Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Mechanical Properties of Anhydrous Oxalic Acid and Oxalic Acid Dihydrate

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Table S1. Bond distances in oxalic acid dihydrate (in Å).

Bond	Exp.[1] (X-Ray)	Exp.[2] (Neutron)	DFT
Oxalic acid molecule $(COOH)_2$			
C1—C1$^{\#}$	1.538	1.536	1.555
C1—O1	1.285	1.291	1.286
C1—O2	1.212	1.212	1.241
O1—H1	0.89	1.026	1.125
Water molecule H_2O			
O3—H2	0.84	0.964	0.992
O3—H3	0.79	0.956	0.988
Hydrogen bonds (D-H···A)			
H1···O3	1.63	1.480	1.315
O1- - -O3	2.512	2.506	2.439
H2···O2	2.03	1.917	1.753
O3- - - O2	2.864	2.864	2.722
H3···O2	2.17	1.979	1.787
O3- - -O2	2.883	2.881	2.725

Table S2. Bond angles in oxalic acid dihydrate (in deg.).

Angle	Exp.[1] (X-Ray)	Exp.[2] (Neutron)	DFT
O1—C1—O2	126.8	126.6	126.76
O1—C1—C1$^{\#}$	112.1	112.4	113.39
O2—C1—C1$^{\#}$	121.1	121.0	119.85
C1—O1—H1	114.3	114.4	114.00
Water molecule H_2O			
H2—O3—H3	101.5	105.9	105.91
Hydrogen bonds (D-H···A)			
O1—H1···O3	177.4	179.3	176.74
H1···O3—H2	113.6	112.8	111.97
O3—H2···O2	171.0	166.9	165.85
H2···O2—C1	124.8	122.8	122.91
O3—H3···O2	150.2	156.6	156.59
H3···O2—C1	130.9	129.5	129.12

Table S3. Bond distances in the α and β polymorphic forms of anhydrous oxalic acid (in Å).

Material	α-Oxalic acid		β-Oxalic acid	
Source	Exp.[3]	Calc.	Exp.[3]	Calc.
C1-C1$^{\#}$	1.537	1.550	1.537	1.544
C1-O1	1.207	1.225	1.222	1.230
C1-O2	1.306	1.307	1.290	1.306
O2-H1	0.931	1.013	0.95	1.027
O1- - -O2	2.652	2.603	2.702	2.685

Table S4. Bond angles in the α and β polymorphic forms of anhydrous oxalic acid (in deg.).

Material	α-Oxalic acid		β-Oxalic acid	
Source	Exp.[3]	Calc.	Exp.[3]	Calc.
O1-C-O2	126.92	126.77	126.67	126.32
C1-O2-H1	107.1	113.93	108.0	109.76
O1-C1-C1$^{\#}$	122.5	122.43	120.28	121.06
O2-C1-C1$^{\#}$	110.57	110.80	113.05	111.87
O2-H1···O1	146.0	156.50	174.0	177.04

Table S5. Displacement of some of the most intense reflections in the X-ray powder diffraction pattern of oxalic acid dihydrate under the effect of external pressures directed along U_{min}^{L}. The 2θ and d values associated to the XRD pattern of oxalic acid dihydrate at zero pressure are also given. The values of 2θ and d associated with each reflection [hkl] are given degrees and Å, respectively.

[hkl]	2θ (P=0)	d(P=0)	Δ(0.0-0.047)	Δ(0.047-0.095)	Δ(0.095-0.161)	Δ(0.161-0.212)	Δ(0.212-0.280)	Δ(0.280-0.327)
[002]	15.782	5.611	-0.013	-0.018	-0.025	-0.023	-0.025	-0.013
[-202]	30.807	2.900	0.059	0.053	0.038	0.040	0.042	0.048
[112]	35.408	2.553	-0.057	-0.027	-0.019	-0.016	-0.014	0.001
[104]	38.813	2.318	0.003	0.004	0.001	0.000	0.002	0.029
[-104]	31.804	2.811	0.008	0.000	-0.008	-0.006	-0.010	-0.026
[113]	40.616	2.219	-0.026	-0.019	-0.014	-0.013	-0.011	0.004
[011]	26.406	3.373	-0.104	-0.078	-0.054	-0.045	-0.043	-0.044
[100]	15.134	5.849	0.121	0.123	0.101	0.100	0.117	0.232
[-204]	38.636	2.329	0.028	0.020	0.010	0.011	0.009	-0.006
[014]	41.036	2.198	-0.032	-0.027	-0.022	-0.019	-0.019	-0.017
[-102]	19.041	4.657	0.056	0.040	0.020	0.023	0.018	-0.012
[202]	37.979	2.367	0.030	0.032	0.026	0.025	0.031	0.083
[110]	29.494	3.026	-0.060	-0.044	-0.030	-0.025	-0.023	-0.017
[-1-11]	29.563	3.019	-0.060	-0.045	-0.032	-0.026	-0.025	-0.027

Table S6. Displacement of some of the most intense reflections in the X-ray powder diffraction pattern of α-oxalic acid under the effect of external pressures directed along U_{min}^{L}. The 2θ and d values of associated to the XRD pattern of α-oxalic acid at zero pressure are also given. The values and increments of 2θ and d associated with each reflection [hkl] are given degrees and Å, respectively.

[hkl]	2θ (P=0)	d(P=0)	Δ(0.0-0.455)	Δ(0.455-0.959)	Δ(0.959-1.411)	Δ(1.411-1.811)
[004]	60.245	1.5349	-0.036	-0.029	-0.030	-0.041
[420]	60.948	1.5189	0.022	0.027	0.032	0.060
[242]	64.015	1.4533	-0.011	-0.015	-0.013	-0.017
[112]	34.253	2.6158	-0.040	-0.033	-0.035	-0.046
[241]	57.820	1.5934	-0.007	-0.013	-0.011	-0.013
[020]	23.358	3.8052	-0.039	-0.062	-0.055	-0.076
[212]	41.800	2.1593	-0.010	-0.004	-0.004	-0.001
[040]	47.765	1.9026	-0.020	-0.031	-0.027	-0.038
[211]	32.868	2.7227	0.018	0.026	0.030	0.058
[220]	35.911	2.4987	0.016	0.014	0.019	0.038
[012]	31.396	2.8470	-0.061	-0.053	-0.054	-0.073
[221]	38.881	2.3144	0.005	0.004	0.007	0.018
[202]	40.007	2.2518	-0.009	-0.001	-0.002	0.004
[200]	26.888	3.3131	0.064	0.083	0.099	0.189
[022]	37.616	2.3893	-0.043	-0.043	-0.042	-0.057
[201]	30.638	2.9157	0.027	0.040	0.045	0.087
[111]	22.927	3.8758	-0.022	-0.019	-0.018	-0.018

Table S7. Displacement of some of the most intense reflections in the X-ray powder diffraction pattern of β-oxalic acid under the effect of external pressures directed along U_{min}^{L}. The 2θ and d values of associated to the XRD pattern of β-oxalic at zero pressure are also given. The values and increments of 2θ and d associated with each reflection [hkl] are given in degrees and Å, respectively.

[hkl]	2θ (P=0)	d(P=0)	Δ(-0.157-(-0.097))	Δ(-0.097-0.0)	Δ(0.0-1.124)	Δ(0.124-0.210)
[040]	61.872	1.4984	-0.023	0.001	-0.011	0.016
[-2-32]	62.121	1.4930	0.009	0.002	0.020	0.028
[002]	36.622	2.4518	0.049	0.007	-0.002	0.017
[-1-11]	24.743	3.5954	0.055	0.006	0.083	0.082
[012]	39.686	2.2693	0.034	0.006	-0.004	0.017
[-2-12]	42.955	2.1039	0.054	0.004	0.074	0.059
[020]	29.789	2.9968	-0.047	0.002	-0.022	0.033
[-2-11]	37.314	2.4079	0.005	-0.002	0.001	-0.011
[021]	35.064	2.5571	-0.014	0.004	-0.015	0.025
[011]	23.421	3.7953	0.023	0.008	-0.013	0.032

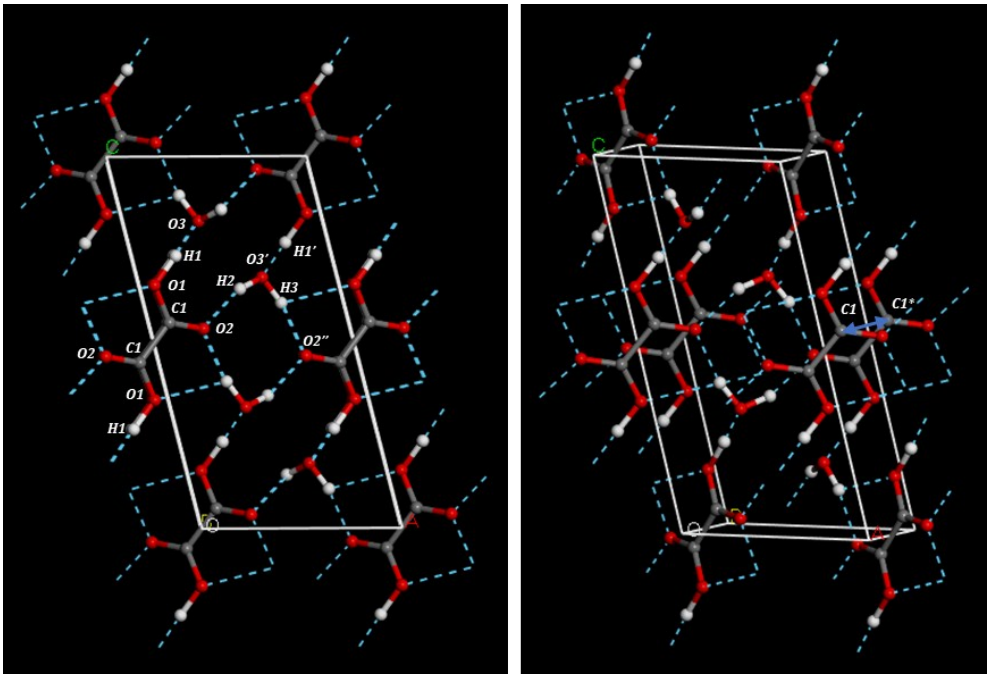

Figure S1. Atom numbering convention employed for oxalic acid dihydrate crystal structure.

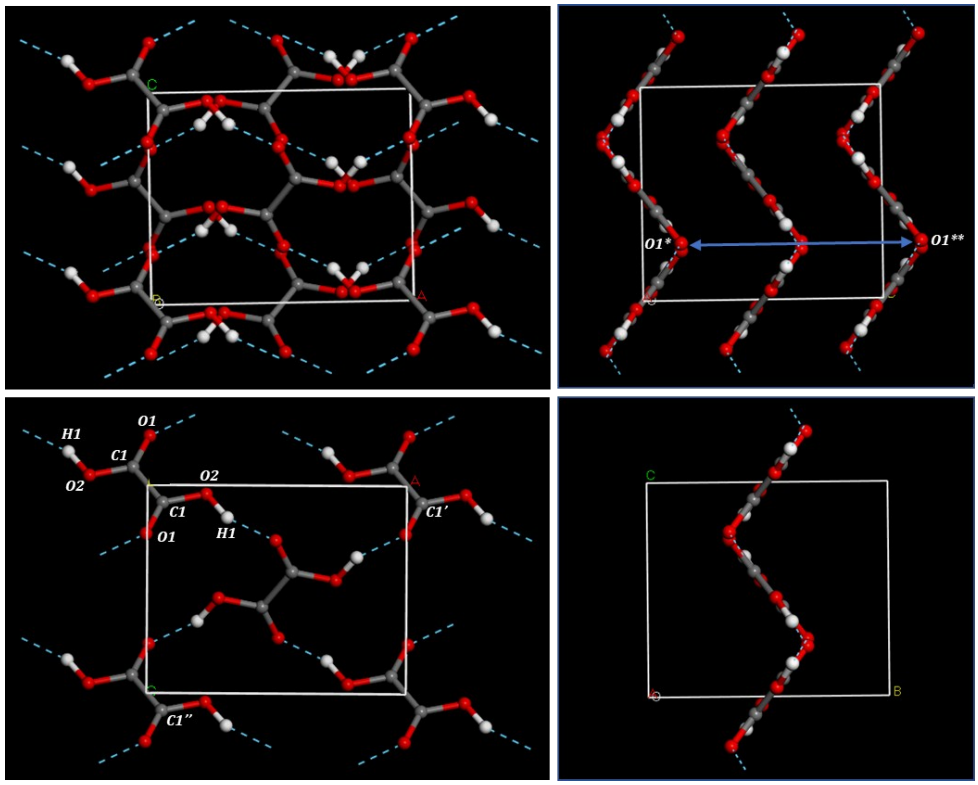

Figure S2. Atom numbering convention employed for α-oxalic acid crystal structure.

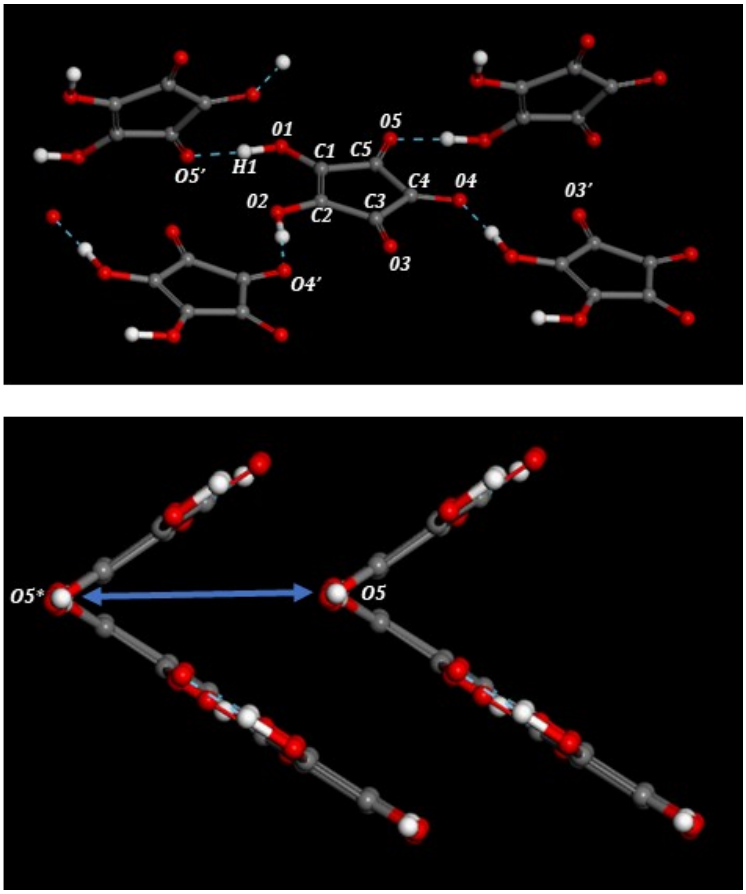

Figure S3. Atom numbering convention employed for β-oxalic acid crystal structure.

References

1 T. M. Sabine, G. W. Cox and B. M. Craven, *Acta Crytallogr. B*, 1969, 25, 2437.

2 R. G. Delaplane and J. A. Ibers, *Acta Crytallogr. B*, 1969, **25**, 2423.

3 J. L. Derisen and P. H. Smit, *Acta Crystallogr. B*, 1974, **30**, 2240.