

Supplementary

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Table S1. Crystal data, data collection and refinement of α , $\beta 1$, $\beta 2$ at 293, αD , $\beta 1D$ and $\beta 2D$.

Crystal structure	α	$\beta 1$	$\beta 2$	αD	$\beta 1D$	$\beta 2D$
Formula of compound	$C_4H_2O_4 \cdot 2H_2O$	$C_4H_2O_4 \cdot 2H_2O$	$C_4H_2O_4 \cdot 2H_2O$	$C_4D_2O_4 \cdot 2D_2O$	$C_4D_2O_4 \cdot 2D_2O$	$C_4D_2O_4 \cdot 2D_2O$
M_r	150.08	150.08	150.08	156.12	156.12	156.12
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c, No. 14	P2 ₁ /c, No. 14	P2 ₁ /c, No. 14	P2 ₁ /c, No. 14	P2 ₁ /c, No. 14	P2 ₁ /c, No. 14
a [Å]	7.9831(7)	7.0611(6)	6.9954(4)	7.9965(6)	7.0918(6)	7.0143(5)
b [Å]	3.8666(4)	5.4510(4)	5.4828(4)	3.8710(3)	5.4471(5)	5.4727(4)
c [Å]	11.0665(12)	9.8228(13)	9.7714(9)	11.0626(8)	9.8523(14)	9.7669(12)
β [°]	97.909(9)	115.867(8)	117.155(6)	98.042(7)	115.886(9)	117.175(8)
V [Å ³]	338.35(6)	340.20(6)	333.47(4)	339.07(4)	342.40(6)	333.54(5)
No. of formula units, Z	2	2	2	2	2	2
D_x [Mg m ⁻³]	1.473	1.465	1.495	1.529	1.514	1.555
F_{000}	156	156	156	156	156	156
X-Ray radiation	Cu K α	Cu K α	Mo K α	Mo K α	Mo K α	Mo K α
Wavelength, λ [Å]	1.54184	1.54184	0.71073	0.71073	0.71073	0.71073
μ [mm ⁻¹]	1.293	1.286	0.147	0.144	0.143	0.147
T [K]	293(2)	263(2)	150(2)	293(2)	263(2)	150(2)
Colour	colourless	colourless	colourless	colourless	colourless	colourless
Dimensions of crystal [mm]	0.32x0.29x0.09	0.35x0.30x0.25	0.31x0.27x0.08	0.34x0.30x0.15	0.42x0.30x0.25	0.42x0.30x0.25
No. of measured reflections	1314	1367	1775	1805	3065	3045

No. of unique reflections	688	690	880	894	925	905
R_{int} , [%]	0.0173	0.0116	0.0241	0.0158	0.0349	0.0624
No of ($F^2 > 2.0\sigma(F^2)$) reflections	571	635	677	621	591	609
Θ maximal [°]	75.02	74.97	30.16	30.37	30.23	30.11
$R[F^2 > 2\sigma(F^2)]$	0.0550	0.0366	0.041	0.043	0.0486	0.0451
$wR(F^2)$	0.1519	0.1044	0.1104	0.1045	0.1163	0.1155
Goof, S	1.088	1.058	1.092	1.042	1.087	1.100
No. of contributing reflections	688	690	880	894	925	905
No. of parameters	58	58	58	58	58	58
(Δ/σ) maximal	0.002	0.000	0.000	0.000	0.000	0.000
$(\Delta\rho)$ —maximal [e Å ⁻³]	0.198	0.218	0.252	0.206	0.185	0.232
$(\Delta\rho)$ —minimal Å ⁻³]	−0.225	−0.150	−0.230	−0.143	−0.224	−0.253

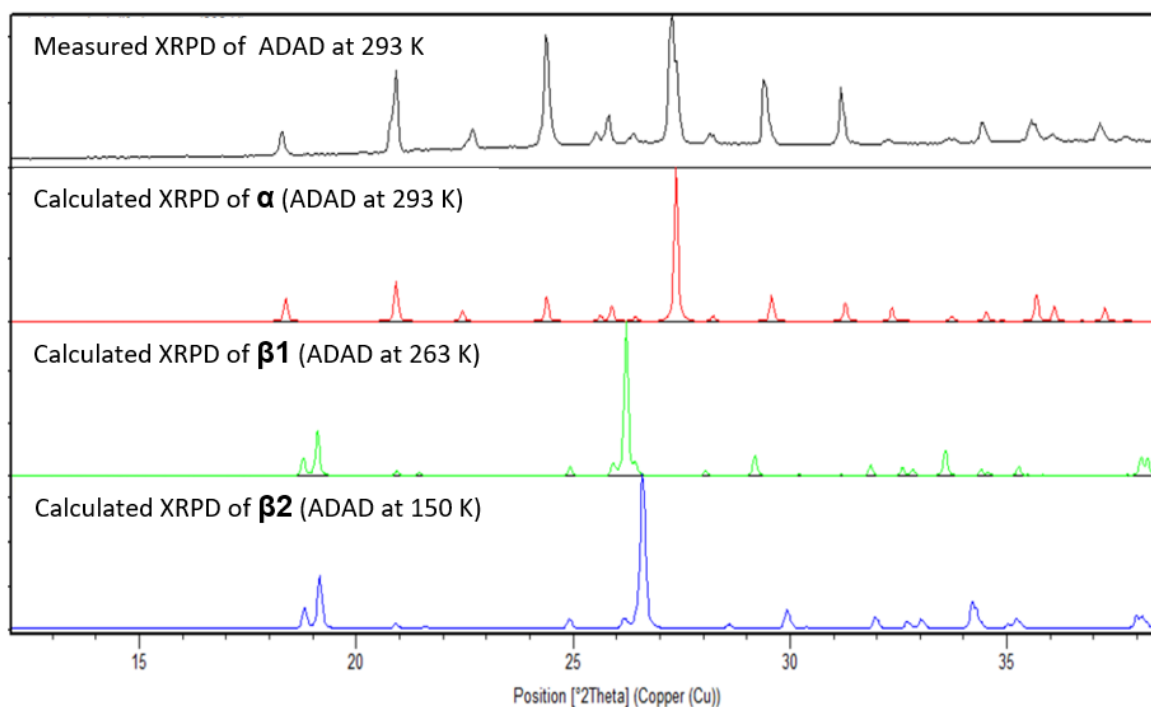


Figure S1. X-ray powder diffraction patterns (XRPD) of ADAD.

Table S2. Bond lengths and angles.

Bond length (Å)	α	β1	β2	αD	β1D	β2D
C1—C1 ⁱ	1.181(4)	1.185(2)	1.189(3)	1.183(3)	1.189(3)	1.191(3)
C1—C2	1.465(2)	1.4615(16)	1.465(2)	1.464(2)	1.461(2)	1.465(2)
C2—O2	1.204(2)	1.2091(16)	1.2143(18)	1.2046(19)	1.209(2)	1.2104(19)
C2—O1	1.285(3)	1.2892(17)	1.2991(19)	1.287(2)	1.294(2)	1.295(2)
O1—H1	0.95(4)	0.92(2)	0.91(3)	0.93(3)	0.94(3)	0.89(2)
O3—H2	0.77(5)	0.93(3)	0.81(3)	0.80(3)	0.81(3)	0.79(2)
O3—H3	0.99(3)	0.88(2)	0.97(2)	0.88(3)	0.89(3)	0.99(2)
Bonding angle (°)	α	β1	β2	αD	β1D	β2D
C1 ⁱ —C1—C2	176.2(3)	176.85(19)	176.7(2)	176.1(2)	176.7(3)	176.6(2)
O2—C2—O1	125.26(16)	125.66(11)	125.78(13)	125.45(14)	125.47(15)	125.73(15)
O2—C2—C1	120.42(17)	121.05(11)	120.87(13)	120.55(15)	121.32(16)	121.03(14)
O1—C2—C1	114.32(16)	113.29(11)	113.35(13)	114.00(15)	113.20(16)	113.24(15)
C2—O1—H1	110(2)	107.2(15)	112.2(17)	108.8(15)	110.9(15)	110.6(15)
H2—O3—H3	105(3)	109(2)	107(2)	112(3)	114(2)	107.1(18)

(i) $-x, -y, -z+2$

Table S3. Geometric parameters of hydrogen bonds in protic (upper table) and deuterated (lower table) ADAD .

α	X—H (Å)	H...Y (Å)	X...Y (Å)	X—H...Y (°)
O1—H1...O3	0.95(3)	1.60(3)	2.542(2)	172(3)
O3—H2...O2 ⁱ	0.77(5)	2.27(5)	2.904(2)	141(4)
O3—H2...O3 ⁱ	0.77(5)	2.59(4)	3.098(3)	125(3)
O3—H3...O2 ⁱⁱ	1.00(3)	1.81(3)	2.774(2)	163(3)
β1				
O1—H1...O3	0.91(2)	1.63(3)	2.5394(18)	174(3)
O3—H2...O2 ⁱ	0.93(3)	2.01(3)	2.8671(18)	152(3)

O3—H2...O3 ⁱ	0.93(3)	2.57(3)	3.1329(16)	120(2)
O3—H3...O2 ⁱⁱ	0.88(2)	1.92(2)	2.7724(16)	164(2)
β_2				
O1—H1...O3	0.92(3)	1.62(3)	2.5328(19)	176(2)
O3—H2...O2 ⁱ	0.81(3)	2.10(3)	2.8513(18)	154(3)
O3—H2...O3 ⁱ	0.81(3)	2.614(3)	3.1100(16)	121(2)
O3—H3...O2 ⁱⁱ	0.97(2)	1.80(2)	2.7654(16)	172(2)

αD	X—D (Å)	D...Y (Å)	X...Y (Å)	X—D...Y (°)
O1—D1...O3	0.93(2)	1.62(2)	2.552(2)	174(2)
O3—D2...O2 ⁱ	0.80(3)	2.20(3)	2.909(2)	149(2)
O3—D2...O3 ⁱ	0.80(3)	2.55(3)	3.088(3)	126(3)
O3—D3...O2 ⁱⁱ	0.87(3)	1.91(3)	2.782(2)	175(3)
β_{1D}				
O1—D1...O3	0.94(3)	1.61(3)	2.553(2)	179(4)
O3—D2...O2 ⁱ	0.81(3)	2.16(3)	2.882(2)	149(3)
O3—D2...O3 ⁱ	0.81(3)	2.59(3)	3.137(2)	126(3)
O3—D3...O2 ⁱⁱ	0.89(3)	1.91(3)	2.782(2)	167(3)
β_{2D}				
O1—D1...O3	0.89(3)	1.65(3)	2.542(2)	178(3)
O3—D2...O2 ⁱ	0.79(2)	2.13(2)	2.860(2)	153(2)
O3—D2...O3 ⁱ	0.79(2)	2.617(3)	3.103(2)	121(2)
O3—D3...O2 ⁱⁱ	0.99(2)	1.80(2)	2.770(2)	169(2)

(i) $1-x, 1/2+y, 3/2-z$; (ii) $x, -1/2-y, -1/2+z$;

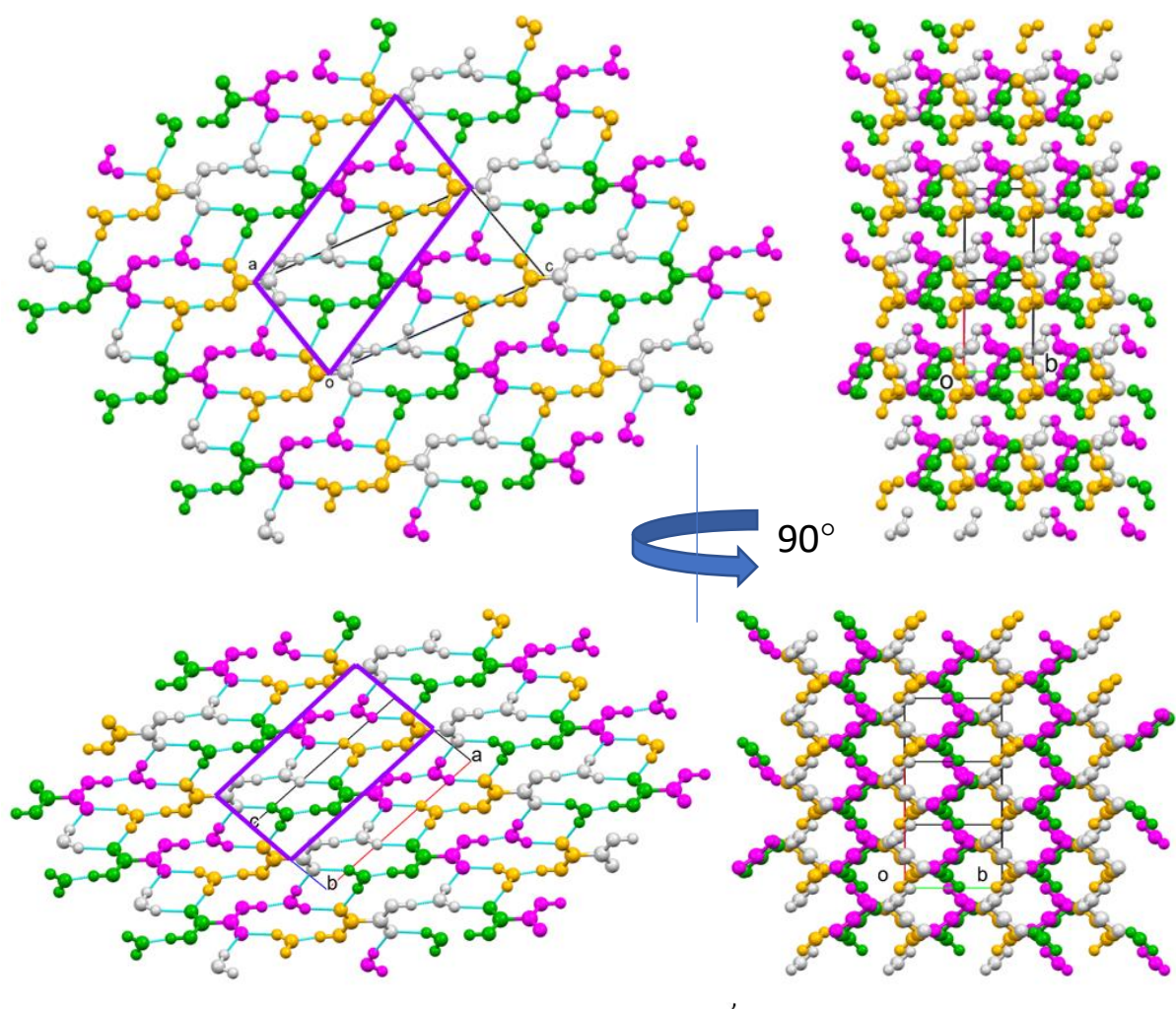


Figure S2. Presentation of crystal packing of molecules in OADH using colouring for symmetry operations: asymmetric unit is drawn in light grey, inversion symmetry in yellow, 2-fold screw axis.

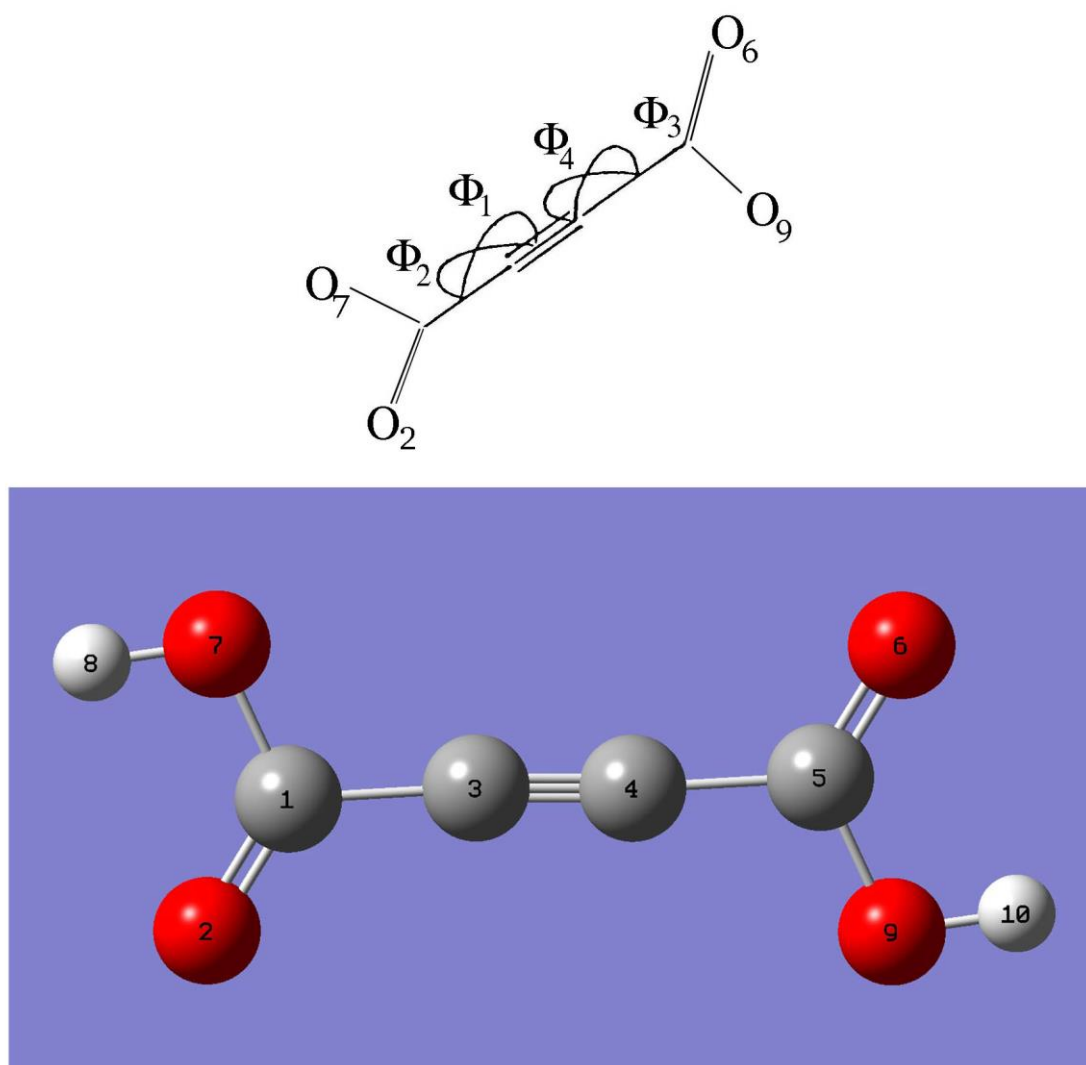


Figure S3. The definition and assignment of torsion angles and atom numbers used in QM calculations.

Table S4. Definition of internal coordinates in *trans* acetylenedicarboxylic acid. Atom numbering is shown in Supplementary Figure S3.

Deformations of bond stretching coordinates

1. $\Delta T = \Delta(C_3 \equiv C_4)$
2. $\Delta D_1 = \Delta(C_1=O_2)$
3. $\Delta D_2 = \Delta(C_5=O_6)$
4. $\Delta R_1 = \Delta(C_1 - C_3)$
5. $\Delta R_2 = \Delta(C_4 - C_5)$
6. $\Delta S_1 = \Delta(C_1 - O_7)$
7. $\Delta S_2 = \Delta(C_5 - O_9)$
8. $\Delta l_1 = \Delta(O_7 - H_8)$
9. $\Delta l_2 = \Delta(O_9 - H_{10})$
10. $\Delta \epsilon_1 = \Delta(C_1 - O_7 - H_8)$
11. $\Delta \epsilon_2 = \Delta(C_5 - O_9 - H_{10})$
12. $\Delta \eta_1 = \Delta(O_2 - C_1 - O_7)$
13. $\Delta \eta_2 = \Delta(O_6 - C_5 - O_9)$
14. $\Delta \kappa_1 = \Delta(O_2 - C_3 - C_1)$
15. $\Delta \kappa_2 = \Delta(O_6 - C_5 - C_4)$
16. $\Delta \lambda_1 = \Delta(\text{out of plane } C_1 - O_7 \text{ bending})$
17. $\Delta \lambda_2 = \Delta(\text{out of plane } C_5 - O_9 \text{ bending})$
18. $\Delta \Phi_1 = \Delta(\text{linear bending } O_2 - C_1 - C_3 - C_4 \text{ in the molecular plane})$
19. $\Delta \Phi_2 = \Delta(\text{linear bending } O_2 - C_1 - C_3 - C_4 \text{ perpendicular to the molecular plane})$
20. $\Delta \Phi_3 = \Delta(\text{linear bending } O_6 - C_5 - C_4 - C_3 \text{ in the molecular plane})$
21. $\Delta \Phi_4 = \Delta(\text{linear bending } O_6 - C_5 - C_4 - C_3 \text{ perpendicular to the molecular plane})$
22. $\Delta \tau_{OH_1} = \Delta(\text{torsion } H_8 - O_7 - C_1 - C_3)$
23. $\Delta \tau_{OH_2} = \Delta(\text{torsion } H_{10} - O_9 - C_5 - C_4)$
24. $\Delta \tau_{COOH} = \Delta(\text{torsion } O_6 - C_5 - C_4 - O_7 + \text{torsion } O_2 - C_1 - C_3 - O_9)$

Table S5. Definition of symmetrized coordinates for *trans* acetylenedicarboxylic acid with C_{2h} symmetry.

9 A_g

1. $S_1 = \Delta T$
2. $S_2 = \Delta D_1 + \Delta D_2$
3. $S_3 = \Delta R_1 + \Delta R_2$
4. $S_4 = \Delta S_1 + \Delta S_2$
5. $S_5 = \Delta l_1 + \Delta l_2$
6. $S_6 = \Delta \varepsilon_1 + \Delta \varepsilon_2$
7. $S_7 = \Delta \eta_1 + \Delta \eta_2$
8. $S_8 = \Delta \kappa_1 + \Delta \kappa_2$
9. $S_9 = \Delta \Phi_1 + \Delta \Phi_3$

3 B_g

10. $S_{10} = \Delta \lambda_1 - \Delta \lambda_2$
11. $S_{11} = \Delta \Phi_2 + \Delta \Phi_4$
12. $S_{12} = \Delta \tau OH_1 - \Delta \tau OH_2$

4 A_u

13. $S_{13} = \Delta \lambda_1 + \Delta \lambda_2$
14. $S_{14} = \Delta \tau OH_1 + \Delta \tau OH_2$
15. $S_{15} = \Delta \Phi_2 - \Delta \Phi_4$
16. $S_{16} = \Delta \tau COOH$

8 B_u

17. $S_{17} = \Delta D_1 - \Delta D_2$
18. $S_{18} = \Delta R_1 - \Delta R_2$
19. $S_{19} = \Delta S_1 - \Delta S_2$
20. $S_{20} = \Delta l_1 - \Delta l_2$
21. $S_{21} = \Delta \varepsilon_1 - \Delta \varepsilon_2$
22. $S_{22} = \Delta \eta_1 - \Delta \eta_2$
23. $S_{23} = \Delta \kappa_1 - \Delta \kappa_2$
24. $S_{24} = \Delta \Phi_1 - \Delta \Phi_3$

Table S6. Unscaled normal modes of *trans* acetylenedicarboxylic acid with C_{2h} symmetry with potential energy distribution (PED) among symmetrized coordinates calculated by BALGA[†] program are compared with the observed bands of crystal. Contributions greater than 10% are given. Torsional frequency of carboxyl groups is calculated as imaginary.

symmetry C_{2h}	observed Raman crystal 293 K	observed infrared crystal 295 K	calculated	PED (%)	approximate description
A_g	3402 2246 2004 br 1688,1649 1454,1445 1332,1288 758 609 415 212	inactive	2365 3761 1816 1374 1188 734 615 358 204	100 S ₅ 84 S ₁ + 16 S ₃ 89 S ₂ 45 S ₆ + 28 S ₄ + 19 S ₇ 46 S ₄ + 41 S ₆ 33 S ₇ + 22 S ₃ + 22 S ₄ 56 S ₈ + 35 S ₉ 49 S ₃ + 44 S ₇ 63 S ₉ + 36 S ₈	water sym. OH str. C≡C stretch. sym. O-H stretching C=O sym. str. COH bend.+C-O str. C-O str. + COH bend O=C-O scissor O=C-C bend. C-C str.+O=C-C sciss. in pl. CC≡CC bend.
B_g	3470 sh 808, 794 637 315,285	inactive	767 627 327	88 S ₁₀ 93 S ₁₂ 80 S ₁₁	water OH str out of plane C-O bend OH torsion out of pl.CC≡CC bend
A_u	inactive	3508 758 1071	767 614 120 35i	91 S ₁₃ 97 S ₁₄ 97 S ₁₅ 100 S ₁₆	water asym. OH str. out of plane C-O bend OH torsion o.of pl. CC≡CC bend COOH torsion
B_u	inactive	3382 1968 br 1647,1602 1435 1257,1271 994	3761 1823 1401 1196 986 599 542 81	100 S ₂₀ 87 S ₁₇ 35 S ₂₁ + 24 S ₁₉ + 23 S ₁₈ 52 S ₂₁ + 28 S ₁₉ + 15 S ₁₈ 55 S ₁₈ + 38 S ₁₉ 47 S ₂₂ + 35 S ₂₃ 46 S ₂₃ + 40 S ₂₂ 86 S ₂₄	water sym. OH str. antisym.O-H stretch. antisym.C=O sym. str COH bend.+C-O str. COH bend.+C-O str C-C str.+C-O str O=C-O scissor O=C-C bend in pl. CC≡CC bend.

[†] G. Keresztury, G. Jalsovszky J. Mol. Struct. 10 (1971) 304.

H. Rostkowski, L. Lapinski, M. Nowak Vib. Spectrosc. 49 (2009) 43.

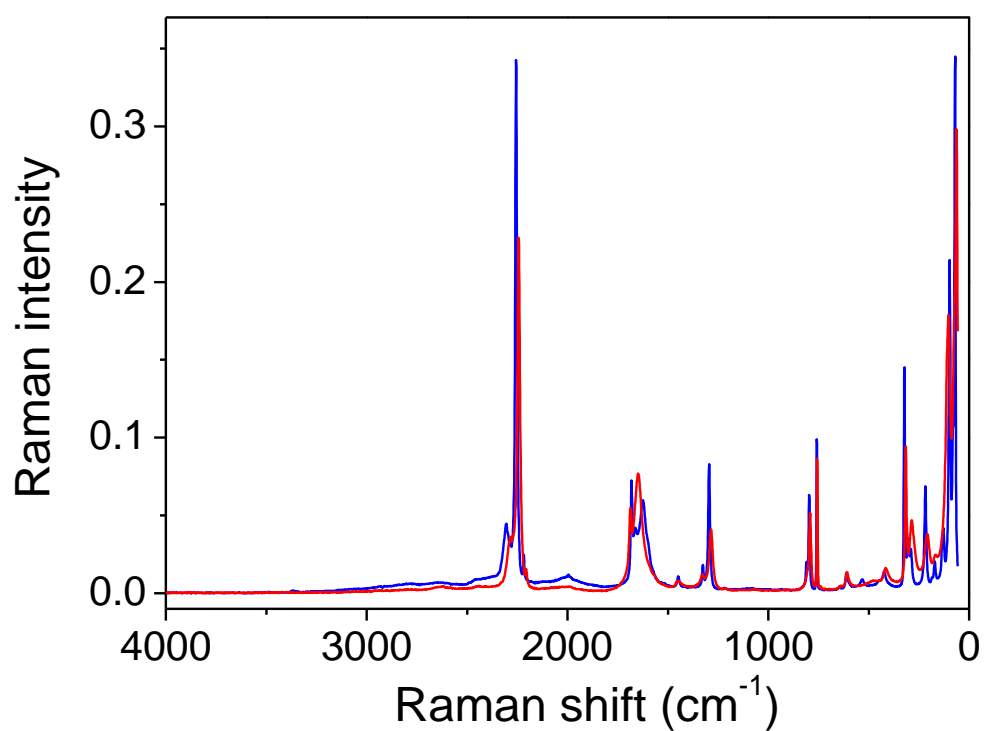


Figure S4. The FT-Raman spectrum of ADAD recorded at $T=25^{\circ}\text{C}$ (red line) and $T=-110^{\circ}\text{C}$ (blue line).

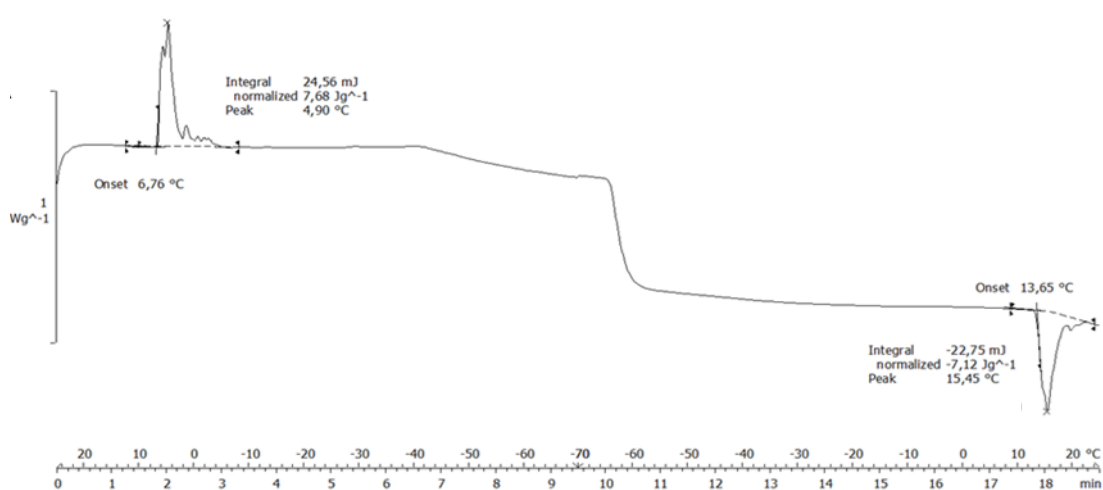


Figure S5. DSC curve of ADAD.

Additional X-ray data

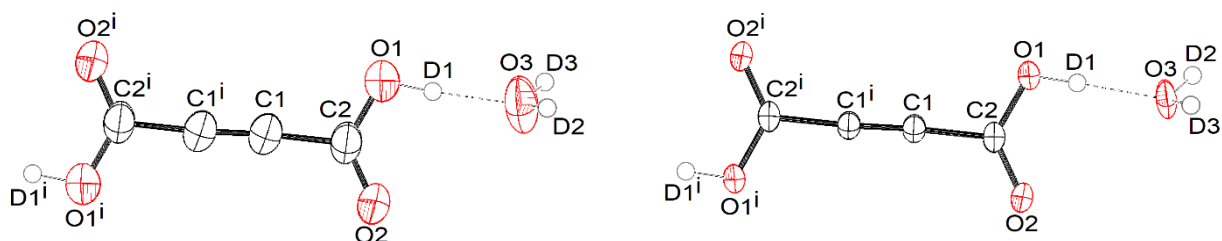


Figure S6. Ortep drawings with atom labelling scheme of water and acetylenecarboxylic acid molecules in α D (left) and β 2D (right) structure. Displacement ellipsoids are at 50% probability level. (i: $-x, -y, -z+2$).

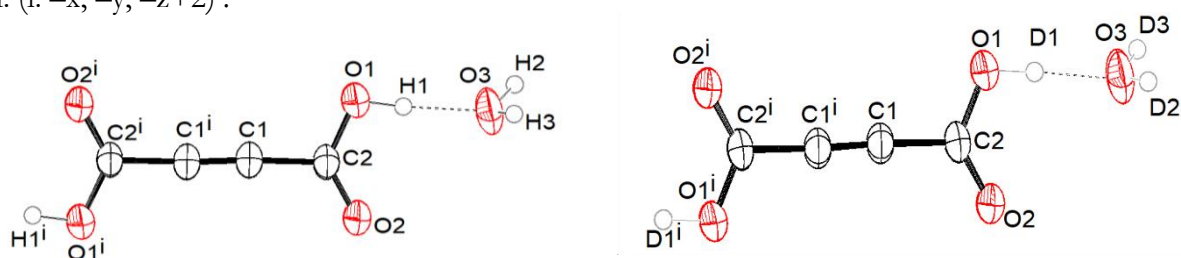


Figure S7. Ortep drawings with atom labelling scheme of water and acetylenecarboxylic acid molecules in β 1 (left) and β 1D (right) structure. Displacement ellipsoids are at 50% probability level. (i: $-x, -y, -z+2$).

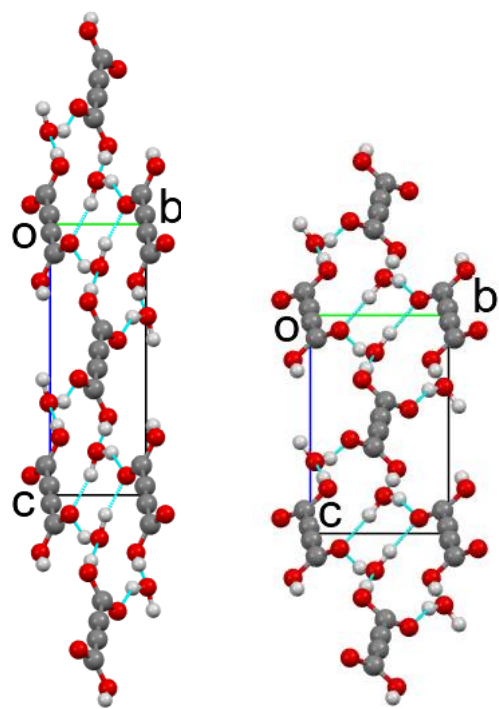


Figure S8. Drawings of molecular packing of α (left) and β_2 (right) structure viewed along a axis. Blue lines represent hydrogen bonds.

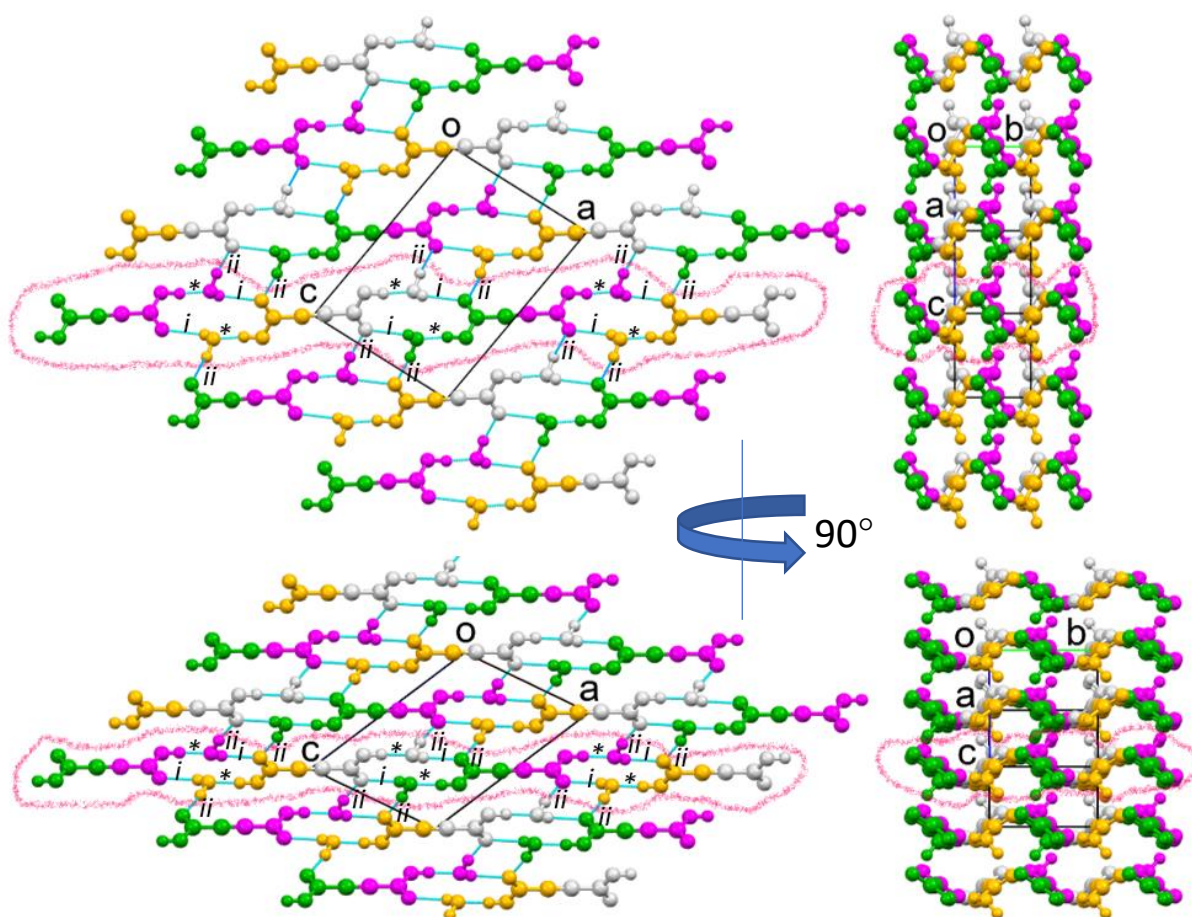


Figure S9. Presentation of crystal packing of molecules in ADAD using colouring for symmetry operations: asymmetric unit is drawn in light grey, inversion symmetry in yellow, 2-fold screw axis in green, and c glide plane in pink. Left drawings represent a view on structures of α (top) and β_2 (bottom) along b axis and right drawings a view on the structures rotated for 90° with b axis lying in plane of paper.

in green, and c glide plane in pink. Left drawings represent a view on structures of α (top) OXACDH28 and β (bottom) OXACDH29 along b axis and right drawings a view on the structures rotated for 90° with b axis lying in plane of paper. The purple lines represent unit cells after cell transformation on the same coordinate system.

OXACDH28, OXACDH29: [6]

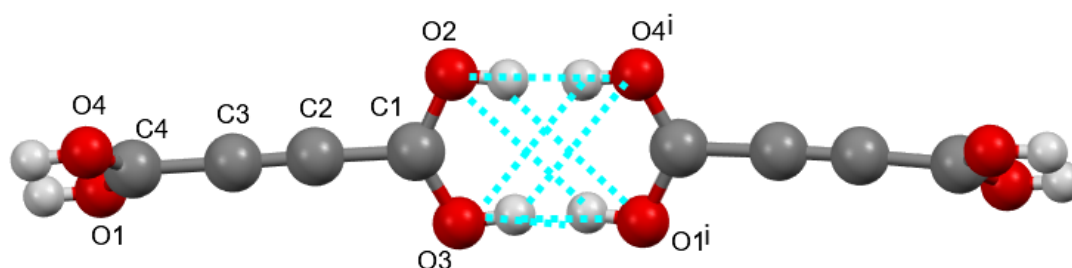


Figure S10: Presentation of molecules of acetylenedicarboxylic acid in anhydrous structure (ADCA) [32]. The lengths of bonds between carbon atoms in ADCA [(C2≡C3 1.188, C1–C2 1.454 and C3–C4 1.455 Å) are similar to that of ADAD. On the other hand, the bond lengths C1≈O2 1.262, C1≈O3 1.245, C4≈O1 1.259 and C4≈O4 1.246 Å and H atoms positions with 50% occupancy reflect that carboxyl groups in ADCA are disordered which is not the case in ADAD. The conformation of acid molecules in anhydrous structure also differs from that of hydrated. In ADAD molecules are centrosymmetric and nearly planar while in ADCA molecules are asymmetric and twisted with torsion angle O2–C1–C4–O4 of $\approx 60^\circ$. Hydrogen bonds between acid and water molecules in ADAD are significantly stronger than hydrogen bonds between acid molecules in ADCA (O3...Oⁱ 2.656 and O2...O4ⁱ 2.694 Å, $i: -1/2+x, 1.5-y, 1/2+z$). The structure of ADCA was determined also at high pressures from 0.18 up to 5.2 GPa) [32]. At high pressure the structure of ADCA remains to be disordered, with twisted molecules and hydrogen bonds of moderate strength.