

Supplementary Information

**Controlling the pH of aqueous maleic and succinic acids analyzed by X-ray
absorption spectroscopy**

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1. Conformation of maleic and succinic acids

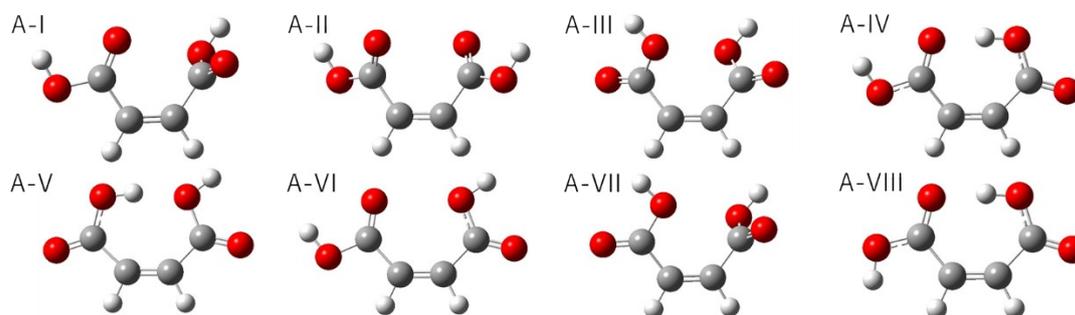


Fig. S1. Structure of neutral maleic acid.

Table S1. Relative total energy of neutral maleic acid.

	Gas ^a / kJ mol ⁻¹	PCM ^b / kJ mol ⁻¹
A-I	9.93	13.47
A-II	13.20	16.96
A-III	14.86	19.04
A-IV	0.0	0.0
A-V	22.37	21.67
A-VI	26.08	31.91
A-VII	14.39	18.11
A-VIII	23.63	12.36

^a Single maleic acid in the gas phase.

^b Single maleic acid by the PCM method.

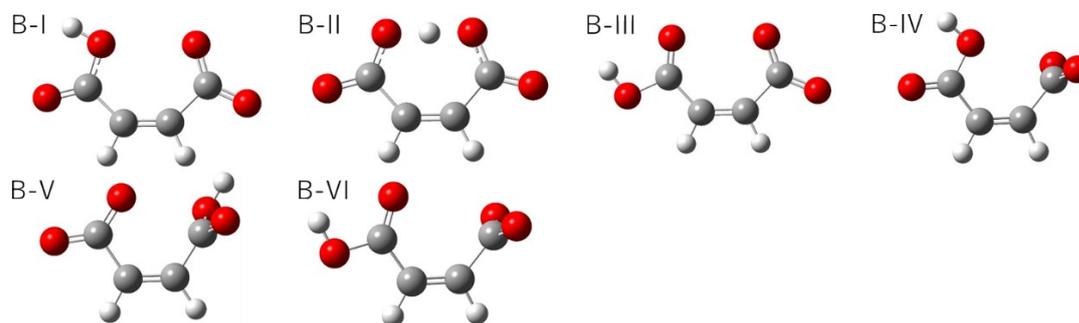


Fig. S2. Structure of anionic maleic acid.

Table S2. Relative total energy of anionic maleic acid.

	Gas ^a / kJ mol ⁻¹	PCM ^b / kJ mol ⁻¹
B-I	105.93	54.19
B-II	99.24	58.26
B-III	97.70	56.45
B-IV	127.62	80.96
B-V	0.0	0.0
B-VI	120.68	83.53

^a Single maleic acid in the gas phase.

^b Single maleic acid by the PCM method.

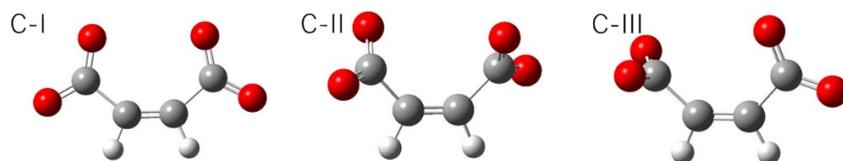


Fig. S3. Structure of dianionic maleic acid.

Table S3. Relative total energy of dianionic maleic acid.

	Gas ^a / kJ mol ⁻¹	PCM ^b / kJ mol ⁻¹
C-I	0.0	0.0
C-II	0.72	1.77
C-III	15.37	28.96

^a Single maleic acid in the gas phase.

^b Single maleic acid by the PCM method.

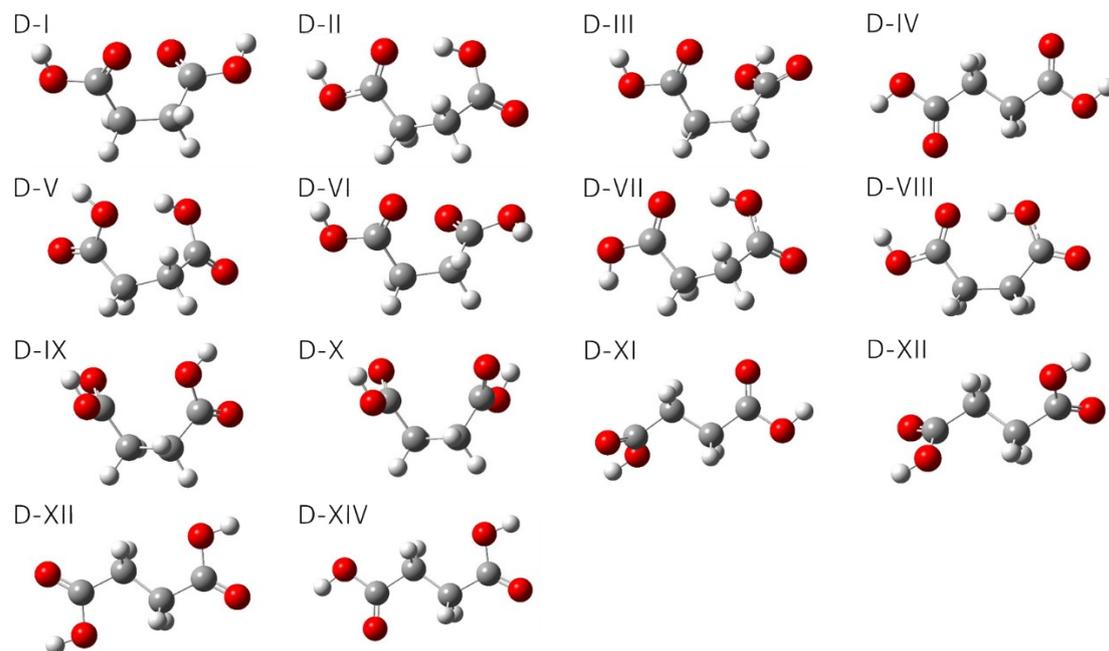


Fig. S4. Structure of neutral succinic acid.

Table S4. Relative total energy of neutral succinic acid.

	Gas ^a / kJ mol ⁻¹	PCM ^b / kJ mol ⁻¹
D-I	0.0	0.0
D-II	11.95	3.34
D-III	6.14	3.83
D-IV	4.48	5.16
D-V	28.25	18.75
D-VI	21.51	9.84
D-VII	32.98	13.19
D-VIII	54.68	41.10
D-IX	13.91	9.35
D-X	13.88	12.75
D-XI	9.54	9.66
D-XII	14.76	14.42
D-XIII	18.85	17.09
D-XIV	11.80	11.02

^a Single succinic acid in the gas phase.

^b Single succinic acid by the PCM method.

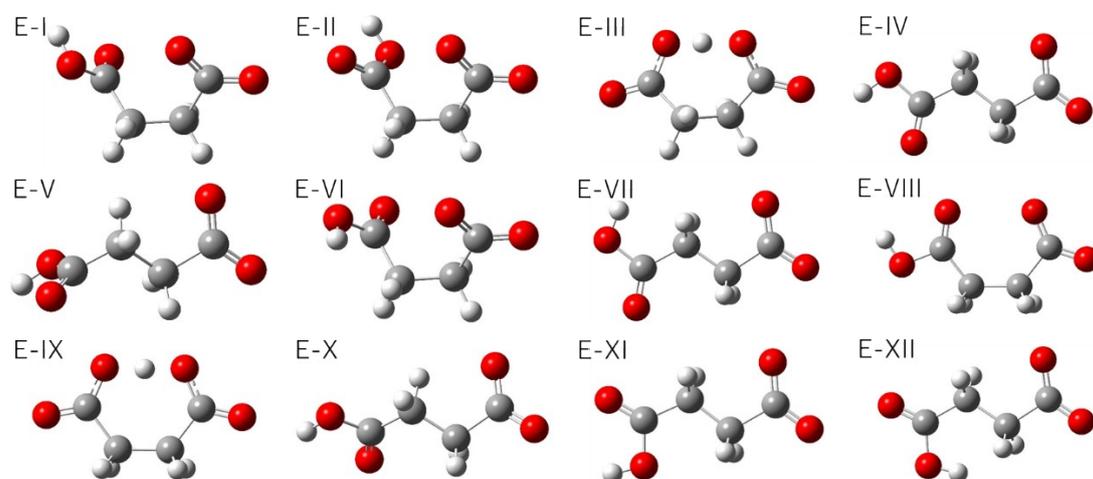


Fig. S5. Structure of anionic succinic acid.

Table S5. Energy of anionic succinic acid.

	Gas ^a / kJ mol ⁻¹	PCM ^b / kJ mol ⁻¹
E-I	79.52	39.37
E-II	0.0	0.0
E-III	79.73	41.37
E-IV	85.06	47.12
E-V	79.69	47.54
E-VI	—	47.58
E-VII	92.59	55.59
E-VIII	173.98	121.92
E-IX	37.25	36.10
E-X	82.82	—
E-XI	88.65	52.57
E-XII	80.74	59.36

^a Single succinic acid in the gas phase.

^b Single succinic acid by the PCM method

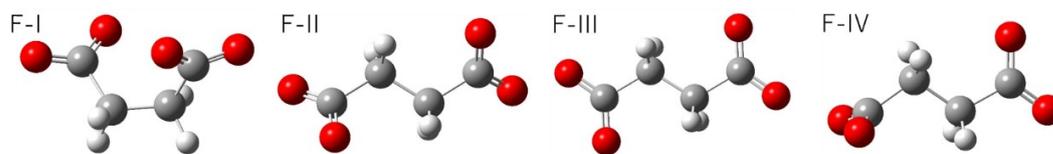


Fig. S6. Structure of dianionic succinic acid.

Table S6. Relative total energy of dianionic succinic acid.

	Gas ^a / kJ mol ⁻¹	PCM ^b / kJ mol ⁻¹
F-I	0.0	—
F-II	—	0.0
F-III	3.55	3.46
F-IV	—	1.57

^a Single succinic acid in the gas phase.

^b Single succinic acid by the PCM method

2. force constants of maleic and succinic acids

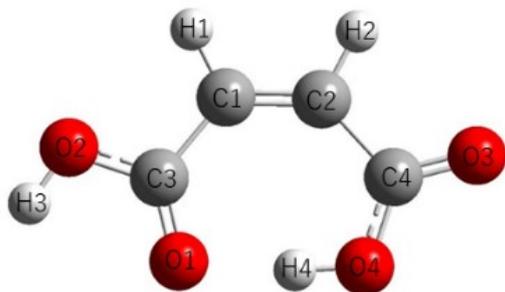


Table S7. Force constants of neutral maleic acid (bond)

bond	Length / nm	force constant / $\text{kJ mol}^{-1} \text{nm}^{-2}$
C1-C2	0.134559	521779.4
C1-C3	0.147353	292554.1
C1-H1	0.108050	345553.7
C2-C4	0.150092	247004.8
C2-H2	0.108161	342943.4
C3-O1	0.122071	702804.6
C3-O2	0.134083	372958.4
O2-H3	0.096996	471898.7
C4-O3	0.121308	720864.8
C4-O4	0.132855	399541.8
O4-H4	0.098449	378463.4

Table S8. Force constant of neutral maleic acid (angle)

angle	Angle / degree	force constant / $\text{kJ mol}^{-1} \text{rad}^{-2}$
C1-C3-O1	127.536	966.759
C1-C3-O2	110.633	946.250
C1-C2-C4	133.512	919.358
C1-C2-H2	116.293	551.118
H1-C1-C3	114.049	543.779
H1-C1-C2	117.718	550.260
C2-C1-C3	128.233	901.592
C2-C4-O4	120.052	1036.868

C2-C4-O3	117.848	961.214
H2-C2-C4	110.195	530.773
C3-O2-H3	106.258	435.729
O1-C3-O2	121.831	1136.299
C4-O4-H4	110.583	560.361
O3-O4-H4	122.100	1105.623

Table S9. Force constant of neutral maleic acid (dihedral)

dihedral	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅
C2-C1-C3-O2, C1-C2-C4-O3	5.8576	-6.6944	-12.552	0.0000	0.0000	0.0000
C2-C1-C3-O1, C1-C2-C4-O4	5.8576	6.6944	-12.552	0.0000	0.0000	0.0000

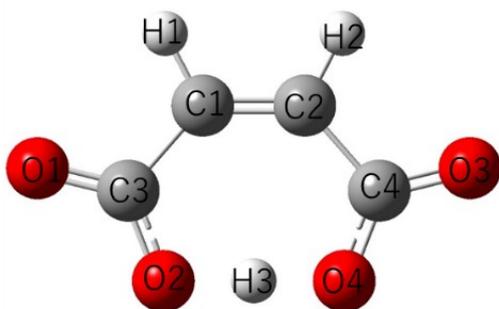


Table S10. Force constant of anionic maleic acid (bond)

bond	length/nm	force constant /kJ mol ⁻¹ nm ⁻²
C1-C2	0.13465	517328.2
C1-C3	0.15049	324286.9
C1-H1	0.10837	335078.4
C3-O1	0.12350	688553.4
C3-O2	0.12939	525860.0
O2-H3	0.11939	289030.3

Table S11. Force constant of anionic maleic acid (angle)

angle	angle/degree	force constant /kJ mol ⁻¹ rad ⁻²
C1-C2-H2	116.1246	494.282

C1-C2-H4	132.2323	571.318
C2-C1-H1	114.2489	493.774
C2-C1-C3	135.8351	492.526
H1-C1-C3	109.9161	428.656
H2-C2-C4	111.6432	449.340
H1-C1-C3	111.8575	513.520
C3-O2-H3	110.8496	1456.775
O1-C3-O2	125.0717	1529.762

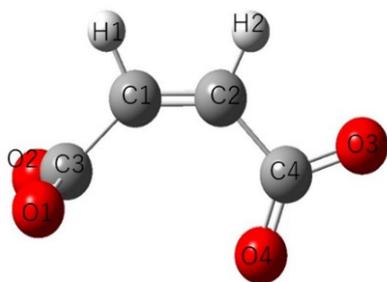


Table S12. Force constant of dianionic maleic acid (bond)

bond	length/nm	force constant /kJ mol ⁻¹ nm ⁻²
C1-C2	0.13482	507012.2
C1-C3	0.15281	210439.4
C1-H1	0.10937	307529.8
C2-C4	0.15257	213489.4
C2-H2	0.10897	315751.6
C3-O1	0.12587	603928.1
C4-O3	0.12727	525871.8
C4-O4	0.12529	591943.4

Table S13. Force constant of dianionic maleic acid (angle)

angle	angle/degree	force constant /kJ mol ⁻¹ rad ⁻²
C1-C2-H2	116.1246	494.282
C1-C2-H4	132.2323	571.318
C2-C1-H1	114.2489	493.774

C2-C1-C3	135.8351	492.526
H1-C1-C3	109.9161	428.656
H2-C2-C4	111.6432	449.340
C1-C3-O1	115.4693	1400.531
O1-C3-O2	128.5353	1133.808
C2-C4-O3	113.1595	986.284
C2-C4-O4	119.0152	873.808
O3-C4-O4	127.8254	1160.736

Table S14. Force constant of dianionic maleic acid (dihedral)

dihedral	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅
C2-C1-C3-O1, C2-C1-C3-O2	-5.8576	0.0000	12.552	0.0000	0.0000	0.0000
C1-C2-C4-O3, C1-C2-C4-O4	5.8576	0.0000	-12.552	0.0000	0.0000	0.0000

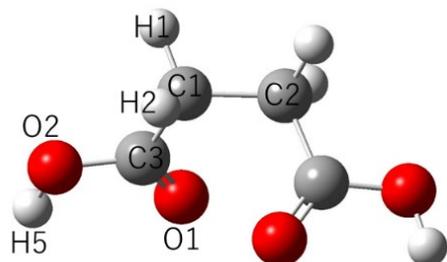


Table S15. Force constant of neutral succinic acid (bond)

bond	length/nm	force constant /kJ mol ⁻¹ nm ⁻²
C1-C2	0.151254	272808.7
C1-H1	0.108760	324714.7
C1-H1	0.109004	320395.2
C1-C3	0.150236	267981.5
C3-O1	0.121243	732561.0
C3-O2	0.134622	345872.2
O2-H5	0.097030	470616.5

Table S16. Force constant of neutral succinic acid (angle)

angle	angle/degree	force constant /kJ mol ⁻¹ rad ⁻²
H1-C1-C2	111.513	451.484
H2-C1-C2	110.537	433.721
H1-C1-H2	107.001	394.909
H1-C1-C3	108.500	422.480
H2-C1-C3	107.417	409.033
C2-C1-C3	111.670	724.619
C1-C3-O1	125.374	871.490
C1-C3-O2	111.583	879.809
O3-C3-O2	123.034	1066.086
C3-O2-H5	106.674	416.427

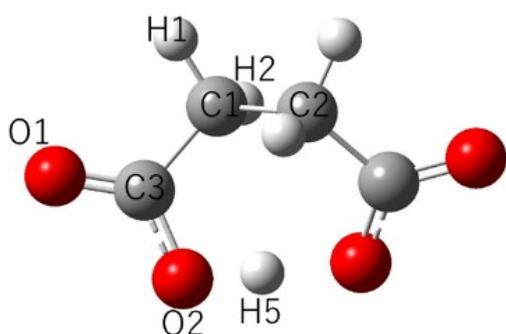


Table S17. Force constant of anionic succinic acid (bond)

bond	length/nm	force constant /kJ mol ⁻¹ nm ⁻²
C1-C2	0.153282	315517.3
C1-H1	0.108667	329777.3
C1-H1	0.109226	319349.9
C1-C3	0.151666	385538.5
C3-O1	0.122597	633841.0
C3-O2	0.131489	472378.2
O2-H5	0.108657	462750.4

□

Table S18. Force constant of anionic succinic acid (angle)

angle	angle/degree	force constant /kJ mol ⁻¹
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		rad ²
H1-C1-C2	110.024	481.704
H2-C1-C2	109.458	461.869
H1-C1-H2	107.349	394.700
H1-C1-C3	106.890	469.148
H2-C1-C3	107.683	418.029
C2-C1-C3	115.129	518.159
C1-C3-O1	121.628	788.302
C1-C3-O2	116.086	1041.276
O3-C3-O2	122.284	1073.169
C3-O2-H5	108.823	539.297

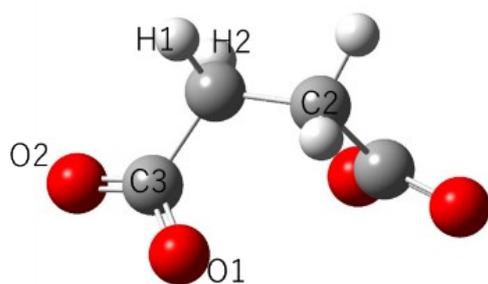


Table S19. Force constant of dianionic succinic acid (bond)

bond	length/nm	force constant /kJ mol ⁻¹ nm ⁻²
C1-C2	0.151555	285889.9
C1-H1	0.10947	313135.5
C1-H1	0.108816	318252.5
C1-C3	0.153568	277270.5
C3-O1	0.126069	984203.3
C3-O2	0.126286	539840.0

Table S20. Force constant of dianionic succinic acid (angle)

angle	angle/degree	force constant /kJ mol ⁻¹ rad ²
H1-C1-C2	109.998	502.782

H2-C1-C2	110.132	462.296
H1-C1-H2	106.791	487.255
H1-C1-C3	106.742	745.996
H2-C1-C3	108.146	455.034
C2-C1-C3	114.687	826.926
C1-C3-O1	117.545	969.208
C1-C3-O2	116.128	978.581
O3-C3-O2	126.294	1327.996
