Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2009

Hydrogen migration in oxalic acid di-hydrate at high pressure?

Nicola Casati,* Piero Macchi,* Angelo Sironi

Department of Structural Chemistry and Inorganic Stereochemistry, University of Milan, via Venezian 21 20133 Milano Italy

Supporting Information

Details of the X-ray data collection and analysis

The experiments were conducted in a Merrill-Basset Diamond Anvil Cell (DAC), equipped with Be backing plates and with 0.6 mm diamond culets, using a standard Mo Kα source with a Bruker APEXII detector. A tungsten gasket, pre-indented to 0.15 mm, was filled with a pentane: isopentane mixture and a small ruby chip for the pressure measurement was placed together with two small crystals (both of dimensions ~0.1 x 0.1 x 0.1 mm), carefully pre-oriented in different directions.

As data were collected on two sides of the DAC, four different unit cells were indexed with SMART5.054[1] (two crystals for two DAC orientations except for the last pressure, where only one crystal could be indexed) and refined during the integration. They resulted slightly different in dimensions, due to the lower precision of the crystallographic direction parallel with the DAC main axis, but quite similar in volume: averaged values of the cell parameters are reported in Table S2. Data were integrated with SAINT6.45 using dynamic masks corrected for diamond overlaps to avoid integration in shaded areas.[2] Absorption correction for the DAC was performed with Absorb6.0[3] while crystal correction was performed with Sadabs.[4] The data were merged with Xprep and refined with Shelxl.[5]

Thermal parameters have been refined anisotropically except for the last pressure. Distances for the water H's have been set to neutron diffraction observation for this compound, while the acidic one has been fixed at each pressure according to the theoretical calculations.

Pressure was measured by the ruby fluorescence method,[6] using a JASCO TRS-300 spectrometer equipped with a Kr laser source.

Careful inspection of the CCD images did not reveal any change of the crystalline metrics. No supercell was detected (by inspecting reciprocal space with visualization programs and integrating the images using a multiple unit cell). No change in the systematic absences was found. Thus, the RP description in $P2_1/n$ remains valid at high pressure as well. Noteworthy, also powder neutron diffraction experiments carried out at lower pressure regimes[7] did not give evidence of any change in the crystal lattice.

Periodic DFT calculations were carried out using the program CRYSTAL06.[8] The functional B3LYP was used with a 6-31G(2d,2p) basis set. Geometries were optimised in the unit cell at constant cell volumes (but the individual cell parameters being free to vary). At each equilibrium geometry, frequencies zero point vibration, thermal energy and Entropy contributions were computed (using frequencies evaluated at Γ point). Internal energy, Enthalpy and Free Energy were then computed at Temperature of 298 K and pressure obtained from the experimental P/V fitting. PV work shown in Figure S3 was computed after 2nd order fitting of experimental values of P as a function of V and then evaluating $\int P(V)dV$.

The absence of imaginary frequencies at Γ point suggests that no breaking of the crystal symmetry is expected, in particular of the inversion centre (that would be difficult to establish from X-ray data only). In other regions of the Brillouin space, we did not compute frequencies (as this is not yet implemented in the CRYSTAL06 suite) to test possibility of super-cell formation. Anyway, the absence of super-cell reflections in the X-ray diffraction patterns suggests that in fact no change of the lattice metrics can be envisaged.

---

[1] Bruker (1997). SMART (Version 5.054) and SAINT (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.

[2] N. Casati, P. Macchi, A. Sironi, *J.Appl.Cryst.* **2007** *40* 628-630

[3] R. J. Angel, *J. Appl. Cryst.* **2004** *37*, 486–492.

[4] Siemens (1996). SADABS. Siemens Industrial Automation Inc., Madison,Wisconsin, USA.

[5] Sheldrick, G. M. *Acta Cryst.* **2008**, A*64*, 112-122.

[6] G. J. Piermarini, S. Block, J. D. Barnett, R. A. Forman, *J.Appl. Phys.* **1975** *46* 2774-2780.

[7] Putkonen, M.-L.; Feld, R.; Vettier, C.; Lehmann, M. S. Acta Cryst. 1985, B41, 77-79. See also Marshall, W. G.; Pulham C. R.; Allan, D. R. *Isis experimental reports* 14428, **2004**.

[8] Dovesi, R.; Saunders, V.R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N.M.; Bush, I.J.; D'Arco, P.; Llunell M. CRYSTAL06 User's Manual, University of Torino, Torino, **2006**.

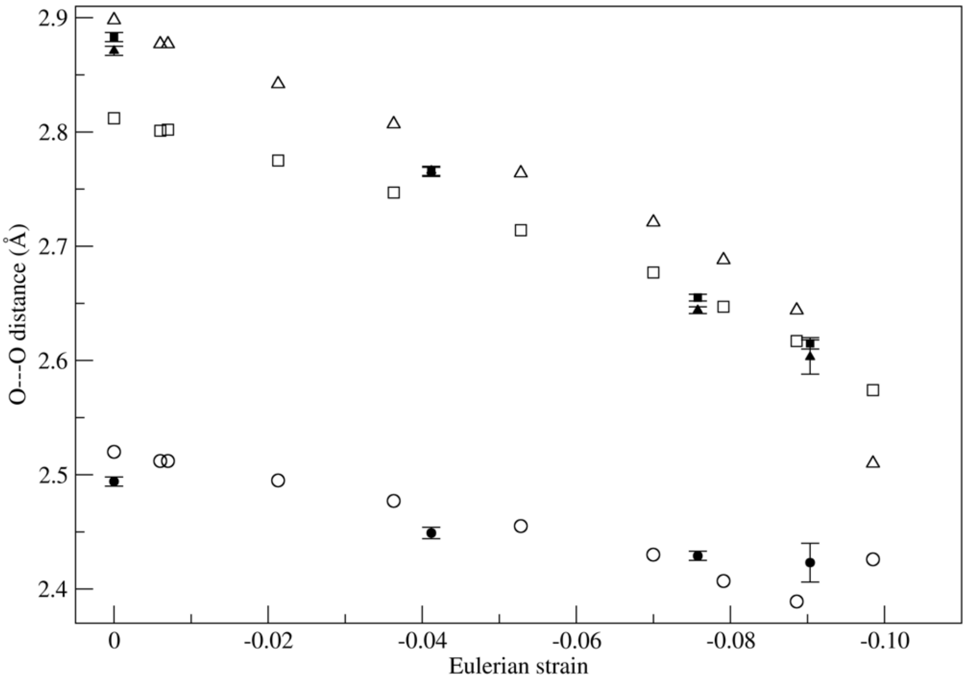

Figure S1. The evolution of the O---O intermolecular distances as a function of |ε|, computed from periodic DFT calculations (empty symbols) or observed from HP single crystal diffraction (filled symbols, with error bars). Circles refer to O1—Ow distances, triangles and squares to Ow---O2 distances (two independent contacts are present).

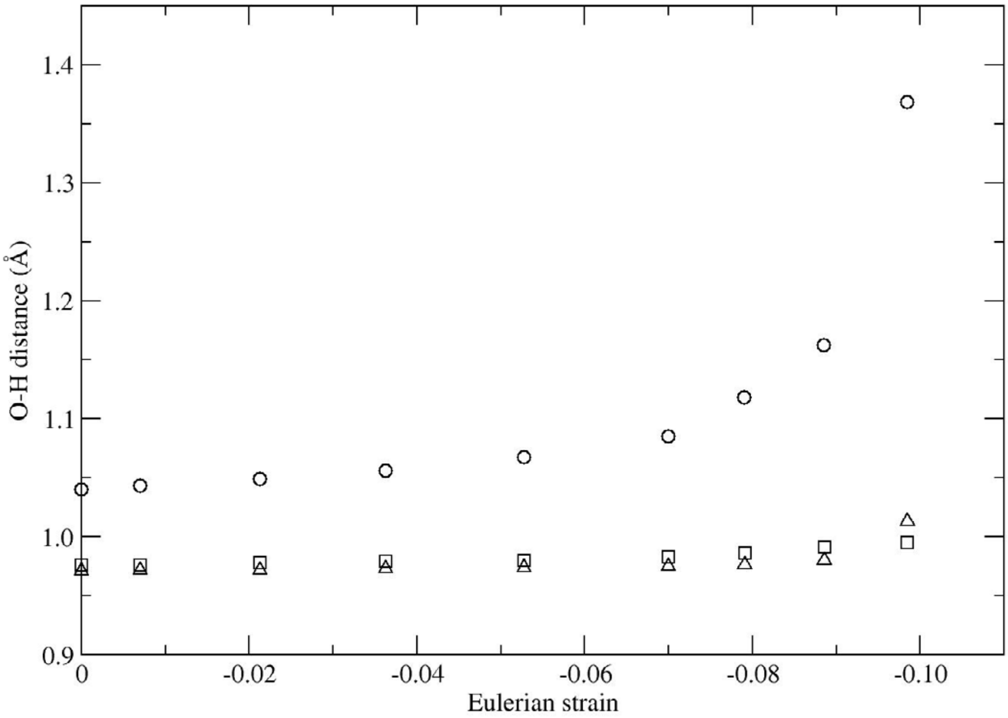

Figure S2. O-H distances, from periodic DFT calculations, as a function of |ε|. Circles refer to the O1-H1 bond, triangles and squares to the two Ow-H bonds.

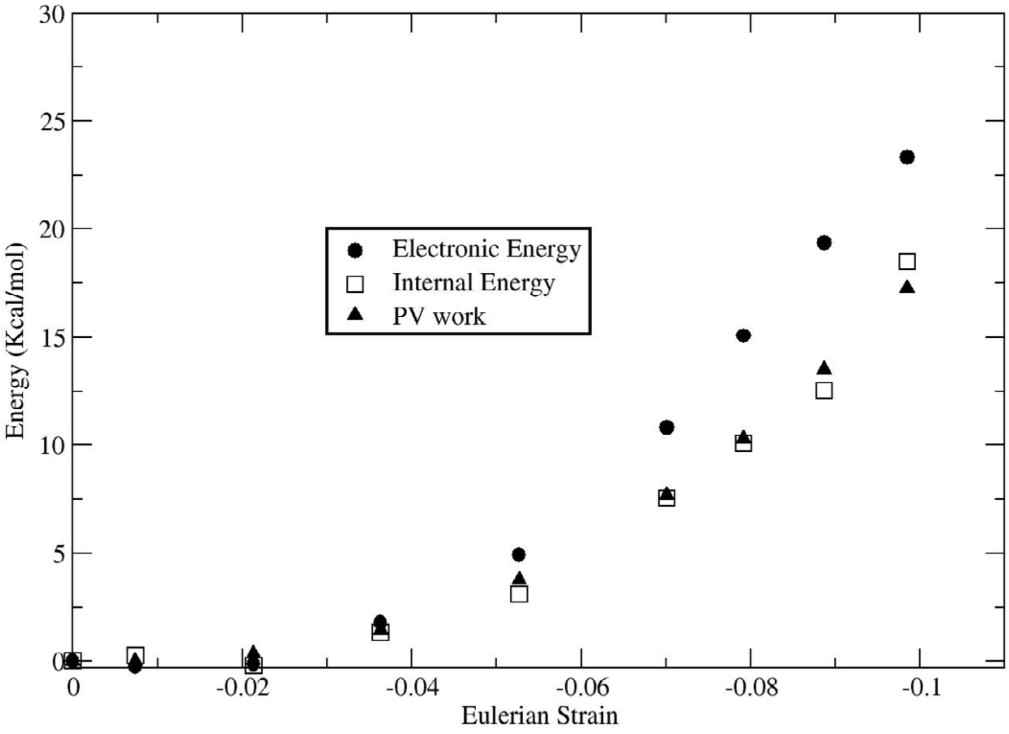

Figure S3. Electronic energy, internal energy and PV work of a unit cell (in kcal/mol) as a function of |ε|, from periodic DFT calculations or from observed pressures and volumes (PV work).

Table S1 Structural data of crystal structures of **1** optimised at several volume constraints. The first column refers to geometry optimisation without volume constraints, the second column to optimisation at volume constrained at the experimental determination at room pressure. All interatomic distances are in Å and refer to the labeling scheme of Figure 1 in the manuscript. At each point, frequencies calculations were carried out, computing internal energies and entropies (data reported in Figure 6). Based on experimental Pressure-Volume data, we report for each volume the simulated pressure.

	No constraints	**RP Volume**	**250**	**240**	**230**	**220**	**210**	**205**	**200**	**195**
a (Å)	6.2243	6.2449	6.2465	6.2305	6.1969	6.1320	6.0432	5.9634	5.8881	5.6423
b (Å)	3.5754	3.6206	3.5466	3.4309	3.3224	3.2264	3.1451	3.1220	3.0957	3.0885
c (Å)	11.8069	11.8370	11.8073	11.7420	11.6787	11.6107	11.5344	11.4760	11.4127	11.5903
β (°)	107.29	107.39	107.23	107.13	107.04	106.98	106.88	106.48	106.04	105.09
V (Å^3)	250.9	255.4	249.8	239.9	229.9	219.8	209.8	204.9	199.9	195.0
P (GPa)	-	0.001	0.06	0.45	1.13	2.11	3.37	4.09	4.89	5.76
ε	-0.006	0	-0.007	-0.021	-0.036	-0.053	-0.070	-0.079	-0.089	-0.098
C1-C1'	1.545	1.546	1.545	1.543	1.54	1.536	1.532	1.531	1.529	1.529
C1-O2	1.226	1.225	1.226	1.227	1.228	1.229	1.231	1.234	1.239	1.252
C1-O1	1.292	1.293	1.292	1.289	1.286	1.282	1.277	1.271	1.264	1.247
O1-H1	1.043	1.040	1.043	1.049	1.056	1.067	1.085	1.118	1.162	1.368
Ow-Hw1	0.976	0.976	0.976	0.978	0.979	0.98	0.983	0.986	0.991	0.995
Ow-Hw2	0.972	0.971	0.972	0.972	0.973	0.974	0.975	0.976	0.98	1.013
O1--Ow	2.512	2.520	2.512	2.495	2.477	2.455	2.43	2.407	2.389	2.426
Ow--O2	2.801	2.812	2.802	2.775	2.747	2.714	2.677	2.647	2.617	2.574
Ow--O2	2.877	2.898	2.877	2.842	2.807	2.764	2.721	2.688	2.644	2.51

Table S2 Structural data and refinement parameters for oxalic acid di-hydrated at different pressure values. All interatomic distances are in Å and and refer to the labeling scheme in Figure 1 of the manuscript. For all values the refined formula is $C_2O_6H_6$, M=126.07 , Spacegroup is P2_1/n, and T = 295 K.

P(GPa)	**0.0001**	**1.6**	**3.6**	**5.3**
a (Å)	6.1169(15)	5.983(3)	5.8093(7)	5.744(3)
b (Å)	3.6053(8)	3.331(4)	3.1657(9)	3.098(4)
c (Å)	12.050(3)	11.833(6)	11.676(4)	11.630(4)
β (°)	106.30(1)	106.15(1)	106.01(4)	106.15(1)
V (Å^3)	255.05(1)	226.5(5)	206.4(1)	198.8(1)
ε	0	-0.04118	-0.07576	-0.09035
ρ_{calc}(g/cm^3)	1.642	1.848	2.029	2.106
μ(mm^{-1})	0.174	0.196	0.215	0.223
θ range (°)	4.31/25.05	4.40/25.15	4.50/25.03	4.55/24.48
reflections measured/unique	2802/263	2447/218	2220/198	1086/113
Rint	0.0756	0.0796	0.0654	0.0635
R_1/wR_2 (all data)	0.0707/0.1325	0.0560/0.1043	0.0479/0.0984	0.0659/0.1624
data/parameters/restraints	263/43/2	218/43/2	198/43/2	113/23/2
min/max diff. peaks (e/Å^3)	-0.195/0.157	-0.208/0.180	-0.196/0.162	-0.285/0.256
C1-C1'	1.513(8)	1.518(9)	1.514(8)	1.532(29)
C1-O2	1.218(4)	1.226(4)	1.239(3)	1.257(16)
C1-O1	1.292(4)	1.278(5)	1.267(5)	1.268(7)
O1-H1	*1.040*	*1.059*	*1.106*	*1.365*
Ow-Hw1	*0.976*	*0.978*	*0.979*	*0.995*
Ow-Hw2	*0.972*	*0.972*	*0.973*	*1.013*
O1--Ow	2.494(4)	2.449(5)	2.429(4)	2.423(17)
Ow--O2	2.883(4)	2.765(4)	2.655(3)	2.615(5)
Ow--O2	2.871(4)	2.766(4)	2.644(3)	2.603(15)