Supporting Information

Conformational dependence of the circular dichroism spectrum of α-hydroxyphenylacetic acid: A ChiraSac study

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Table S1. Coordinates (in Å) of the most stable conformation, Δ=0º (Δ1=0º, Δ2=0º or Δ3=0º) of α-hydroxyphenylacetic acid (HPAA).

Atom (See Figure 2)	X	Y	Z
C_1*	-1.08975	-0.27733	0.776661
H_2	-1.24894	0.253274	1.72652
C_3	0.380655	-0.13758	0.377177
C_4	1.087667	1.034777	0.667064
C_5	2.422126	1.165433	0.283581
C_6	3.062548	0.123401	-0.39081
C_7	2.361596	-1.04929	-0.67585
C_8	1.025424	-1.17996	-0.29398
H_9	0.592993	1.848148	1.192163
H_{10}	2.96353	2.07825	0.517633
H_{11}	4.103847	0.223094	-0.68558
H_{12}	2.855775	-1.8675	-1.19322
H_{13}	0.480345	-2.09703	-0.4906
O_{14}	-1.49204	-1.619	0.916038
H_{15}	-2.13064	-1.78445	0.196472
C_{16}	-1.98767	0.387781	-0.27021
O_{17}	-2.74062	-0.24208	-0.98496
O_{18}	-1.86034	1.723854	-0.31579
H_{19}	-2.44853	2.040688	-1.02756

Table S2. 1 and 2^1A excited states for COOH, OH and phenyl rotations.

COOH rotation								
	1^1A				2^1A			
Δ1 [a]	EE [b]	Osc [c]	Rot [d]	θ [e]	EE [b]	Osc [c]	Rot [d]	θ [e]
0	4.66	0.0007	-0.25	102.3	5.45	0.027	55.70	49.9
30	4.61	0.0002	0.43	79.5	5.36	0.004	28.72	34.8
60	4.60	0.0001	-0.91	112.9	5.03	0.002	-16.32	123.5
90	4.60	0.0002	-0.98	153.8	4.88	0.003	-26.08	168.3
120	4.65	0.0001	-0.40	130.8	5.04	0.012	-31.56	128.8
150	4.63	0.0001	-0.35	125.8	5.13	0.023	-16.12	100.5
180	4.62	0.0006	-0.04	93.9	5.24	0.013	10.04	80.6
210	4.57	0.0004	-0.09	97.4	5.19	0.002	0.65	88.0
240	4.61	0.0000	0.05	13.8	5.06	0.001	-10.14	138.9
270	4.60	0.0001	-0.10	159.0	4.89	0.002	-13.37	143.7
300	4.59	0.0004	-0.10	100.7	5.04	0.011	-10.34	101.2
330	4.64	0.0001	-0.45	155.6	5.21	0.030	18.02	78.7
OH rotation								
	1^1A				2^1A			
Δ2 [a]	EE [b]	Osc [c]	Rot [d]	θ [e]	EE [b]	Osc [c]	Rot [d]	θ [e]
0	4.66	0.0007	-0.25	102.3	5.45	0.027	55.70	49.9
30	4.66	0.0001	-0.23	115.6	5.50	0.023	59.05	47.0
60	4.64	0.0000	-0.38	112.2	5.37	0.020	64.20	44.3
90	4.62	0.0001	-0.39	106.4	5.30	0.016	49.91	44.0
120	4.67	0.0000	-0.38	139.2	5.28	0.015	39.21	48.4
150	4.67	0.0002	-0.11	97.6	5.28	0.015	38.89	50.3
180	4.65	0.0004	-0.10	93.7	5.29	0.016	48.49	48.5
210	4.64	0.0006	-0.18	96.9	5.31	0.016	48.29	48.6
240	4.64	0.0006	-0.29	106.7	5.26	0.015	44.79	53.5
270	4.61	0.0004	-0.06	93.8	5.19	0.015	41.65	51.3
300	4.63	0.0007	-0.05	92.5	5.23	0.017	38.71	52.7
330	4.63	0.0007	0.11	85.7	5.34	0.024	55.77	49.8
Phenyl rotation								
	1^1A				2^1A			
Δ3 [a]	EE [b]	Osc [c]	Rot [d]	θ [e]	EE [b]	Osc [c]	Rot [d]	θ [e]
0	4.66	0.0007	-0.25	102.3	5.45	0.027	55.70	49.9
30	4.63	0.0002	-0.12	96.0	5.53	0.020	52.52	46.3
60	4.65	0.0001	0.36	61.1	5.55	0.007	28.72	50.6
90	4.68	0.0001	0.07	82.8	5.57	0.002	14.76	52.4
120	4.61	0.0000	-0.21	118.9	5.49	0.002	12.29	47.9
150	4.68	0.0003	0.25	75.3	5.50	0.014	36.12	48.8

[a] Δ1, Δ2 and Δ3 are dihedral angle change for COOH, OH and phenyl rotations, respectively. [b] Excitation energy (in eV). [c] Oscillator strength. [d] Rotatory strength (10^{-40} cgs). [d] Angle in Eq.(3).

Table S3. Top 14 highest existence ratios among the 864 conformers of α-hydroxyphenylacetic acid from the Boltzmann distributions using the single point CCSD/6-31G(d) energies at the B3LYP/6-31G(d) geometries at 27°C and 527ºC.

Dihedral angle change (º) [a]			Existence ratio (%)		Relative energy (kcal/mol)
phenyl (Δ3)	COOH (Δ1)	OH (Δ2)	27°C	527ºC	
0	0	0	23.9	2.8	0.00
30	0	0	8.2	1.9	0.64
150	0	0	7.9	1.8	0.67
150	0	30	5.9	1.7	0.83
0	30	330	5.6	1.6	0.87
0	0	330	5.3	1.6	0.90
150	330	30	4.7	1.5	0.98
0	0	30	4.0	1.4	1.07
30	0	330	3.0	1.3	1.24
0	330	30	2.2	1.1	1.41
30	30	330	2.0	1.1	1.47
30	0	30	1.9	1.1	1.52
60	0	0	1.4	1.0	1.71
30	330	30	1.4	1.0	1.71
120	0	30	1.3	0.9	1.72
60	0	30	1.1	0.9	1.83
Other 848 conformers			20.3	77.4	

[a]Δ =0º at the most stable conformation.

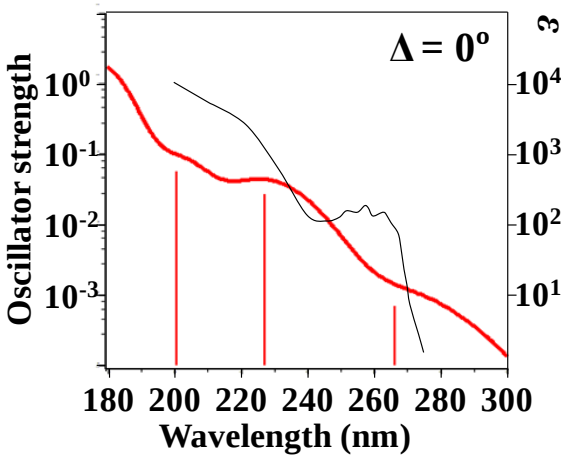


Figure S1. SAC-CI UV spectrum of α-hydroxyphenylacetic acid at the most stable conformation, Δ=0º (Δ1=0º, Δ2=0º or Δ3=0º), compared with the experimental UV spectrum (black line) [47].

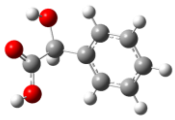
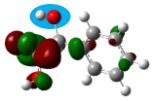
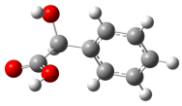
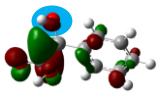
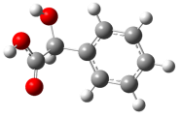
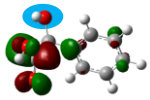
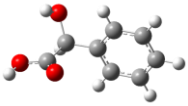
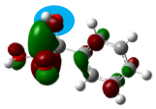
Conformation in COOH rotation		LUMO+2
Δ1=0º		
Δ1=90º		
Δ1=180º		
Δ1=270º		

Figure S2. Molecular orbital pictures of the π* orbital of the COOH group at at Δ1=0, 90, 180 and 270° in the COOH rotation. The aqua blue circles represent the OH group. The contour value of the isosurfaces is 0.05.

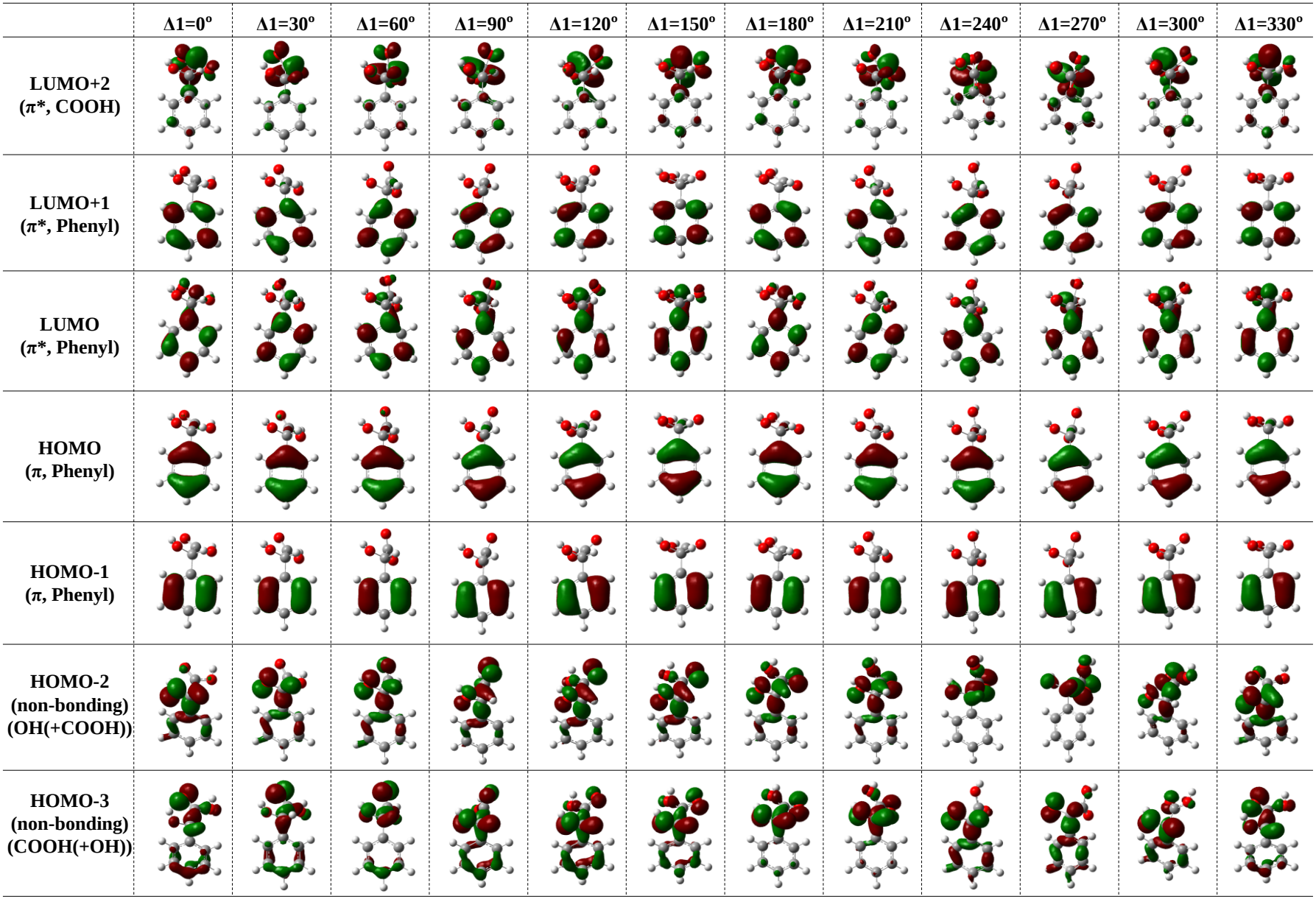


Figure S3. Molecular orbital pictures from HOMO-3 to LUMO+2 at several conformational angles of the carboxyl (COOH) rotation. The contour value of the isosurfaces is 0.05.

Figure S4. Molecular orbital pictures from HOMO-3 to LUMO+2 at several conformational angles of the hydroxyl (OH) rotation. The contour value of the isosurfaces is 0.05.

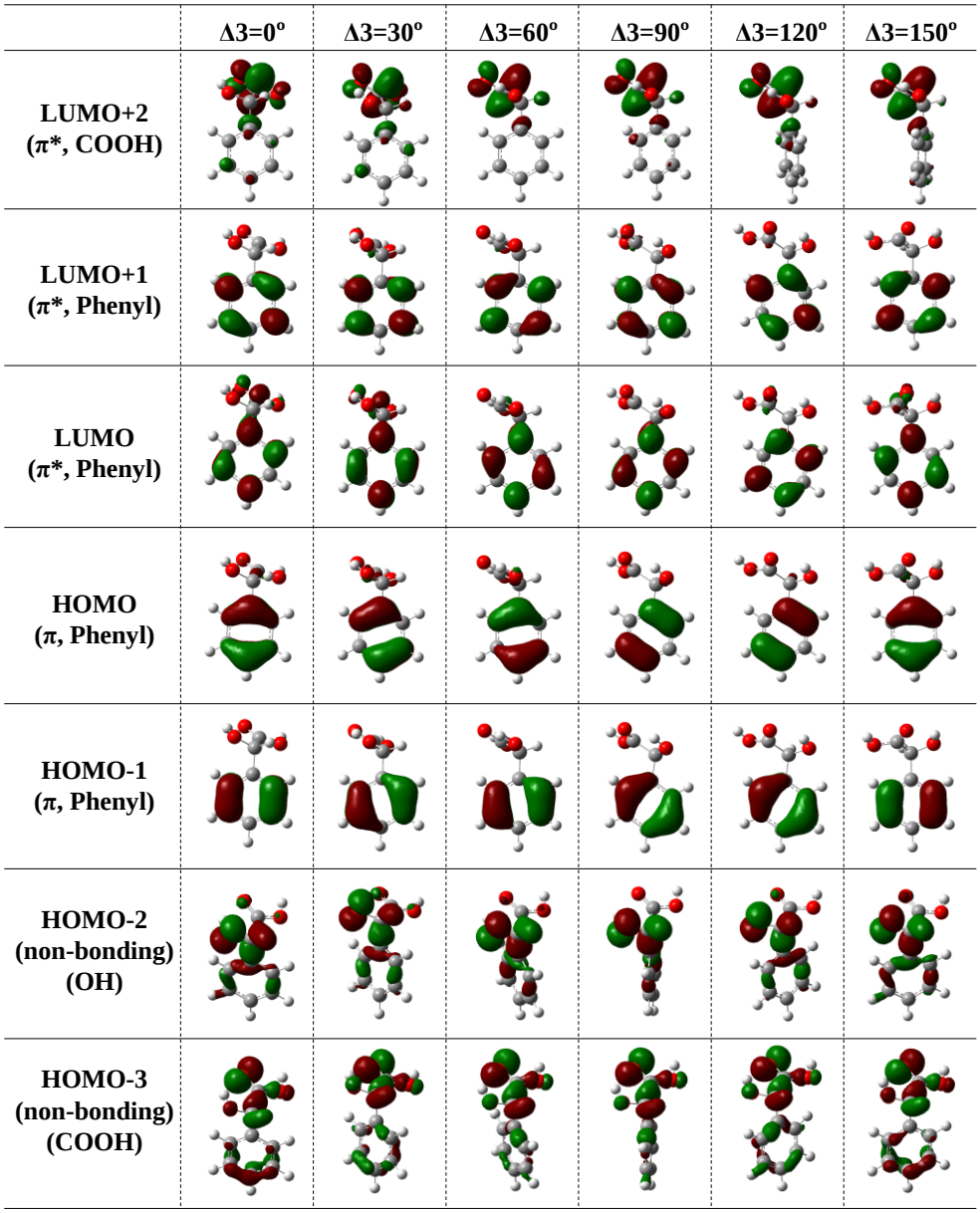


Figure S5. Molecular orbital pictures from HOMO-3 to LUMO+2 at several conformational angles of the phenyl rotation. The contour value of the isosurfaces is 0.05.

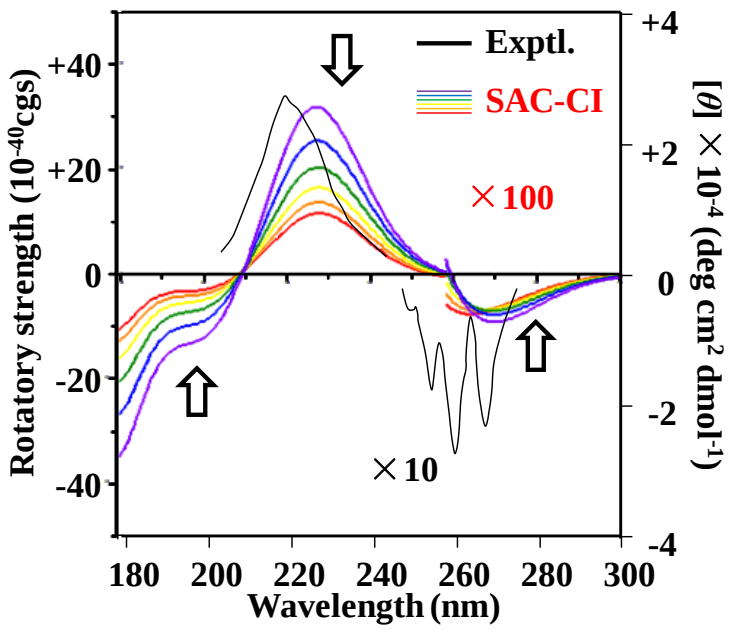


Figure S6. Boltzmann averaged SAC-CI CD spectra using the single point CCSD/6-31G(d) energies at the B3LYP/6-31G(d) geometries of α-hydroxyphenylacetic acid at 27 (purple line), 127 (blue line), 227 (green line) , 327 (yellow line), 427 (orange line) and 527 (red line)^{o}C, compared with the experimental CD spectrum (27°C, black line) [47]. Arrows indicates the changes in raising the temperature