Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Enantiomeric crystallization of (±)-*trans*-1,2-diaminocyclohexane under pressure

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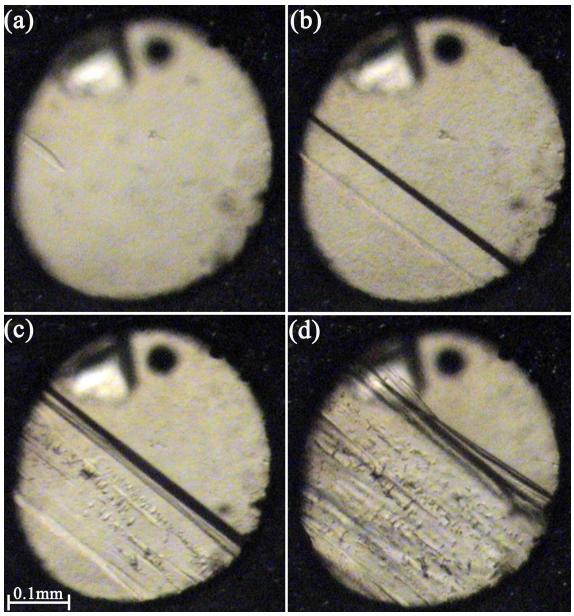

Fig. S1 Isochoric growth of a single crystal of neat (±)-DACH in the DAC chamber: (a) a crystal seed in the left part of the chamber at 383 K; (b) at 363 K; (c) at 343 K ; (d) the single crystal filling *ca*. 60% of the DAC chamber at 0.36 GPa/296 K. A ruby chip for pressure calibration lies at the upper edge of the chamber, close to a small metal ball used for viscosity measurement of (±)-DACH.

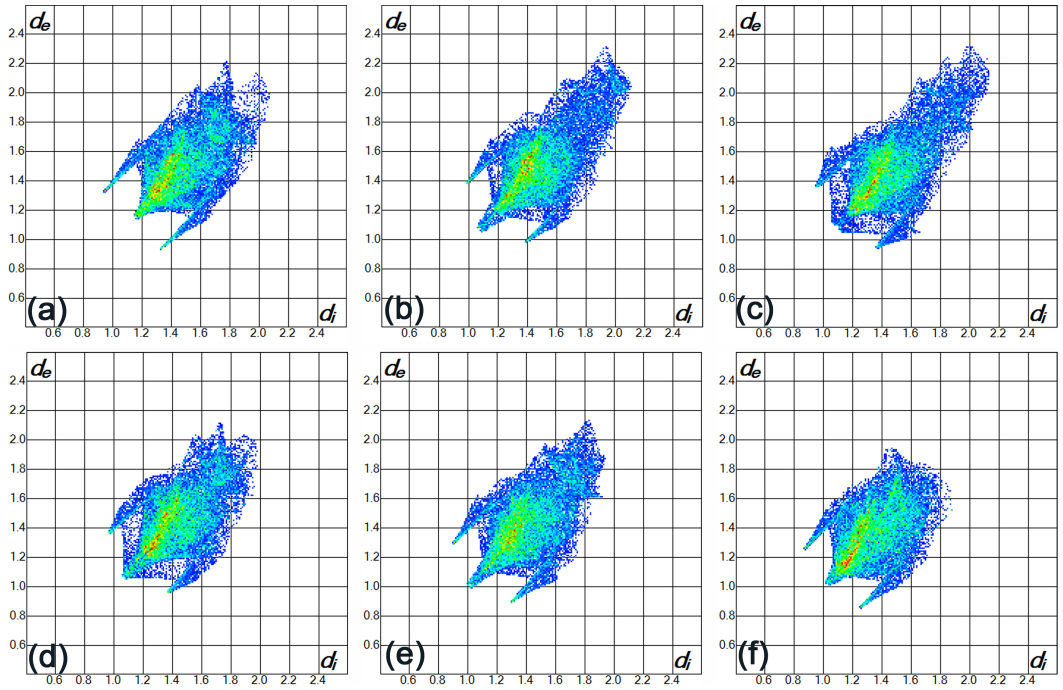

Fig. S2 2D fingerprint plots of (±)-DACH structures at (a) 0.1 MPa/ 110 K; (b) 0.36 GPa/296 K; (c) 0.52 GPa/296 K; (d) 0.65 GPa/296 K; (e) 1.19 GPa/296 K; and (f) 2.04 GPa/296 K.

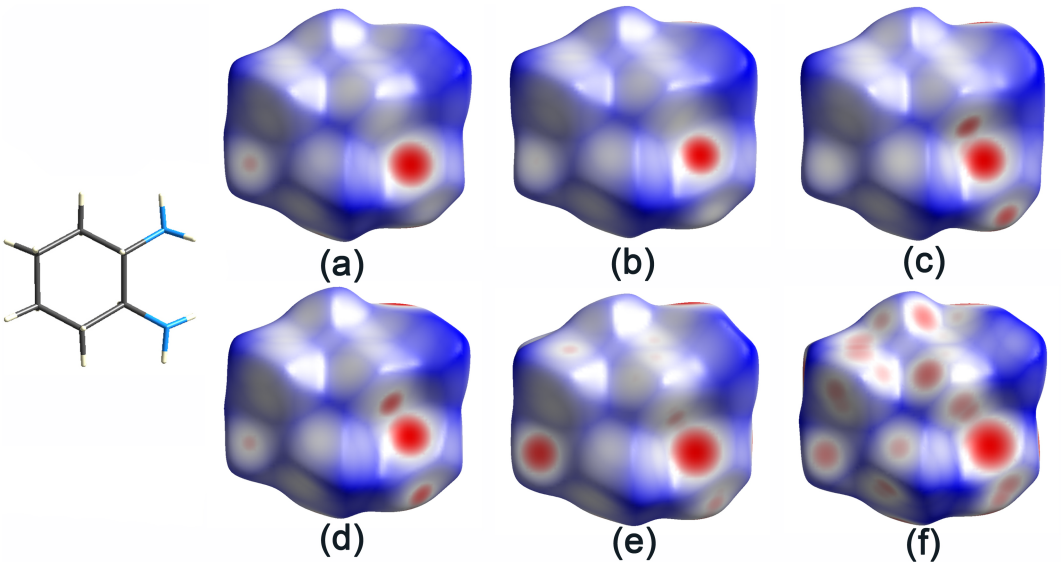

Fig. S3 Normalized intermolecular contacts mapped on the Hirshfeld surfaces of (±)-DACH structures at (a) 0.1 MPa/110 K; (b) 0.36 GPa/296 K; (c) 0.52 GPa/296 K; (d) 0.65 GPa/296 K; (e) 1.19 GPa/296 K; and (f) 2.04 GPa/296 K. The colour scale describes distances longer (navy-blue), equal (white), and shorter (red) than the van der Waals radii.

Table S1 Crystal data of (±)-DACH at 0.36, 0.52, 0.65, 1.19 and 2.04 GPa/296 K

Pressure	0.36 GPa	0.52 GPa	0.65 GPa [a]	1.19 GPa	2.04 GPa [a]
Temperature	296 K	296 K	296 K	296 K	296 K
Crystal size (mm)	0.40/0.32/0.28	0.36/0.28/0.12	0.37/0.30/0.14	0.32/0.30/0.28	0.34/0.20/0.12
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12$	$P2_12_12$	$P2_12_12$	$P2_12_12$	$P2_12_12$
a/Å	8.5210(17)	8.40(6)	8.345(8)	8.200(13)	8.08 (3)
b/Å	5.2696(11)	5.159 (5)	5.150(7)	5.13 (3)	4.914(16)
c/Å	7.7240(15)	7.61(3)	7.558(10)	7.40 (2)	7.33 (2)
V/Å^3	346.83(12)	330(3)	324.8(7)	311(2)	291.1(16)
Z	2	2	2	2	2
ρ_{cal} (g /cm^3)	1.093	1.150	1.168	1.218	1.303
θ range (°)	3.56−27.32	4.77−28.80	3.64−28.60	3.71−28.95	2.78−25.43
μ (mm^{-1})	0.067	0.071	0.072	0.075	0.080
F(000)	128	128	128	128	128
Limiting indices	$-8 \le h \le 8$	$-6 \le h \le 7$	$-10 \le h \le 10$	$-10 \le h \le 11$	$-5 \le h \le 5$
	$-6 \le k \le 6$	$-6 \le k \le 6$	$-4 \le k \le 4$	$-4 \le k \le 3$	$-5 \le k \le 5$
	$-5 \le l \le 5$	$-8 \le l \le 8$	$-8 \le l \le 8$	$-8 \le l \le 8$	$-8 \le l \le 8$
R_{int}	0.1472	0.3243	0.2199	0.4098	0.1491
Data/restrains/parameters	201 / 8 / 40	300/ 2 / 30	351 / 2 / 35	268 / 28 / 35	181 / 5 / 20
R_1/wR_2 (I>4σI)	0.0535/0.1201	0.1889/0.3133	0.0939/0.1492	0.1269/0.1922	0.1732/0.2397
R_1/wR_2 indices (all data)	0.0715/0.1278	0.4255/0.4550	0.1395/0.1724	0.3808/0.2649	0.2368/0.2645
Weighting scheme: x; y [b]	0.0692; 0	0.1515; 0.40	0.0517; 0.03	0.0136; 1.05	0.0849; 0.11
Goodness-of-fit on F_0^2	1.155	1.144	1.139	1.014	1.198
Largest peak/hole (e·Å^{-3})	0.10/−0.08	0.26/−0.24	0.16/−0.16	0.20 /−0.19	0.20/−0.22
CCDC number	821655	821656	821657	821658	821659

a. Crystals were obtained with volume ratio (±)-DACH: methanol = 4:1
b. $w = 1/[\sigma^2(F_o^2)+(xP)^2+yP]$, where $P = (\mathrm{Max}(F_o^2,0)+2F_c^2)/3$

Table S2 Selected bond distances (Å) and angles (˚) of (±)-DACH at 0.36, 0.52, 0.65, 1.19 and 2.04 GPa/296 K

Pressure	0.1 MPa [1]	0.36 GPa	0.52 GPa	0.65 GPa	1.19 GPa	2.04 GPa
Temperature	110 K	296 K	296 K	296 K	296 K	296 K
N1−C1	1.474(3)	1.490(16)	1.40(3)	1.445(7)	1.48(3)	1.52(3)
C1−C2	1.524(3)	1.446(19)	1.51(2)	1.515(7)	1.49(2)	1.475(19)
C1−C1^i	1.534(4)	1.558(14)	1.59(5)	1.496(10)	1.66(4)	1.45(3)
C2−C3	1.524(3)	1.600(18)	1.48(2)	1.514(7)	1.43(2)	1.545(16)
C3−C3^i	1.533(5)	1.551(12)	1.54(5)	1.494(11)	1.44(4)	1.56(2)
∠N1−C1−C2	109.8(2)	112.9(14)	115(2)	111.1(3)	109.4(10)	107.1(17)
∠C2−C1−C1^i	109.8(1)	109.5(4)	107.0(14)	110.6(3)	108.8(11)	111.1(11)
∠N1−C1−C1^i	109.9(2)	109.5(5)	112.5(15)	112.4(3)	114.6(15)	113.6(11)
∠C1−C2−C3	111.3(2)	114.4(13)	117(3)	112.0(3)	110.0(12)	111.7(16)
∠C2−C3−C3^i	111.0(2)	108.2(5)	107.8(14)	110.8(4)	116.5(13)	109.2(8)

Symmetry code: (i) $-x+1, -y, z$

Table S3 Intermolecular distances (Å), angles (˚) and torsion angles (˚) of (±)-DACH in low temperature and high pressure structures

Pressure	0.1 MPa [1]	0.1 MPa [2]	0.36 GPa	0.52 GPa	0.65 GPa	1.19 GPa	2.04 GPa
Temperature	110 K	220 K	296 K	296 K	296 K	296 K	296 K
N1−H1	0.91	0.92	0.86	0.846	0.86	0.86	0.90
N1−H2	0.88	0.95	0.86	0.840	0.86	0.86	0.90
N1−H2···N1^i	2.39	2.40(2)	2.523	2.476	2.464	2.351	2.224
N1···N1^i	3.257(3)	3.284(2)	3.355(11)	3.282(29)	3.255(5)	3.210(18)	3.091(26)
N1−H2···C1^{ii}	3.141	3.133	3.170	3.008	2.992	2.964	2.902
C1−H3···N1^{iii}	2.907	2.955	3.038	2.942	2.891	2.797	2.643
∠N1−H2···N1^i	165.43	162.49	163.10	161.25	153.20	176.32	161.53
∠N1−C1−C2−C3	−178.9(2)	−178.9(2)	−178.6(6)	−175.8(18)	−178.2(4)	−177.5(17)	−176.1(12)
∠C1^{iv}−C1−C2−C3	57.8(1)	−	59.1(11)	58(3)	56.1(5)	61.1(16)	59.3(25)
∠C1−C2−C3−C3^{iv}	−55.5(1)	−	−56.8(10)	−60 (3)	−55.9(6)	−52(3)	−54.9(20)

Symmetry codes: (i) $1.5-x, 0.5+y, 2-z$; (ii) $0.5+x, 0.5-y, 2-z$; (iii) $x-0.5, 0.5-y, 2-z$; and (iv) $-x+1, -y, z$

[1] R. G. Kostyanovsky, F. A. Lakhvich, P. M. Philipchenko, D. A. Lenev, V. Y. Torbeev and K. A. Lyssenko, *Mendeleev Commun.,* 2002, **12**, 147−148.
[2] S. Hanessian, A. Gomtsyan, M. Simard and S. Roelens, *J. Am. Chem. Soc.,* 1994, **116**, 4495−4496.