Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information: Chiral aggregation hierarchy in high-pressure resolved 2-butanol and 2,3-butanediol

Marcin Podsiadło, Ewa Patyk and Andrzej Katrusiak*

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

*E-mail: katran@amu.edu.pl

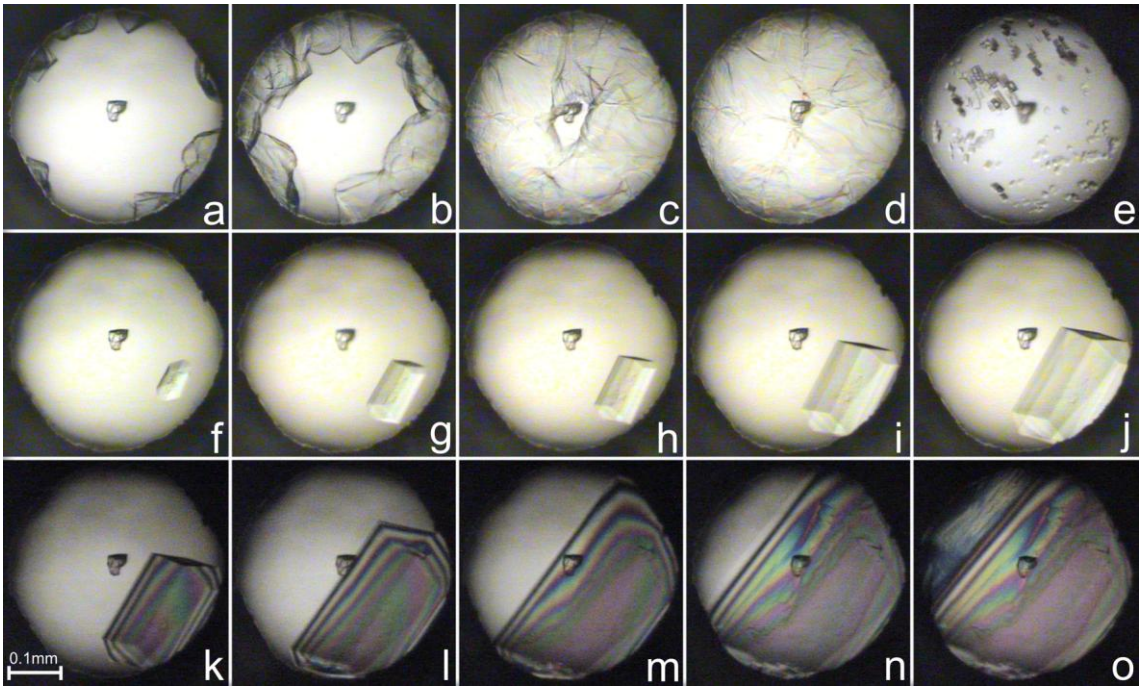

Figure S1. (±)-2-Butanol inside the DAC chamber: (a-d) isothermal freezing into polycrystalline mass at 295 K; (e) most of crystal grains melted at 360 K; (f) one crystal seed at 360 K and (g-n) its isochoric growth when cooled to 320 K; (o) the chamber nearly completely filled by the single-crystal at 295 K and 2.14 GPa. The ruby chip for pressure calibration lies at the central part of the DAC chamber. Photographs a-e and k-o were made in partly polarized light. The whole crystallization took 5 h.

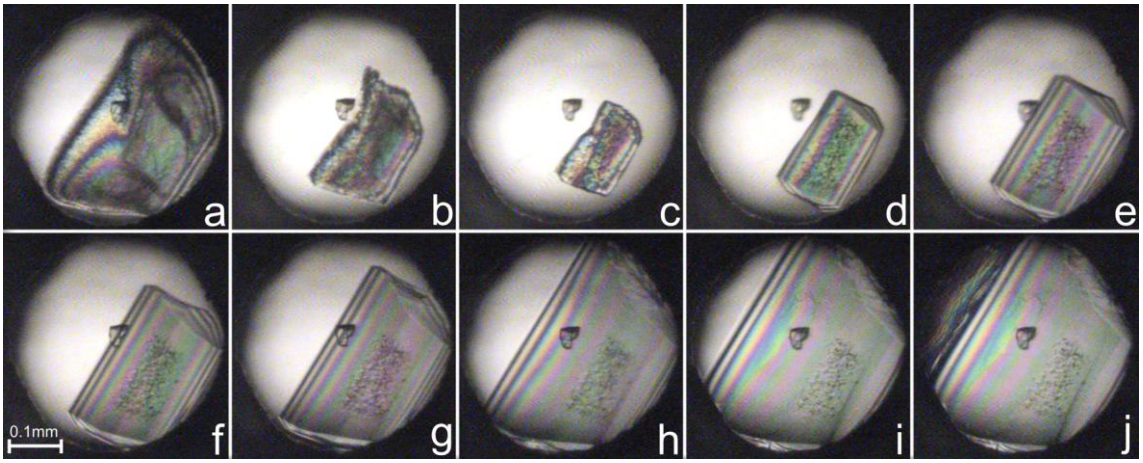

Figure S2. Isochoric 2-butanol single-crystal growth inside the DAC chamber (polarized-light mode): (a) one crystal seed at 450 K; (b) 480 K; (c) *ca*. 500 K after reducing the chamber volume; (d-i) the growing crystal on lowering temperature; (j) one crystal filling the whole DAC chamber at 2.33 GPa/295 K. The ruby chip is located as in Figure S1.

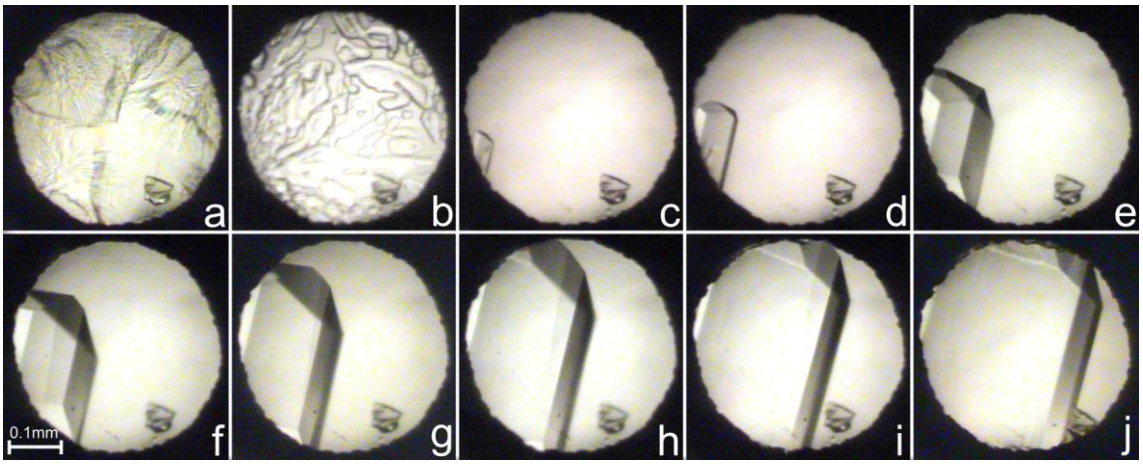

Figure S3. Stages of the 2,3-butanediol crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 295 K; (b) polycrystal-liquid equilibrium at 340 K; (c) one crystal seed at 350 K; (d-i) its growth on cooling to 300 K; and (j) the sample nearly filling the DAC chamber at 295 K and 0.43 GPa. The ruby chip for pressure calibration lies in the bottom part of the DAC chamber.

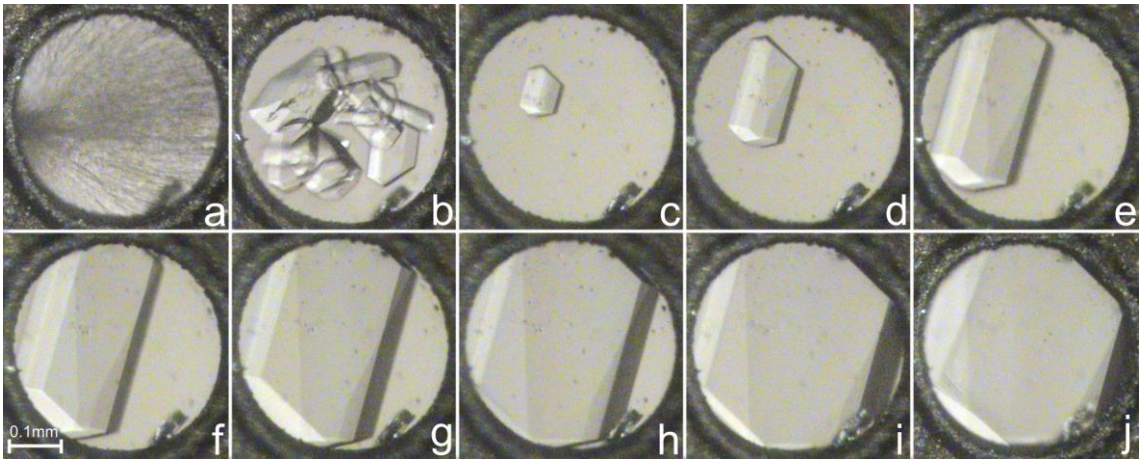

Figure S4. Stages of the 2,3-butanediol single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 295 K; (b) polycrystal-liquid equilibrium at 480 K; (c) one crystal seed at 500 K; (d-i) the single-crystal cooled to 410 K and (j) nearly filling the DAC chamber at 380 K and 0.72 GPa. The ruby chip for pressure calibration lies in the bottom part of the DAC chamber.

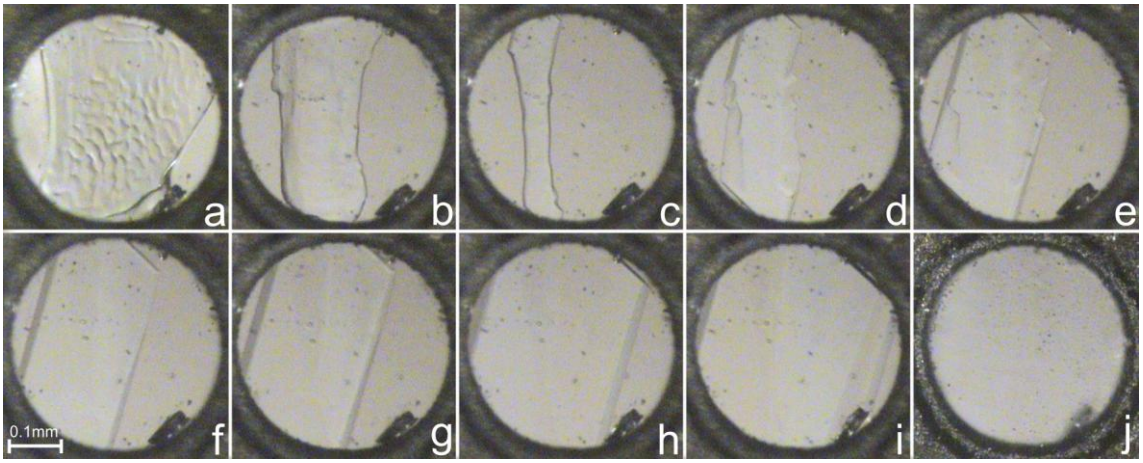

Figure S5. Isochoric 2,3-butanediol single-crystal growth inside the DAC chamber: (a) one crystal at 450 K; (b) 480 K; (c) *ca*. 530 K after reducing the chamber volume; (d-i) the growing crystal on lowering temperature; (j) one crystal filling the whole DAC chamber at 0.97 GPa/295 K. The ruby chip is located as in Figure S4.

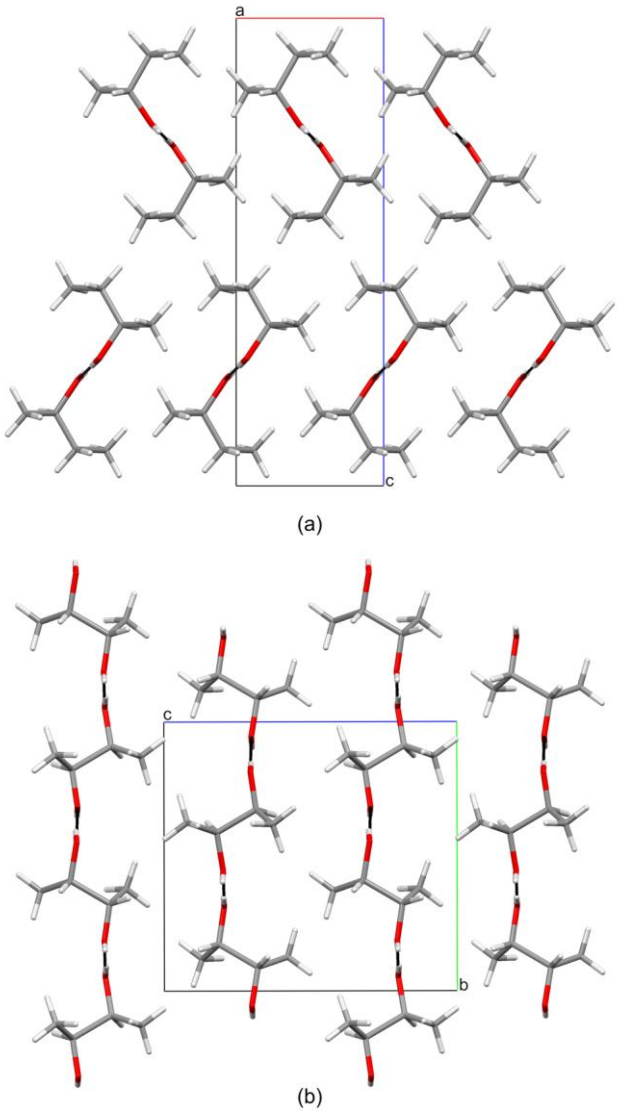

Figure S6. The crystal structure of: (a) 2-butanol at 2.14 GPa and (b) 2,3-butanediol at 0.43 GPa viewed along the O−H···O bonded aggregates.

Table S1. Crystal data and details of the refinements of 2-butanol at 2.14(5) and 2.33(5) GPa, and of 2,3-butanediol at 0.43(5), 0.63(5), 0.72(5) and 0.97(5) GPa (all at 295 K).

	$C_4H_{10}O$	$C_4H_{10}O$	$C_4H_{10}O_2$	$C_4H_{10}O_2$	$C_4H_{10}O_2$	$C_4H_{10}O_2$
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
Pressure (GPa)	2.14(5)	2.33(5)	0.43(5)	0.63(5)	0.72(5)	0.97(5)
Formula weight	74.12	74.12	90.12	90.12	90.12	90.12
Crystal colour	colourless	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)	0.46x0.46x0.22	0.46x0.46x0.21	0.42x0.42x0.22	0.41x0.41x0.21	0.41x0.41x0.27	0.39x0.39x0.25
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell *a* (Å)	5.0580(10)	5.0122(10)	5.0482(10)	5.0292(10)	4.9973(10)	4.9467(10)
b (Å)	5.2221(10)	5.0885(10)	9.4220(19)	9.3989(19)	9.4478(19)	9.3791(19)
c (Å)	16.054(3)	16.044(3)	10.250(2)	10.186(2)	10.076(2)	9.834(2)
Volume (Å^3)	424.04(14)	409.20(14)	487.56(17)	481.46(17)	475.72(16)	456.25(16)
Z	4	4	4	4	4	4
D_x (g cm^{-3})	1.161	1.203	1.228	1.243	1.258	1.312
Wavelength MoKα; λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.08	0.10	0.10	0.10	0.10
F(000) (e)	168	168	200	200	200	200
2θ max (°)	49.88	49.84	49.96	49.92	50.00	56.24
min./max. indices h,k,l	-5/5, -6/6, -17/16	-4/4, -6/6, -15/15	-6/6, -6/6, -12/12	-5/5, -5/5, -11/11	-5/5, -10/10, -4/4	-6/6, -11/12, -3/3
Reflections collected/unique	3268/565	2975/408	3678/467	3408/432	1832/318	1954/284
R_{int}	0.1303	0.1644	0.0642	0.1126	0.0321	0.0413
Observed reflections (I>4σ(I))	320	304	369	315	310	268
Data/parameters	565/46	408/46	467/55	432/55	318/55	284/25
Goodness of fit on F^2	1.025	1.101	1.126	1.157	1.090	1.126
Final R_1 indices (I>4σ(I))	0.0805	0.1118	0.0489	0.1013	0.0369	0.0451
R_1/wR_2 indices (all data)	0.1265/0.2255	0.1301/0.3005	0.0619/0.1333	0.1224/0.3079	0.0375/0.0935	0.0481/0.1045
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.24, -0.16	0.32, -0.39	0.16, -0.16	0.42, -0.36	0.10, -0.09	0.09, -0.10
Weighting scheme x; y[a]	0.1091; 0	0.1937; 0.11	0.0603; 0.18	0.1970; 0.23	0.0525; 0.19	0.0437; 0.32
Absorption corrections	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal
DAC transmission min/max	0.63 / 0.90	0.64 / 0.92	0.63 / 0.92	0.63 / 0.92	0.91 / 1.00	0.91 / 1.00
Gasket shadowing min/max	0.59 / 0.95	0.65 / 0.97	0.56 / 0.96	0.56 / 0.96	0.62 / 0.93	0.61 / 0.95
Sample transmission min/max	0.98 / 0.98	0.98 / 0.98	0.97 / 0.98	0.97 / 0.98	0.97 / 0.97	0.97 / 0.98

[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S2. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for 2-butanol at 2.14 and 2.33 GPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
2.14 GPa/295 K				
O1	740(11)	3513(7)	7734(3)	75(2)
H1	252	4930	7576	112
C1	−1157(19)	6174(10)	9240(5)	83(3)
H11	−2057	6184	9767	124
H12	−2424	5980	8800	124
H13	−220	7758	9170	124
C2	859(18)	3877(11)	9216(5)	73(2)
H21	2119	4064	9667	88
H22	−89	2284	9299	88
C3	2249(16)	3769(9)	8443(5)	54(2)
H31	3269	5357	8390	65
C4	4239(15)	1515(10)	8452(4)	57(2)
H41	5167	1460	7931	86
H42	3302	−64	8532	86
H43	5480	1753	8897	86
2.33 GPa/295 K				
O1	644(16)	3215(10)	7751(4)	68(3)
H1	102	4629	7574	102
C1	−1118(21)	6155(12)	9256(6)	60(3)
H11	−2020	6166	9784	90
H12	−2400	5941	8817	90
H13	−186	7786	9182	90
C2	884(22)	3870(12)	9233(6)	57(3)
H21	2155	4093	9683	68
H22	−68	2239	9330	68
C3	2394(19)	3651(13)	8422(5)	46(3)
H31	3432	5254	8325	55
C4	4241(18)	1284(13)	8453(5)	46(2)
H41	5216	1161	7940	69
H42	3205	−284	8532	69
H43	5468	1480	8909	69

Table S3. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for 2,3-butanediol at 0.43, 0.63, 0.72 and 0.97 GPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
0.43 GPa/295 K				
O1	3033(7)	−537(8)	2016(3)	73(3)
H1	1592	−938	1991	109
O2	1930(7)	3132(8)	2953(3)	58(3)
H2	3432	3463	2972	70
C1	637(9)	1267(10)	789(4)	56(2)
H11	849	667	40	84
H12	856	2241	536	84
H13	−1101	1135	1149	84
C2	2691(9)	888(11)	1800(4)	39(2)
H21	4388	1252	1479	47
C3	2038(10)	1743(11)	3141(5)	46(2)
H31	3453	1545	3769	55
C4	−560(9)	1195(9)	3704(5)	56(2)
H41	−1089	1785	4421	84
H42	−324	238	4004	84
H43	−1904	1215	3042	84

0.63 GPa/295 K				
O1	3021(14)	−553(14)	2008(5)	50(2)
H1	1565	−944	1982	75
O2	1908(13)	3147(14)	2968(6)	42(2)
H2	3404	3492	2985	50
C1	627(19)	1298(20)	762(9)	51(3)
H11	822	703	3	77
H12	901	2274	517	77
H13	−1129	1187	1117	77
C2	2711(15)	864(18)	1812(6)	25(2)
H21	4428	1215	1493	30
C3	2070(18)	1751(21)	3120(7)	31(3)
H31	3494	1560	3752	38
C4	−574(18)	1148(19)	3707(9)	48(3)
H41	−1129	1733	4430	73
H42	−287	193	4009	73
H43	−1929	1150	3043	73
0.72 GPa/295 K				
O1	3077(4)	−528(2)	1991(5)	45(2)
H1	1626	−933	1966	67
O2	1915(4)	3159(2)	2940(5)	41(2)
H2	3432	3488	2960	49
C1	669(7)	1246(4)	674(9)	42(4)
H11	993	607	−50	63
H12	859	2204	370	63
H13	−1113	1105	1005	63
C2	2687(5)	961(3)	1783(8)	33(4)
H21	4407	1350	1490	40
C3	2033(6)	1652(3)	3145(8)	31(4)
H31	3491	1443	3765	37
C4	−573(6)	1204(3)	3765(8)	42(5)
H41	−1008	1834	4481	63
H42	−406	257	4100	63
H43	−1966	1235	3110	63
0.97 GPa/295 K				
O1	3112(4)	−548(2)	1948(8)	24(1)
H1	1650	−960	1923	36
O2	1896(5)	3167(2)	2944(7)	24(1)
H2	3430	3497	2965	29
C1	641(8)	1241(4)	631(13)	33(1)
H11	951	597	−112	49
H12	826	2205	319	49
H13	−1150	1099	982	49
C2	2701(6)	956(3)	1752(11)	21(1)
H21	4427	1359	1450	26
C3	2014(7)	1645(3)	3149(11)	21(1)
H31	3476	1431	3790	26
C4	−650(7)	1188(4)	3774(12)	31(1)
H41	−1110	1823	4503	46
H42	−485	234	4119	46
H43	−2042	1216	3094	46

Table S4. Dimensions of O−H···O hydrogen bonds in 2-butanol at 2.14 and 2.33 GPa/295 K; and in 2,3-butanediol at 0.43, 0.63, 0.72 and 0.97 GPa/295 K.

D−H···A	H···A (Å)	D···A (Å)	D−H···A (°)	symmetry code
2-butanol: 2.14 GPa/295 K				
O1−H1···O1	2.000	2.818(4)	175.19	–*x*, 0.5+*y*, 1.5–*z*
2.33 GPa/295 K				
O1−H1···O1	1.934	2.745(4)	170.16	–*x*, 0.5+*y*, 1.5–*z*
2,3-butanediol: 0.43 GPa/295 K				
O1−H1···O2	1.983	2.802(6)	176.34	–*x*, –0.5+*y*, 0.5–*z*
O2−H2···O1	2.018	2.835(6)	174.38	1–*x*, 0.5+*y*, 0.5–*z*
0.63 GPa/295 K				
O1−H1···O2	1.945	2.764(12)	176.53	–*x*, –0.5+*y*, 0.5–*z*
O2−H2···O1	2.009	2.828(11)	176.65	1–*x*, 0.5+*y*, 0.5–*z*
0.72 GPa/295 K				
O1−H1···O2	1.969	2.786(3)	175.08	–*x*, –0.5+*y*, 0.5–*z*
O2−H2···O1	1.977	2.795(3)	174.25	1–*x*, 0.5+*y*, 0.5–*z*
0.97 GPa/295 K				
O1−H1···O2	1.940	2.757(3)	173.66	–*x*, –0.5+*y*, 0.5–*z*
O2−H2···O1	1.933	2.750(3)	174.51	1–*x*, 0.5+*y*, 0.5–*z*

Table S5. Donohue angles (Donohue, J. (1952). *J. Phys. Chem.* **56**, 502-510.) of O−H···O hydrogen bonds in 2-butanol and 2,3-butanediol.

C−O−H···O−C	C−O···O* (º)	O···O*−C* (º)	*symmetry code
2-butanol: 2.14 GPa/295 K			
C3−O1−H1···O1−C3	106.1(3)	117.2(3)	–*x*, 0.5+*y*, 1.5–*z*
2.33 GPa/295 K			
C3−O1−H1···O1−C3	103.0(4)	121.2(5)	–*x*, 0.5+*y*, 1.5–*z*
2,3-butanediol: 0.43 GPa/295 K			
C2−O1−H1···O2−C3	109.1(3)	118.5(4)	–*x*, –0.5+*y*, 0.5–*z*
C3−O2−H2···O1−C2	113.5(4)	123.2(4)	1–*x*, 0.5+*y*, 0.5–*z*
0.63 GPa/295 K			
C2−O1−H1···O2−C3	109.4(6)	119.5(6)	–*x*, –0.5+*y*, 0.5–*z*
C3−O2−H2···O1−C2	111.8(6)	122.0(6)	1–*x*, 0.5+*y*, 0.5–*z*
0.72 GPa/295 K			
C2−O1−H1···O2−C3	108.6(2)	118.3(2)	–*x*, –0.5+*y*, 0.5–*z*
C3−O2−H2···O1−C2	113.5(2)	124.1(2)	1–*x*, 0.5+*y*, 0.5–*z*
0.97 GPa/295 K			
C2−O1−H1···O2−C3	107.9(2)	117.6(2)	–*x*, –0.5+*y*, 0.5–*z*
C3−O2−H2···O1−C2	113.1(2)	124.2(2)	1–*x*, 0.5+*y*, 0.5–*z*