Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Pressure effects on H-ordering in hydrogen bonds and interactions in benzoic acid

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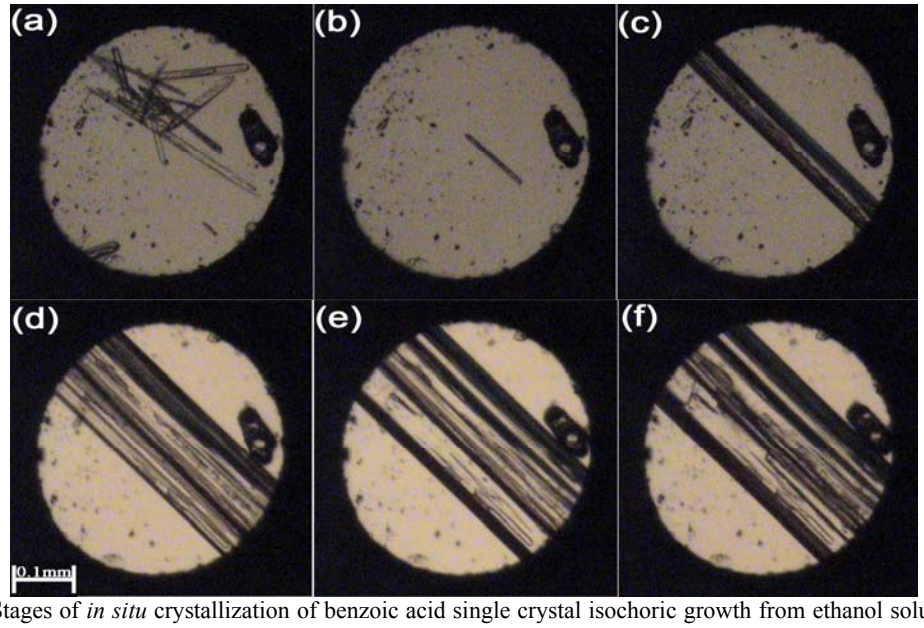

Fig. S1 Stages of *in situ* crystallization of benzoic acid single crystal isochoric growth from ethanol solution. The concentration of the solution was 9:11 (benzoic acid: ethanol). After polycrystalline benzoic acid was obtained at 0.38 GPa, the sample was heated to 363 K when several crystals dissolved but one single crystal left; (a and b) at 363 K; (c) at 358 K; (d) at 343 K; (e) at 333 K and (f) the final pressure stabilized at 0.21 GPa/296 K. A ruby chip for pressure calibration is placed at the right side of the chamber.

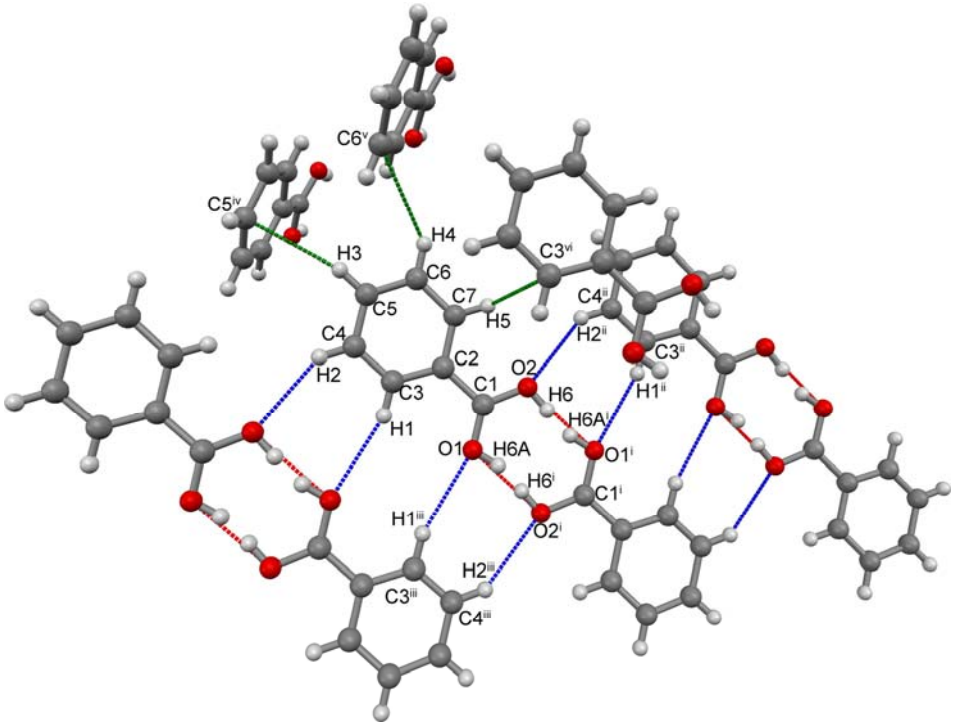

Fig. S2 Crystal packing of benzoic acid molecules at 1.12 GPa/296 K. The intermolecular contacts C−H···O (blue dashes) and C−H···C (green dashes) between adjacent dimers have been indicated by dotted lines. Symmetry codes: (i) –*x*, –*y*, –*z*; (ii) 1–*x*, 1–*y*, –*z*; (iii) *x*–1, *y*–1, *z*; (iv) 1–*x*, 0.5+*y*, 0.5–*z* ; (v) –*x*, *y*+0.5, 0.5–*z* ; and (vi) –1+*x*, *y*, *z*.

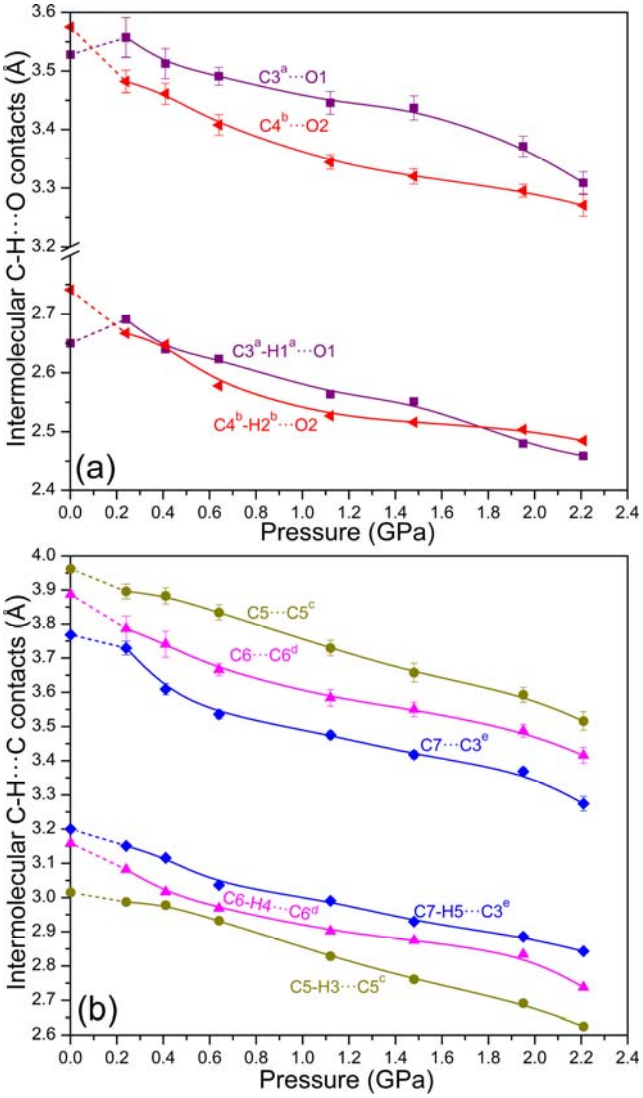

Fig. S3 Intermolecular contacts (a) C−H···O and (b) C−H···C between adjacent dimers in benzoic acid as the function of pressure. Symmetry codes: (a) 1–*x*, 1–*y*, –*z*; (b) *x*–1, *y*–1, *z;* (c) 1–*x*, 0.5+*y*, 0.5–*z* ; (d) –*x*, *y*+0.5, 0.5–*z* ; and (e) –1+*x*, *y*, *z*.

Table S1 Crystal data of benzoic acid at 0.21, 0.42, 0.64, 1.12, 1.48, 1.96, and 2.21 GPa/296 K

Pressure	0.21 GPa	0.42 GPa	0.64 GPa	1.12 GPa	1.48 GPa	1.96 GPa	2.21 GPa
Temperature	296 K	296 K	296 K	296 K	296K K	296K	296K
Crystal size(mm)	0.42/0.25/0.18	0.38/0.37/0.24	0.38/0.37/0.24	0.38/0.37/0.24	0.38/0.37/0.24	0.38/0.37/0.24	0.38/0.37/0.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	5.402(4)	5.3454(15)	5.2959(8)	5.2087(10)	5.1578(11)	5.1036(11)	5.077(14)
b/Å	5.067(3)	5.0400(16)	5.0110(8)	4.9632(11)	4.9334(11)	4.8981(10)	4.893(9)
c/Å	21.751(15)	21.688(17)	21.651(14)	21.469(15)	21.302(15)	21.176(16)	21.10(6)
β/°	98.10(6)	98.36(8)	98.78(4)	99.48(6)	99.82(6)	100.38(6)	100.6(4)
V/Å^3	589.3(7)	578.1(5)	567.8(4)	547.4(4)	534.1(4)	520.7(4)	515(2)
Z	4	4	4	4	4	4	4
ρ_{cal} (g/cm^3)	1.376	1.403	1.428	1.482	1.519	1.558	1.574
θ range(°)	5.72–27.98	4.15–28.14	4.49–28.41	3.97–28.43	4.15–28.63	4.27–29.18	4.28 –27.14
μ(mm^{-1})	0.101	0.103	0.105	0.109	0.112	0.115	0.116
F(000)	256	256	256	256	256	256	256
Limiting indices	$-5\le h\le5$	$-7\le h\le6$	$-7\le h\le7$	$-6\le h\le7$	$-6\le h\le6$	$-6\le h\le7$	$-6\le h\le6$
	$-6\le k\le6$	$-6\le k\le6$	$-6\le k\le6$	$-6\le k\le6$	$-6\le k\le6$	$-6\le k\le6$	$-6\le k\le6$
	$-16\le l\le16$	$-7\le l\le7$	$-7\le l\le7$	$-7\le l\le7$	$-7\le l\le7$	$-8\le l\le8$	$-12\le l\le12$
R_{int}	0.1626	0.2304	0.2105	0.1640	0.1591	0.2626	0.3204
Data/parameters	218/72	170/82	200/82	189/82	202/82	214/82	162/82
R_1/wR_2 ($I>4\sigma(I)$)[a]	0.0875/0.0767	0.0999/0.1986	0.0927/0.1775	0.0509/0.1324	0.0667/0.0990	0.0765/0.0919	0.0982/0.1083
R_1/wR_2 indices(all data)	0.1365/0.0847	0.1250/0.2153	0.1081/0.1883	0.0716/0.1503	0.0886/0.1053	0.1128/0.1048	0.2213/0.1479
Goodness-of-fit on F_0^2	1.477	1.314	1.211	1.131	1.353	1.301	1.269
Largest peak/hole (e·Å^{-3})	0.03/–0.04	0.07/–0.06	0.09/–0.09	0.06 /–0.08	0.08/–0.07	0.05/–0.07	0.07/–0.08
CCDC number	864020	864019	864018	864023	864022	864021	864024

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$ for $F_o^2>2\sigma(F_o^2)$; $wR_2=\sum[w(F_o^2-F_c^2)]/\sum[w(F_o^2)^2]^{1/2}$,where $w=1/[\sigma^2F_o^2+(AP)^2+BP]$, and $P=(Fo^2+2Fc^2)/3$

Table S2 Bond lengths (Å) and angles (°) of benzoic acid at 0.21, 0.42, 0.64, 1.12, 1.48, 1.96, and 2.21 GPa/296 K

Pressure	0.21 GPa	0.42 GPa	0.64 GPa	1.12 GPa	1.48 GPa	1.96 GPa	2.21 GPa
C(1)–O(1)	1.32(2)	1.294(19)	1.24(2)	1.259(12)	1.245(18)	1.270(16)	1.34(3)
C(1)–O(2)	1.244(15)	1.265(6)	1.309(8)	1.294(5)	1.299(6)	1.299(6)	1.278(13)
C(1)–C(2)	1.466(16)	1.43(3)	1.47(3)	1.456(19)	1.48(2)	1.460(17)	1.51(3)
C(2)–C(3)	1.38(2)	1.368(10)	1.383(10)	1.384(7)	1.390(7)	1.372(7)	1.378(14)
C(2)–C(7)	1.19(5)	1.40(4)	1.41(4)	1.42(2)	1.39(2)	1.40(2)	1.42(3)
C(3)–C(4)	1.42(4)	1.37(3)	1.30(2)	1.342(19)	1.342(19)	1.358(15)	1.34(4)
C(4)–C(5)	1.29(4)	1.31(3)	1.39(3)	1.41(2)	1.40(2)	1.40(2)	1.48(3)
C(5)–C(6)	1.37(2)	1.383(11)	1.377(9)	1.377(7)	1.373(6)	1.377(6)	1.363(14)
C(6)–C(7)	1.45(2)	1.40(3)	1.41(3)	1.40(2)	1.40(2)	1.434(19)	1.40(3)
O(1)–C(1)–O(2)	124.4(14)	122.9(14)	125.7(15)	123.6(9)	123.9(12)	121.5(10)	121(3)
O(1)–C(1)–C(2)	114.5(17)	116.2(9)	119.9(8)	120.4(6)	120.2(6)	119.8(6)	119.1(10)
O(2)–C(1)–C(2)	120.9(18)	120.8(16)	114.3(16)	116.0(11)	115.6(14)	118.6(11)	117.7(15)
C(3)–C(2)–C(7)	118.6(13)	116(2)	114.2(19)	117.4(14)	117.1(13)	118.3(13)	118(2)
C(3)–C(2)–C(1)	123(2)	126(2)	124.7(18)	122.1(14)	121.5(14)	122.4(14)	122.6(14)
C(7)–C(2)–C(1)	119(2)	117.8(9)	121.0(9)	120.6(6)	121.4(6)	119.2(6)	118.4(10)
C(4)–C(3)–C(2)	119(2)	123.0(19)	127.0(16)	122.4(14)	122.8(14)	121.6(13)	121.8(13)
C(3)–C(4)–C(5)	118.2(17)	119.6(10)	117.4(9)	119.6(7)	119.2(7)	120.4(6)	116.3(10)
C(6)–C(5)–C(4)	123.7(15)	122.6(17)	122.7(12)	121.5(12)	120.7(13)	121.4(11)	123.1(17)
C(7)–C(6)–C(5)	113(2)	116.8(19)	116.5(13)	117.4(14)	118.3(13)	116.7(12)	114.7(13)
C(6)–C(7)–C(2)	127(2)	122.1(10)	122.1(8)	121.7(6)	121.8(6)	121.5(6)	123.6(11)

Table S3 Selected structural parameters (Å and °) of benzoic acid dimer at 0.21, 0.42, 0.64, 1.12, 1.48, 1.96, and 2.21 GPa/296 K

Pressure	0.21 GPa	0.42 GPa	0.64 GPa	1.12 GPa	1.48 GPa	1.96 GPa	2.21 GPa
SOF H6	0.14(12)	0.20(13)	0.24(13)	0.29(9)	0.37(10)	0.43(9)	0.48(14)
SOF H6A	0.86(12)	0.80(13)	0.76(13)	0.71(9)	0.63(10)	0.57(9)	0.52(14)
O1···O2^{i}	2.663(10)	2.634(13)	2.610(9)	2.600(10)	2.575(11)	2.516(10)	2.445(16)
O1···H6	1.857	1.832	1.797	1.790	1.770	1.713	1.649
O2^{i} ···H6A	1.856	1.826	1.805	1.803	1.774	1.717	1.641
O1···O2^{i}–H6^{i}	167.65	168.20	170.96	169.25	166.57	165.75	163.14
O1−H6A···O2^{i}	166.18	165.69	166.62	163.69	165.06	164.24	166.21
C1−O1···O2^{i}(η_1)	118.4(10)	119.3(6)	118.6(5)	120.7(4)	119.6(4)	119.8(4)	118.1(8)
C1^{i}–O2^{i}···O1(η_2)	117.2(9)	117.6(10)	115.6(9)	115.7(7)	116.5(8)	118.6(6)	117.4(11)
$S = (\eta_1-\eta_2)/2$	0.6(6)	0.9(6)	1.5(5)	2.5(4)	1.6(4)	0.6(4)	0.4(7)

Symmetry code (i) $-x, -y, -z$

Table S4 Dimension of intermolecular contacts C–H···O and C–H···C between adjacent benzoic acid dimers at 0.21, 0.42, 0.64, 1.12, 1.48, 1.96, and 2.21 GPa/296 K

Pressure	0.21 GPa	0.42 GPa	0.64 GPa	1.12 GPa	1.48 GPa	1.96 GPa	2.21 GPa
C3^{i}–H1^{i}···O1							
D–H	0.93	0.93	0.93	0.93	0.93	0.93	0.93
H···A	2.691	2.641	2.623	2.564	2.551	2.480	2.459
D···A	3.557(34)	3.512(25)	3.491(15)	3.445(20)	3.437(21)	3.371(18)	3.309(19)
D–H···A	155.38	156.51	155.48	158.45	159.25	160.49	151.95
C4^{ii}–H2^{ii}···O2							
D–H	0.93	0.93	0.93	0.93	0.93	0.93	0.93
H···A	2.667	2.648	2.578	2.527	2.516	2.503	2.485
D···A	3.482(19)	3.461(18)	3.408(18)	3.344(12)	3.320(13)	3.295(11)	3.271(18)
D–H···A	146.71	146.36	148.83	146.82	144.84	143.14	142.31
C5–H3···C5^{iii}							
D–H	0.93	0.93	0.93	0.93	0.93	0.93	0.93
H···A	2.987	2.977	2.932	2.828	2.761	2.691	2.625
D···A	3.896(22)	3.882(24)	3.834(22)	3.728(22)	3.657(27)	3.593(21)	3.516(27)
D–H···A	166.32	164.73	163.76	163.33	162.11	163.38	160.67
C6–H4···C6^{iv}							
D–H	0.93	0.93	0.93	0.93	0.93	0.93	0.93
H···A	3.082	3.017	2.969	2.902	2.875	2.834	2.738
D···A	3.786(37)	3.741(38)	3.666(18)	3.584(24)	3.550(21)	3.487(19)	3.416(23)
D–H···A	133.82	135.86	132.90	131.24	130.51	128.25	130.49
C7–H5···C3^{v}							
D–H	0.93	0.93	0.93	0.93	0.93	0.93	0.93
H···A	3.151	3.115	3.036	2.990	2.929	2.885	2.843
D···A	3.729(20)	3.609(17)	3.536(13)	3.475(11)	3.418(11)	3.369(10)	3.274(21)
D–H···A	122.18	115.04	115.34	114.10	114.19	113.7	109.58

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x-1, y-1, z$; (iii) $1-x, 0.5+y, 0.5-z$; (iv) $-x, y+0.5, 0.5-z$; and (v) $-1+x, y, z$.