Supplementary Information

Thermal expansion and dimensionality of the hydrogen bond network:

a case study on dimorphic Oxalic acid

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Experimental

Generation of the C2 polymorphs

Crystalline Oxalic acid dihydrate was purchased from Loba Chemie. and used without further purification. Diffraction quality single crystals of **α**-C2 were produced by sublimation of crystalline Oxalic acid dihydrate under high vacuum[S1].

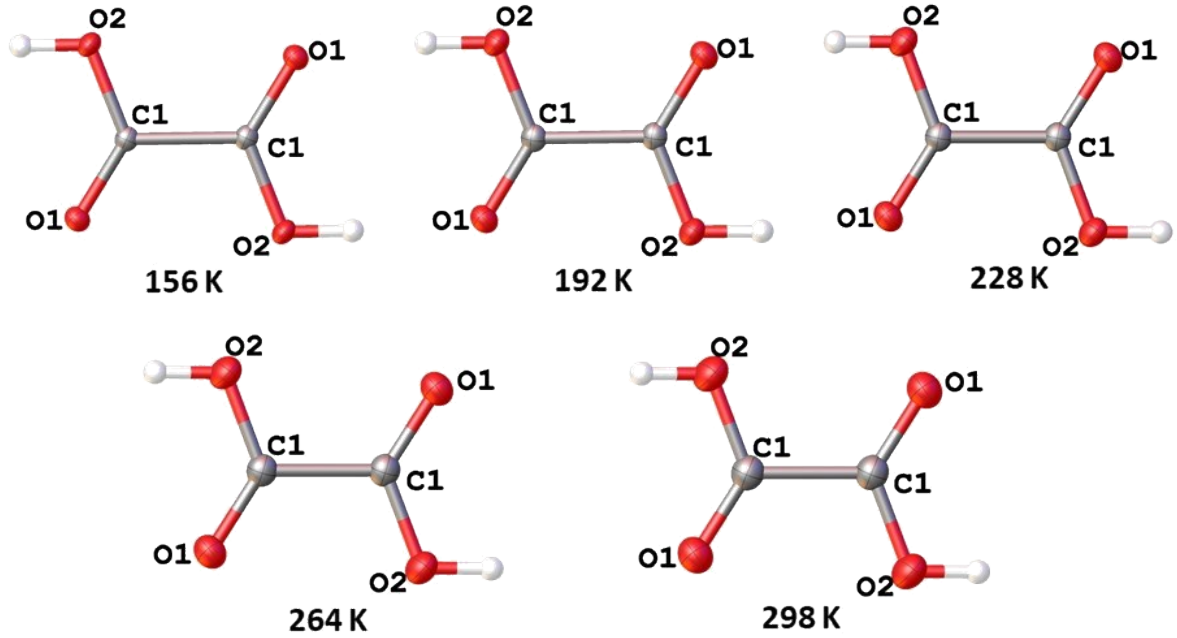
Variable temperature single-crystal diffraction data collection

A good diffraction quality crystal of **α**-C2 was chosen and considered for variable temperature single crystal diffraction measurements. The crystal is mounted on the diffractometer and slowly cooled to 156 K. Five sets of data were collected at temperatures 156 K, 192 K, 228 K, 264 K and 298 K. The temperature was controlled by cryojet using a liquid nitrogen flow. At every temperature, the crystal is maintained for 15 min under the liquid N_2 flow to allow proper temperature equilibration, before the commencement of the data collection. The cell parameters at different temperatures are used for calculation of the thermal expansion coefficients using the PASCal program[S2]. The cell parameters for the **β**-C2 phase were obtained from the cif files deposited in CCDC by Saha and coworkers[S3] regarding their report on alternation in thermal expansion coefficient of aliphatic dicarboxylic acids.

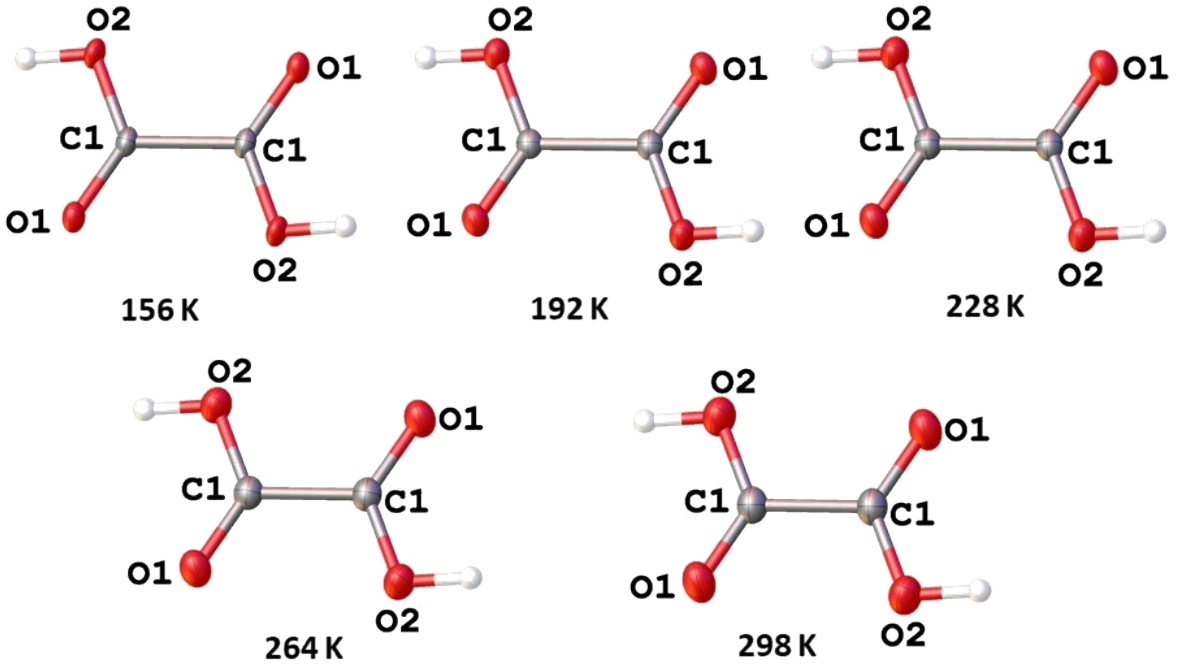
X-Ray crystallography

X-ray crystal data were collected on Xcalibur Eos, Oxford Diffraction Ltd. with Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption correction using spherical harmonics, implemented with SCALE3 ABSPACK scaling algorithm was applied[S4]. Structure solution and refinement were performed with SHELXS[S5] and SHELXL[S6], respectively. The hydrogen atoms of the carboxylic acid group have been placed from refinement with any restraint.

Figure S1: Thermal ellipsoid plot at 50% probability of (a) **α**-C2 (b) **β**-C2



(a)



(b)

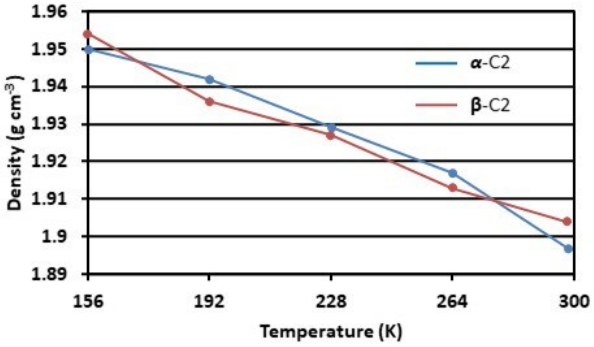
Table S1a: Crystallographic details of **α**-C2 at different temperatures					
Identification code	**α-C2-156**	**α-C2-192**	**α-C2-228**	**α-C2-264**	**α-C2-298**
Empirical formula	$C_2H_2O_4$	$C_2H_2O_4$	$C_2H_2O_4$	$C_2H_2O_4$	$C_2H_2O_4$
Formula weight	90.04	90.04	90.04	90.04	90.04
Temperature/K	156(2)	192(2)	228(2)	264(2)	298(2)
Crystal system	Orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*P*bca	*P*bca	*P*bca	*P*bca	*P*bca
a/Å	6.4914(5)	6.5045(6)	6.5224(11)	6.5399(11)	6.5678(8)
b/Å	6.0556(5)	6.0640(6)	6.0741(8)	6.0841(7)	6.0983(7)
c/Å	7.8020(5)	7.8072(9)	7.8268(12)	7.8385(12)	7.8715(8)
α/°	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	90	90	90	90	90
Volume/Å^3	306.69(4)	307.94(5)	310.08(8)	311.89(8)	315.27(6)
Z	4	4	4	4	4
ρ_{calc}mg/mm^3	1.95	1.942	1.929	1.917	1.897
m/mm^{-1}	0.201	0.2	0.199	0.198	0.196
F(000)	184	184	184	184	184
Crystal size/mm^3	0.44 × 0.4 × 0.38	0.44 × 0.4 × 0.38	0.44 × 0.4 × 0.38	0.44 × 0.4 × 0.38	0.44 × 0.4 × 0.38
Reflections collected	1063	814	823	834	872
Independent reflections	355 R_{int} = 0.0076 R_{sigma} = 0.0107	353 R_{int} = 0.0064 R_{sigma} =0.0087	352 R_{int} =0.0068 R_{sigma} =0.0107	354 R_{int} = 0.0072 R_{sigma} =0.0108	367 R_{int} = 0.0077 R_{sigma} = .0080
Data/restraints/parameters	355/0/32	353/0/32	352/0/32	354/0/33	367/0/33
Goodness-of-fit on F^2	1.109	1.173	1.126	1.122	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0661	R_1 = 0.0266, wR_2 = 0.0668	R_1 = 0.0284, wR_2 = 0.0683	R_1 = 0.0263, wR_2 = 0.0644	R_1 = 0.0254, wR_2 = 0.0661
Final R indexes [all data]	R_1 = 0.0273, wR_2 = 0.0672	R_1 = 0.0287, wR_2 = 0.0684	R_1 = 0.0299, wR_2 = 0.0692	R_1 = 0.0277, wR_2 = 0.0652	R_1 = 0.0281, wR_2 = 0.0671
Largest diff. peak/hole / e Å^{-3}	0.47/-0.21	0.45/-0.18	0.49/-0.18	0.42/-0.15	0.43/-0.13
CCDC Nos	**1854360**	**1854359**	**1854358**	**1854357**	**1854356**

Table S1b: Crystallographic details of **β** -C2 at different temperatures*					
Identification code	**β-C2-156**	**β-C2-192**	**β-C2-228**	**β-C2-264**	**β-C2-298**
Empirical formula	$C_2H_2O_4$	$C_2H_2O_4$	$C_2H_2O_4$	$C_2H_2O_4$	$CO_2H_{0.25}$
Formula weight	90.04	90.04	90.04	90.05	90.05
Temperature/K	156.00(10)	192.00(14)	228.00(14)	264.00(14)	298(2)
Crystal system	monoclinic	monoclinic	Monoclinic	monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	5.3170(15)	5.3369(9)	5.3333(12)	5.3385(15)	5.3266(13)
b/Å	5.9435(12)	5.9570(6)	5.9723(8)	5.9978(14)	6.0126(10)
c/Å	5.3988(14)	5.4144(9)	5.4187(11)	5.4376(15)	5.4456(13)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	116.21(3)	116.18(2)	115.99(3)	116.12(3)	115.80(3)
γ/°	90.00	90.00	90.00	90.00	90.00
Volume/Å^3	153.06(7)	154.47(4)	155.14(5)	156.33(7)	157.01(6)
Z	4	4	4	4	4
ρ_{calc}mg/mm^3	1.954	1.936	1.927	1.913	1.904
m/mm^{-1}	0.200	0.200	0.199	0.196	0.195
F(000)	89.0	92.0	92.0	89.0	89.0
Crystal size/mm^3	0.42 × 0.38 × 0.18	0.42 × 0.38 × 0.18	0.42 × 0.38 × 0.18	0.42 × 0.38 × 0.18	0.42 × 0.38 × 0.18
2Θ range for data collection	10.86 to 58.28°	8.52 to 58.44°	10.9 to 57.6°	8.5 to 58.04°	8.5 to 57.18°
Index ranges	-6 ≤ h ≤ 6, -8 ≤ k ≤ 5, -6 ≤ l ≤ 6	-5 ≤ h ≤ 6, -8 ≤ k ≤ 7, -7 ≤ l ≤ 7	-6 ≤ h ≤ 6, -8 ≤ k ≤ 7, -7 ≤ l ≤ 7	-6 ≤ h ≤ 7, -7 ≤ k ≤ 7, -7 ≤ l ≤ 6	-6 ≤ h ≤ 7, -8 ≤ k ≤ 7, -7 ≤ l ≤ 6
Reflections collected	732	764	749	789	776
Independent reflections	346 R(int) = 0.0262	349 R(int) = 0.0077	348 R(int) = 0.0095	362 R(int) = 0.0082	356 R(int) = 0.0071
Data/restraints/parameters	346/0/32	349/0/32	348/0/32	362/0/32	356/0/32
Goodness-of-fit on F^2	1.109	1.095	1.070	1.146	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1440	R_1 = 0.0303, wR_2 = 0.0802	R_1 =0.0320, wR_2 =0.0859	R_1 =0.0400, wR_2 =0.1048	R_1 =0.0342, wR_2 =0.0859
CCDC Nos	**929767**	**929768**	**929769**	**929770**	**929771**
***Information retrieved from Supplementary information of the paper[S3] and CSD.**					

Table S2: Hydrogen bond geometry parameters of (a) **α**-C2 (b) **β**-C2					
	α-C2-156	**α**-C2-192	**α**-C2-228	**α**-C2-264	**α**-C2-298
O2–H2···O1	2.685(1) 1.88(2) 152(2)	2.689(1) 1.87(2) 153(2)	2.696(1) 1.89(2) 152(9)	2.702(1) 1.89(1) 153(1)	2.714(1) 1.92(2) 152(2)
(a)					
	β-C2-156	**β**-C2-192	**β**-C2-228	**β**-C2-264	**β**-C2-298
O2–H2···O1	2.665(2) 1.77(3) 176(3)	2.676(2) 1.78(3) 176(2)	2.676(2) 1.76(3) 176(2)	2.680(2) 1.75(3) 175(2)	2.674(2) 1.72(3) 174(2)
(b)					

Table S3: (a) C···O interaction distances in **α**-C2 distances at different temperatures. (b) C···O and O···O interaction distances in **β**-C2 distances at different temperatures.					
	α-C2-156	**α**-C2-192	**α**-C2-228	**α**-C2-264	**α**-C2-298
C1···O1	2.853(1)	2.862(2)	2.874(1)	2.885(2)	2.899(2)
C1···O1	2.844(1)	2.853(1)	2.862(1)	2.874(2)	2.889(2)
(a)					
	β-C2-156	**β**-C2-192	**β**-C2-228	**β**-C2-264	**β**-C2-298
C1···O1	2.861(1)	2.871(1)	2.878(1)	2.891(2)	2.903(2)
C1···O1	2.986(1)	2.996(1)	3.006(1)	3.018(2)	3.027(2)
O1···O2	3.152 (2)	3.164 (2)	3.178 (2)	3.194 (2)	3.212 (2)
(b)					

Figure S2: Density Vs Temperature plot of **α**-C2 and **β**-C2.



Reference:

S1. J. L. Derissen and P. H. Smith, *Acta Crystallogr. Sect. B*, 1974, **30**, 2240—2242.

S2. M.J. Cliffe and A.L. Goodwin, *J. Appl. Cryst.*, 2012, **45**, 1321—1329.

S3. S. Bhattacharya, V. G. Saraswatula and B. K. Saha, *Cryst. Growth Des.*, 2016, **16**, 277–284.

S4. CrysAlisPro Agilent Technologies Version 1.171.37.31 (release 14-01-2014 CrysAlis171 .NET) (compiled Jan 14 2014,18:38:05)

S5. G. M. Sheldrick, *Acta Crystallogra. Sect A*, 2008, **64**, 112—122.

S6. G. M. Sheldrick, *Acta Crystallogra. Sect. C*, 2015, **71**, 3—8.