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Supplementary material

Can the thermal expansion be controlled by varying hydrogen bond dimensionality in polymorphs?

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Figure S1. Thermal ellipsoid plots of the system at 50% probability.

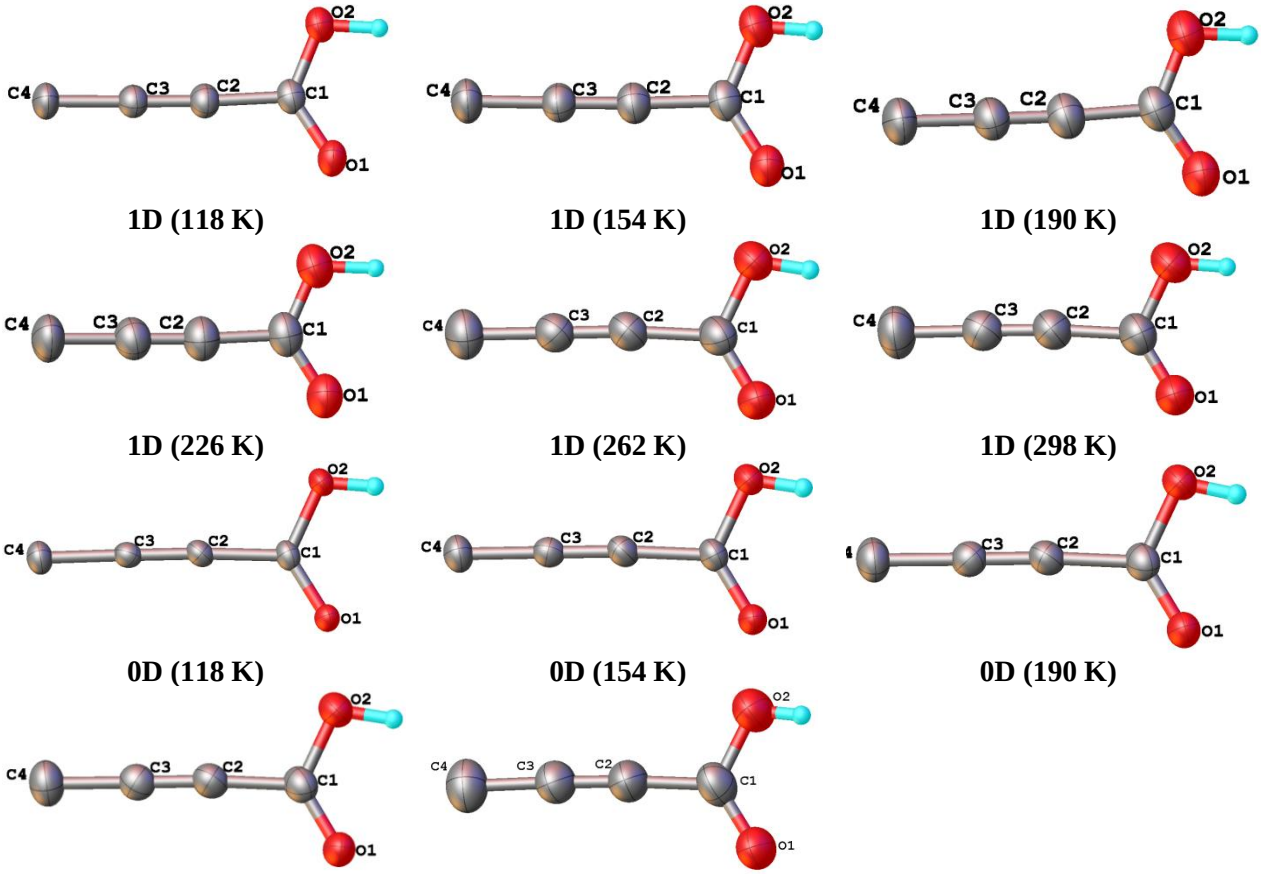
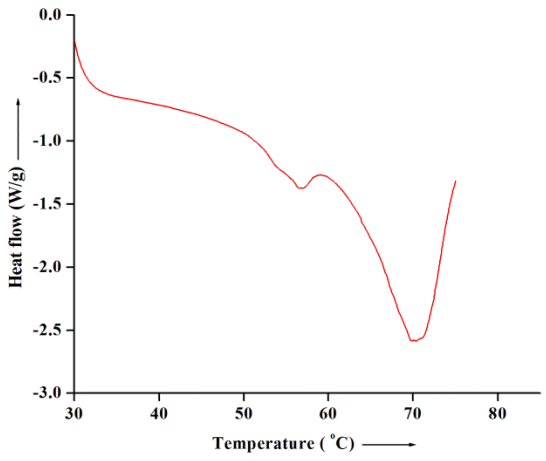
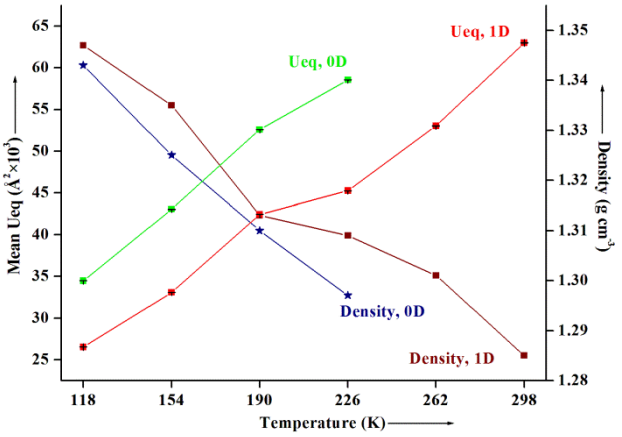


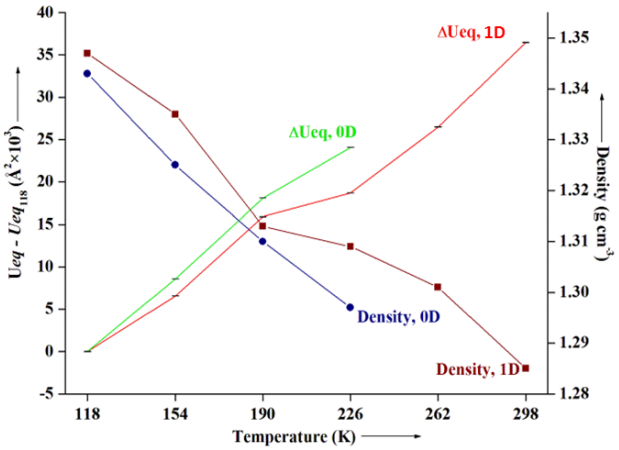
Figure S2: DSC plot of 1D and variation of density, mean Ueq and change in mean Ueq for the systems.



(a) DSC plot of the **1D** form of 2-butynoic acid



(b) Variation of mean Ueq and density of systems at different temperatures.



(c) Change in mean Ueq of the systems at different temperatures and respective densities.

Table –S1: Variable temperature geometry of the hydrogen bonds present in the systems							
0D							
		118 K	**154 K**	**190 K**	**226 K**	**262 K* ($1D^t$)**	
O2–H2···O1	D-H *d* *D* *θ*	0.99(4) 1.66(4) 2.637(2) 170(4)	0.91(3) 1.74(3) 2.640(2) 170(3)	1.00(5) 1.66(6) 2.641(3) 168(5)	1.03(5) 1.61(6) 2.636(3) 172(5)	0.820 1.888 2.649(7) 153.9	
1D							
Hydrogen bonds		**118 K**	**154 K**	**190 K**	**226 K**	**262 K**	**298 K**
O2–H2···O1	D-H *d* *D* *θ*	0.88(4) 1.79(4) 2.641(3) 164(4)	0.88(4) 1.80(4) 2.641(3) 159(4)	0.88(4) 1.84(4) 2.654(3) 154(4)	0.93(4) 1.76(4) 2.649(3) 158(4)	0.91(5) 1.78(5) 2.648(4) 158(4)	0.93(6) 1.74(6) 2.645(4) 164(5)
* (obtained *in situ* from the **0D** (226 K) via SCSCPT)							

Table –S2: Variable temperature geometry of important contacts present in the systems							
0D							
Direction	**Interactions**	**118 K**	**154 K**	**190 K**	**226 K**		
Along X (Me···Me)	C4···C4	3.609(2)	3.628(3)	3.650(4)	3.674(4)		
Along Y	C4-H4A···C2	3.79(3)	3.811(3)	3.824(4)	3.826(4)		
	C4-H4B···O1	3.608(3)	3.616(3)	3.625(4)	3.630(4)		
Along Z	C3···02	3.272(3)	3.303(3)	3.321(4)	3.352(4)		
	C1···O1	3.173(3)	3.197(3)	3.223(4)	3.246(4)		
1D							
		118 K	**154 K**	**190 K**	**226 K**	**262 K**	**298 K**
Along Y	C3···C4	3.520(5)	3.538(5)	3.564(5)	3.579(6)	3.582(6)	3.600(7)
	C4-H4a···C2	3.661(5)	3.667(5)	3.701(5)	3.718(6)	3.722(6)	3.751(7)
	C4-H4a···O2	3.862(4)	3.882(4)	3.910(5)	3.934(5)	3.940(6)	3.981(6)
Along Z	C2···O1	3.319(4)	3.349(4)	3.367(4)	3.375(4)	3.402(5)	3.435(5)

Table S3: Crystallographic parameters for the systems at different temperatures

Identification code	**1D (118 K)**	**1D (154 K)**	**1D (190K)**	**1D (226 K)**	**1D (262 K)**	**1D (298 K)**
Empirical formula	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$
Formula weight	84.07	84.07	84.07	84.07	84.07	84.07
Temperature/K	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a/Å	3.8248(8)	3.8518(5)	3.8856(13)	3.8912(10)	3.9127(7)	3.9417(12)
b/Å	7.0987(7)	7.0956(5)	7.1138(12)	7.1141(12)	7.1074(8)	7.1096(18)
c/Å	7.7801(9)	7.7924(9)	7.8353(16)	7.8453(16)	7.8489(11)	7.878(3)
α/°	90	90	90	90	90	90
β/°	101.058(15)	100.862(12)	100.93(3)	100.80(2)	100.422(16)	100.25(3)
γ/°	90	90	90	90	90	90
Volume/Å^3	207.32(5)	209.16(4)	212.65(9)	213.32(8)	214.67(6)	217.25(12)
Z	2	2	2	2	2	2
ρ_{calc}g/cm^3	1.347	1.335	1.313	1.309	1.301	1.285
μ/mm^{-1}	0.109	0.109	0.107	0.106	0.106	0.104
F(000)	88	88	88	88	88	88
Crystal size/mm^3	0.36×0.28×0.22	0.36×0.28×0.22	0.36×0.28×0.22	0.36×0.28×0.22	0.36×0.28×0.22	0.36×0.28×0.22
Reflections collected	1149	1275	1358	1266	1284	1346
Independent reflections	786	894	899	909	879	858
Parameters	60	60	60	60	60	61
Goodness-of-fit on F^2	1.09	1.086	1.04	1.044	1.075	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0400	R_1 = 0.0426	R_1 = 0.0436	R_1 = 0.0464	R_1 = 0.0460	R_1 = 0.0513
Final R indexes [all data]	wR_2 = 0.0973	wR_2 = 0.1019	wR_2 = 0.1079	wR_2 = 0.1123	wR_2 = 0.1229	wR_2 = 0.1218
CCDC no.	1040242	1040243	1040244	1040245	1040246	1040247

Identification code	**0D (118 K)**	**0D (154 K)**	**0D (190 K)**	**0D (226 K)**	**1D^t (262 K)**
Empirical formula	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$	$C_4H_4O_2$
Formula weight	84.07	84.07	84.07	84.07	84.07
Temperature/K	118(2)	154(2)	190(2)	226(2)	262(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a/Å	5.0156(5)	5.0359(9)	5.0580(9)	5.0673(8)	3.9158(11)
b/Å	6.9262(9)	6.9758(13)	7.0169(17)	7.0638(13)	7.1104(10)
c/Å	7.0836(8)	7.1152(13)	7.1325(15)	7.1630(9)	7.871(3)
α/°	112.956(12)	112.963(18)	112.92(2)	113.064(16)	90
β/°	97.227(10)	97.033(16)	96.962(17)	96.689(12)	100.59(3)
γ/°	107.388(11)	107.706(17)	108.002(19)	108.347(15)	90
Volume/Å^3	207.85(5)	210.80(8)	213.14(9)	215.30(7)	215.40(10)
Z	2	2	2	2	2
ρ_{calc}g/cm^3	1.343	1.325	1.31	1.297	1.296
μ/mm^{-1}	0.109	0.108	0.106	0.105	0.105
F(000)	88	88	88	88	88
Crystal size/mm^3	0.48×0.38×0.06	0.48×0.38×0.06	0.48×0.38×0.06	0.48×0.38×0.06	0.48×0.38×0.06
Reflections collected	2333	2347	2311	2279	1882
Independent reflections	980	976	996	997	939
Parameters	60	60	60	60	57
Goodness-of-fit on F^2	1.052	1.017	1.065	1.081	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0538	R_1 = 0.0575	R_1 = 0.0640	R_1 = 0.0605	R1 = 0.0633
Final R indexes [all data]	wR_2 = 0.1630	wR_2 = 0.1719	wR_2 = 0.2136	wR2 = 0.2071	wR2 = 0.1981
CCDC no.	1040237	1040238	1040239	1040240	1040241