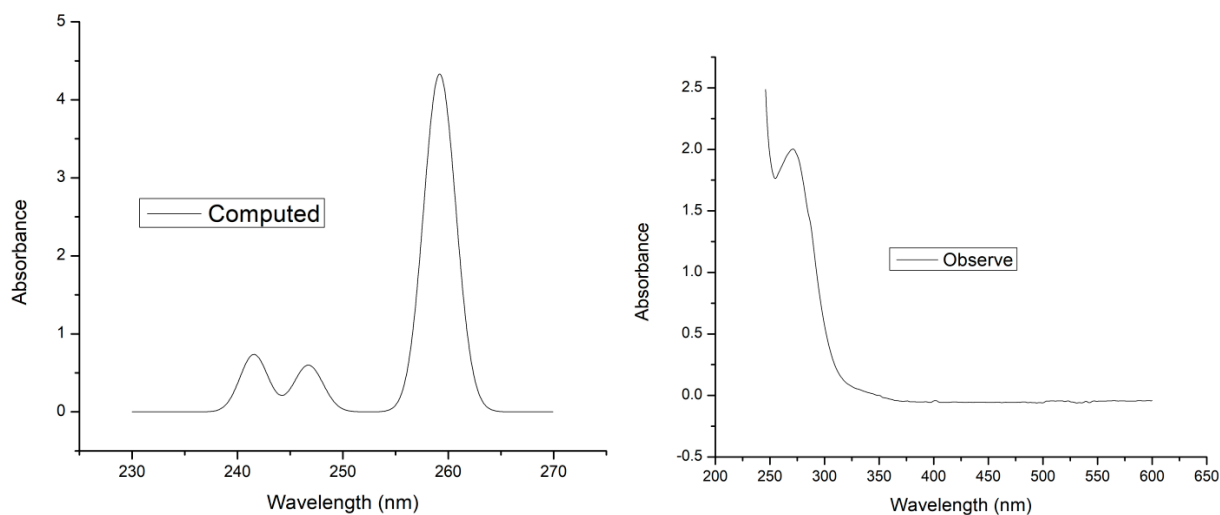**Figure S3.** Computed and observed UV-vis spectra of L-dopa.

SM-Tables:

Table-S1. Some molecular properties of L-dopa.

Molecular properties		C-I	D1
Rotational constants (GHz)	A	1.209	0.227
	B	0.414	0.104
	C	0.359	0.076
Moment of Inertia (a. u.)	I_A	1492	-
	I_B	4357	-
	I_C	5029	-
ZPV Energy (Kcal/mol)		123.913	250.424
E_{th} (Kcal/mol)		132.211	267.463
C_v(Cal/mol-K)		50.626	103.755
S (Cal/mol-K)		114.808	186.281
Dipole moment (Debye)		4.567	0.808
Total energy (Hartree)		-705.47889	-1410.95135

Table-S2(a). Geometrical parameter (bond angles) of the lowest energy conformer C-I and dimer D1 of L-dopa.

[#]Bond angles	C-I (1)	M1 (2)	M2 (3)	Ref.10 (4)	Ref.11 (5)	(2)-(1)	(3)-(1)	(4)-(1)	(5)-(1)
$\alpha(C_2$-C_1-$C_6)$	120.5	120.0	120.0	120.6	120.8	-0.5	-0.5	0.1	0.3
$\alpha(C_2$-C_1-$O_{12})$	124.4	125.1	125.1	124.5	124.7	0.7	0.7	0.1	0.3
$\alpha(C_6$-C_1-$O_{12})$	115.1	114.9	114.9	114.9	114.5	-0.2	-0.2	-0.2	-0.6
$\alpha(C_1$-C_2-$C_3)$	120.7	120.6	120.6	-	120.2	-0.1	-0.1	-	-0.5
$\alpha(C_1$-C_2-$H_7)$	119.2	119.0	119.0	119.3	119.4	-0.2	-0.2	0.1	0.2
$\alpha(C_3$-C_2-$H_7)$	120.1	120.4	120.4	-	120.0	0.3	0.3	-	-0.1
$\alpha(C_2$-C_3-$C_4)$	118.3	118.7	118.7	118.1	118.3	0.4	0.4	-0.2	0
$\alpha(C_2$-C_3-$C_{14})$	120.8	120.7	120.7	121.8	120.3	-0.1	-0.1	1	-0.5
$\alpha(C_4$-C_3-$C_{14})$	120.9	120.6	120.6	120.1	121.4	-0.3	-0.3	-0.8	0.5
$\alpha(C_3$-C_4-$C_5)$	121.1	121.0	121.0	121.3	121.4	-0.1	-0.1	0.2	0.3
$\alpha(C_3$-C_4-$H_8)$	119.8	119.8	119.8	120.6	119.8	0	0	0.8	0
$\alpha(C_5$-C_4-$H_8)$	119.1	119.1	119.1	119.1	118.8	0	0	0	-0.3
$\alpha(C_4$-C_5-$C_6)$	120.1	119.9	119.9	120.2	120.7	-0.2	-0.2	0.1	0.6
$\alpha(C_4$-C_5-$H_9)$	120.9	121.2	121.2	121.1	121.8	0.3	0.3	0.2	0.9
$\alpha(C_6$-C_5-$H_9)$	119.0	118.9	118.9	118.7	118.3	-0.1	-0.1	-0.3	-0.7

	C-I (1)	M1 (2)	M2 (3)	Ref.10 (4)	Ref.11 (5)	(2)-(1)	(3)-(1)	(4)-(1)	(5)-(1)
$\alpha(C_1-C_6-C_5)$	119.3	119.8	119.8	119.1	119.1	0.5	0.5	-0.2	-0.2
$\alpha(C_1-C_6-O_{10})$	120.6	119.7	119.7	-	120.5	-0.9	-0.9	-	-0.1
$\alpha(C_5-C_6-O_{10})$	120.1	120.5	120.5	-	120.2	0.4	0.4	-	0.1
$\alpha(C_6-O_{10}-H_{11})$	108.6	107.4	107.4	-	106.1	-1.2	-1.2	-	-2.5
$\alpha(C_1-O_{12}-H_{13})$	111.0	112.7	112.7	108.9	110.6	1.7	1.7	-2.1	-0.4
$\alpha(C_3-C_{14}-H_{15})$	110.4	111.0	111.0	109.6	110.0	0.6	0.6	-0.8	-0.4
$\alpha(C_3-C_{14}-H_{16})$	109.4	109.4	109.4	109.6	110.1	0	0	0.2	0.7
$\alpha(C_3-C_{14}-C_{17})$	114.6	113.9	113.9	115.9	112.4	-0.7	-0.7	1.3	-2.2
$\alpha(H_{15}-C_{14}-H_{16})$	107.2	107.3	107.3	106.8	107.3	0.1	0.1	-0.4	0.1
$\alpha(H_{15}-C_{14}-C_{17})$	107.7	107.6	107.6	109.3	108.3	-0.1	-0.1	1.6	0.6
$\alpha(H_{16}-C_{14}-C_{17})$	107.2	107.5	107.5	105.3	108.0	0.3	0.3	-1.9	0.8
$\alpha(C_{14}-C_{17}-H_{18})$	107.3	107.7	107.7	107.9	107.8	0.4	0.4	0.6	0.5
$\alpha(C_{14}-C_{17}-C_{19})$	112.3	112.4	112.4	112.9	107.4	0.1	0.1	0.6	-4.9
$\alpha(C_{14}-C_{17}-N_{22})$	115.7	115.4	115.4	109.4	116.1	-0.3	-0.3	-6.3	0.4
$\alpha(H_{18}-C_{17}-C_{19})$	104.2	103.8	103.8	106.1	105.7	-0.4	-0.4	1.9	1.5
$\alpha(H_{18}-C_{17}-N_{22})$	108.0	108.4	108.4	107.4	108.4	0.4	0.4	-0.6	0.4
$\alpha(C_{19}-C_{17}-N_{22})$	108.6	108.5	108.5	112.8	110.3	-0.1	-0.1	4.2	1.7
$\alpha(C_{17}-C_{19}-O_{20})$	113.6	114.6	114.6	116.9	112.0	1	1	3.3	-1.6
$\alpha(C_{17}-C_{19}-O_{21})$	124.1	122.7	122.7	123.0	125.4	-1.4	-1.4	-1.1	1.3
$\alpha(O_{20}-C_{19}-O_{21})$	122.3	122.6	122.6	-	122.6	0.3	0.3	-	0.3
$\alpha(C_{19}-O_{20}-H_{24})$	103.8	104.4	104.4	111.3	106.8	0.6	0.6	7.5	3
$\alpha(C_{17}-N_{22}-H_{23})$	111.5	110.9	110.9	109.7	109.9	-0.6	-0.6	-1.8	-1.6
$\alpha(C_{17}-N_{22}-H_{25})$	111.9	112.4	112.4	109.8	110.4	0.5	0.5	-2.1	-1.5
$\alpha(H_{23}-N_{22}-H_{25})$	107.9	108.4	108.4	105.2	108.1	0.5	0.5	-2.7	0.2

Table-S2(b). Geometrical parameter (dihedral angles) of the lowest energy conformer C-I and dimer D1 of L-dopa

[#]Dihedral angles	C-I (1)	M1 (2)	M2 (3)	Ref.10 (4)	Ref.11 (5)	(2)-(1)	(3)-(1)	(5)-(1)
$\delta(C_2-C_3-C_{14}-C_{17})$	-83.1	-82.7	-82.7	-	-113.1	0.4	0.4	-30
$\delta(C_2-C_3-C_{14}-H_{16})$	156.5	157.1	157.1	-	127.9	0.6	0.6	-28.6
$\delta(C_4-C_3-C_{14}-H_{15})$	-141.8	-142.6	-142.6	-	-167.4	-0.8	-0.8	-25.6
$\delta(C_4-C_3-C_{14}-H_{16})$	-24.0	-24.4	-24.4	-	-50.5	-0.4	-0.4	-26.5
$\delta(C_4-C_3-C_{14}-C_{17})$	96.4	95.8	95.8	-	68.5	-0.6	-0.6	-27.9
$\delta(C_3-C_{14}-C_{17}-H_{18})$	-173.5	-169.6	-169.6	-	-43.4	3.9	3.9	130.1
$\delta(C_3-C_{14}-C_{17}-N_{22})$	-52.9	-48.4	-48.4	-	-159.9	4.5	4.5	-107
$\delta(C_3-C_{14}-C_{17}-C_{19})$	72.5	76.6	76.6	-	73.5	4.1	4.1	1
$\delta(H_{15}-C_{14}-C_{17}-H_{18})$	63.2	66.9	66.9	-	-167.7	3.7	3.7	-230.9
$\delta(H_{15}-C_{14}-C_{17}-C_{19})$	-50.8	-46.8	-46.8	-	-50.8	4	4	0
$\delta(H_{16}-C_{14}-C_{17}-H_{18})$	-51.9	-48.3	-48.3	-	77.9	3.6	3.6	129.8
$\delta(H_{16}-C_{14}-C_{17}-N_{22})$	68.7	72.9	72.9	-	-38.6	4.2	4.2	-107.3
$\delta(H_{16}-C_{14}-C_{17}-C_{19})$	-165.9	-162.0	-162.0	-	-165.2	3.9	3.9	0.7
$\delta(C_{14}-C_{17}-N_{22}-H_{23})$	-95.7	-97.7	-97.7	-	-177.1	-2	-2	-81.4
$\delta(C_{14}-C_{17}-N_{22}-H_{25})$	25.4	23.8	23.8	-	-62.0	-1.6	-1.6	-87.4
$\delta(H_{18}-C_{17}-N_{22}-H_{25})$	24.5	23.2	23.2	-	66.1	-1.3	-1.3	41.6
$\delta(H_{18}-C_{17}-N_{22}-H_{23})$	145.6	144.7	144.7	-	-178.8	-0.9	-0.9	-324.4
$\delta(C_{19}-C_{17}-N_{22}-H_{23})$	-101.9	-103.2	-103.2	-	-50.5	-1.3	-1.3	51.4
$\delta(C_{19}-C_{17}-N_{22}-H_{25})$	137.0	135.3	135.3	-	64.6	-1.7	-1.7	-72.4
$\delta(C_{14}-C_{17}-C_{19}-O_{21})$	-137.7	-136.7	-136.7	-	-56.3	1	1	81.4
$\delta(C_{14}-C_{17}-C_{19}-O_{20})$	44.4	46.0	46.0	-	125.8	1.6	1.6	81.4
$\delta(H_{18}-C_{17}-C_{19}-O_{21})$	106.5	107.2	107.2	-	62.6	0.7	0.7	-43.9
$\delta(H_{18}-C_{17}-C_{19}-O_{20})$	-71.5	-70.1	-70.1	-	-116.3	1.4	1.4	-44.8

δ(N₂₂-C₁₇-C₁₉-O₂₁)	173.6	174.7	174.7	-	179.0	1.1	1.1	5.4
δ(N₂₂-C₁₇-C₁₉-O₂₀)	-8.5	-7.8	-7.8	-	1.1	0.7	0.7	9.6
δ(C₁₇-C₁₉-O₂₀-H₂₄)	2.1	2.5	2.5	-	8.6	0.4	0.4	6.5
δ(O₂₅-C₁₉-O₂₀-H₂₄)	-179.9	-179.8	-179.8	-	-173.4	0.1	0.1	6.5

[#] bond angles(α) and dihedral angles (δ) in (°). [*]M_1 and M_2 are the molecules of the dimer D_1 (Fig.-3)

Table-S3. Normal mode distribution of L-dopa.

Group/moiety[#]		modes in symbolic form[*]	Total
2-ami-nopro-penoic acid	CH_2	$\nu_s+\nu_{as}+\beta_s+\rho+\omega+t$	6
	NH_2	$\nu_s+\nu_{as}+\beta_s+\rho+\omega+\tau$	6
	$CO_2(H)$	$\nu_s+\nu_{as}+\beta_s+\rho+\omega+\tau$	6
	C-H	$\nu+2\delta$	3
	$C_{14}-C'_{17}N'_{22}-C'_{19}$	$3\nu+\alpha+\tau+\beta_s+\omega+\rho+\tau$	9
Phenyl	Ring	$6\nu(R)+3\alpha(R)+3\Phi(R)$	12
	C-OH	$2\nu+2\beta+2\gamma$	6
	$C_3-C'_{14}$	$\nu+\beta+\gamma$	3
	C-H	$3\nu+3\beta+3\gamma$	9
OH	O-H	$3\nu+3\alpha+3\tau$	9

[*] α(R)- is planer ring deformation, υ(R)- is ring stretching, ϕ(R)-is non planer ring deformation,β- planer bending,γ- non planer bending, β_s - is scissoring of group, ρ- is rocking of group, ω- is wigging of the group, τ- is torsion of group, t is twisting of group, ν_{as} is Anti-symmetric stretching, ν_s is symmetric stretching, δ- angle deformation of group δ_s, δ_{as} are symmetric and anti-symmetric angle deformation of group,

[#]C'_{14} is a virtual atom at the centre of the atom C_{14} with mass equivalent to the total mass of 2-aminopropenoic acid moiety; Similarly, the atoms N'_{22} and C'_{19} are the virtual atoms at the centres of the atoms N_{22} and C_{19} with masses of theNH₂ and COOH groups.

Table-S4. Computed vibrational frequencies and their assignments of L-dopa.

Ref. [10]	Ref. [11]	Present			Their differences				Assignments
		C-I	D1						
			M_1	M_2					
(1)	(2)	(3)	(4)	(5)	(3)-(1)	(3)-(2)	(3)-(4)	(3)-(5)	
3834	3848	3824	3467	3457	-10	-24	357	367	ν(O-H)
3778	3789	3773	3762	3762	-5	-16	11	11	ν(O-H)
3684	3758	3255	3336	3337	-429	-503	-81	-82	ν(O-H)
3567	3576	3595	3593	3593	28	19	2	2	ν_as(NH₂)
3491	3494	3501	3484	3484	10	7	17	17	νs(NH₂)
3208	3190	3189	3190	3191	-19	-1	-1	-2	ν(C-H) 2
3184	3173	3170	3180	3180	-14	-3	-10	-10	ν(C-H) 13
3152	3142	3170	3158	3158	18	28	12	12	ν(C-H) 7b
3087	3080	3099	3094	3094	12	19	5	5	ν_as(CH₂)
3040	3064	3061	3051	3051	21	-3	10	10	ν(C-H)
3020	3029	3051	3038	3038	31	22	13	13	νs(CH₂)
1824	1830	1776	1786	1784	-48	-54	-10	-8	ν(C=O)
1676	1661	1648	1654	1654	-28	-13	-6	-6	ν(R) 8
1658	1655	1644	1646	1647	-14	-11	-2	-3	βs(NH₂)
1644	1647	1641	1643	1643	-3	-6	-2	-2	ν(R) 8
1560	1558	1550	1562	1563	-10	-8	-12	-13	ν(R) 19
1495	1491	1479	1485	1485	-16	-12	-6	-6	βs(CH₂)

1474	1474	1469	1479	1478	-5	-5	-10	-9	ν(R) 19
1406	1426	1413	1438	1442	7	-13	-25	-29	α(C-O-H)
1395	1411	1394	1416	1416	-1	-17	-22	-22	ν(R) 14
1362	1359	1392	1400	1401	30	33	-8	-9	δ′(C$_{17}$-H)
1356	1350	1367	1387	1386	11	17	-20	-19	ω(CH$_2$)
1333	1341	1352	1363	1363	19	11	-11	-11	β(C-H) (3)
1313	1310	1303	1312	1311	-10	-7	-9	-8	ν(C-OH)
1289	1299	1289	1297	1297	0	-10	-8	-8	δ(CNCH)
1281	1282	1260	1284	1283	-21	-22	-24	-23	ν(C-OH)
1225	1260	1242	1254	1254	17	-18	-12	-12	ϱ(CH$_2$)
1213	1221	1211	1245	1243	-2	-10	-34	-32	α(C-O-H)
1189	1200	1201	1222	1222	12	1	-21	-21	ν(C-OH)
1176	1182	1178	1216	1212	2	-4	-38	-34	α(C-O-H)
1165	1164	1171	1175	1175	6	7	-4	-4	ϱ(NH$_2$)
1151	1133	1156	1161	1161	5	23	-5	-5	β(C-H)
1139	1123	1123	1135	1135	-16	0	-12	-12	β(C-H)
1121	1092	1096	1091	1091	-25	4	5	5	ν(C$_{17}$-N)
1004	1015	1018	1020	1020	14	3	-2	-2	ν(C$_{14}$-C$_{17}$)
977	969	972	976	976	-5	3	-4	-4	ν(Cph-C)
965	930	951	946	947	-14	21	5	4	γ(C-H)
950	888	929	936	937	-21	41	-7	-8	τ(C-OH)
903	876	911	920	919	8	35	-9	-8	t(CH$_2$)
860	854	888	887	890	28	34	1	-2	γ(C-H)
839	837	864	872	872	25	27	-8	-8	ω(NH$_2$)
804	821	845	844	845	41	24	1	0	α(R)
794	806	822	822	822	28	16	0	0	γ(C-H)
765	775	791	801	801	26	16	-10	-10	ν(R) 1
719	736	771	782	780	52	35	-11	-9	ν(C$_{17}$-C$_{19}$)
699	710	731	738	747	32	21	-7	-16	Φ(R)-4
651	654	723	730	729	72	69	-7	-6	α(R)-12
605	621	655	709	713	50	34	-54	-58	φ(R)
593	597	594	659	660	1	-3	-65	-66	α(R)
559	590	578	602	602	19	-12	-24	-24	β$_s$(CO$_2$H)
543	538	542	580	581	-1	4	-38	-39	δ2(CNCH)
485	520	528	550	555	43	8	-22	-27	ϱ(CO$_2$H)
462	467	483	535	538	21	16	-52	-55	β(C-O)ip
452	458	459	489	493	7	1	-30	-34	φ(R)
433	433	426	477	477	-7	-7	-51	-51	α(R)
388	395	391	452	453	3	-4	-61	-62	τ(C$_6$-O$_{10}$)
326	361	377	428	431	51	16	-51	-54	δ(CNCH)
310	323	351	384	383	41	28	-33	-32	γ(C$_6$-O$_{10}$)
306	312	331	357	359	25	19	-26	-28	τ(C$_{17}$-N$_{22}$)
294	292	316	348	349	22	24	-32	-33	τ(C$_{19}$-O$_{20}$)
270	267	302	334	334	32	35	-32	-32	β(C-O)op
243	238	254	328	328	11	16	-74	-74	τ(C$_1$-O$_{12}$)
215	218	231	242	245	16	13	-11	-14	γ(C$_1$-O$_{12}$)
186	174	194	211	218	8	20	-17	-24	δas″(CHCN)

159	163	164	173	174	5	1	-9	-10	$\alpha(C_3-C_{17}-C_{14})$
84	66	88	89	95	4	22	-1	-7	$\tau(C_{17}-C_{19})$
59	60	68	75	78	9	8	-7	-10	$\tau(C_{14}-C_{17})$
39	44	53	54	62	14	9	-1	-9	$\gamma(C_3-C_{14})$
30	33	36	39	51	6	3	-3	-15	$\tau(C_3-C_{14})$

Table-S5. Geometrical parameter of the first six lower energy conformers of L-dopa.

Parameters#	(I)	(II)	(III)	(IV)	(V)	(VI)
r(C1-C2)	1.387	1.390	1.391	1.389	1.391	1.390
r(C1-C6)	1.403	1.400	1.400	1.403	1.400	1.400
r(C1-O12)	1.376	1.379	1.363	1.361	1.364	1.378
r(C2-C3)	1.404	1.403	1.399	1.402	1.401	1.400
r(C2-H7)	1.086	1.088	1.085	1.084	1.085	1.087
r(C3-C4)	1.398	1.400	1.399	1.398	1.399	1.399
r(C3-C14)	1.514	1.514	1.512	1.514	1.514	1.512
r(C4-C5)	1.396	1.393	1.395	1.398	1.395	1.393
r(C4-H8)	1.085	1.083	1.085	1.085	1.083	1.085
r(C5-C6)	1.388	1.390	1.389	1.386	1.389	1.391
r(C5-H9)	1.083	1.083	1.086	1.086	1.086	1.084
r(C6-O10)	1.363	1.363	1.378	1.377	1.378	1.363
r(O10-H11)	0.966	0.966	0.962	0.962	0.962	0.966
r(O12-H13)	0.963	0.962	0.966	0.966	0.966	0.962
r(C14-H15)	1.092	1.092	1.096	1.092	1.092	1.096
r(C14-H16)	1.094	1.094	1.092	1.094	1.094	1.092
r(C14-C17)	1.549	1.549	1.544	1.549	1.549	1.543
r(C17-H18)	1.096	1.096	1.096	1.095	1.096	1.095
r(C17-C19)	1.547	1.548	1.546	1.548	1.548	1.546
r(C17-N22)	1.471	1.471	1.472	1.472	1.471	1.472
r(C19=O20)	1.337	1.337	1.340	1.338	1.338	1.341
r(C19-O21)	1.205	1.204	1.203	1.204	1.205	1.203
α(C2-C1-C6)	121	121	120	120	120	121
α(C2-C1-O12)	124	124	120	120	120	124
α(C6-C1-O12)	115	115	121	121	121	115
α(C1-C2-C3)	121	121	121	121	121	121
α(C1-C2-H7)	120	119	118	118	118	119
α(C3-C2-H7)	120	120	121	121	121	120
α(C2-C3-C4)	118	118	119	119	119	118
α(C2-C3-C14)	121	120	121	121	120	121
α(C4-C3-C14)	121	122	121	121	121	121
α(C3-C4-C5)	121	121	121	121	121	121
α(C3-C4-H8)	120	120	120	120	120	120
α(C5-C4-H8)	119	119	119	119	120	119
α(C4-C5-C6)	120	121	120	120	120	120
α(C4-C5-H9)	121	121	120	120	120	121
α(C6-C5-H9)	119	119	120	120	120	119

α(C1-C6-C5)	119	119	120	120	120	119
α(C1-C6-O10)	121	121	115	115	115	121
α(C5-C6-O10)	120	120	125	125	125	120
α(C6-O10-H11)	108	109	111	111	111	109
α(C1-O12-H13)	111	111	109	109	108	111
α(C3-C14-H15)	111	110	110	110	110	110
α(C3-C14-H16)	109	110	111	109	110	111
α(C3-C14-C17)	114	114	113	114	114	113
α(H15-C14-H16)	107	107	107	107	107	106
α(H15-C14-C17)	107	107	109	107	107	109
α(H16-C14-C17)	108	108	108	108	108	108
α(C14-C17-H18)	108	108	108	108	108	108
α(C14-C17-C19)	112	112	111	112	112	111
α(C14-C17-N22)	116	116	116	116	116	116
α(H18-C17-C19)	104	104	105	104	104	105
α(H18-C17-N22)	108	108	107	108	108	107
α(C19-C17-N22)	109	110	110	110	109	110
α(C17-C19-O20)	114	114	114	114	114	114
α(C17-C19-O21)	123	123	123	123	123	123
α(O20-C19-O21)	123	123	123	123	123	123

[#] Bond lengths in Å and bond angles in °.