Supplementary Information

Conformational polymorphs of 1,1,2,2-tetrachloroethane: pressure vs. temperature

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Commercially available 1,1,2,2-tetrachloroethane (pure, POCh, Poland) was used without further purification. The isobaric low-temperature crystallization was performed on the diffractometer at a temperature of 215 K with a miniature zone melting procedure using focused infrared-laser- radiation according to: Boese, R.; Nussbaumer, M. *In Situ Crystallization Techniques*, in: Organic Crystal Chemistry, Jones, D. W., Ed., Oxford University Press, Oxford, England, 1994, 20–37.

A single crystal of 1122TCE, for the high-pressure measurement, was grown *in-situ* in a modified Merrill-Bassett diamond-anvil cell, DAC [Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.* **1974**, *45*, 290–294; Bassett, W. A. *High Press. Res.*, **2009**, *29*, 163–186] in isochoric conditions (Fig. S1). A general experimental procedure for the high-pressure crystallization method was previously reported [R. Fourme, *J. Appl. Crystallogr.,* 1968, **1**, 23–30; W. L. Vos, L. W. Finger, R. J. Hemley and H. Mao, *Phys. Rev. Lett.,* 1993, **71**, 3150–3153; D. R. Allan, S. J. Clark, M. J. P. Brugmans, G. J. Ackland and W. L. Vos, *Phys. Rev. B, Condens. Mat.,* 1998, **58**, R11809–R11812; M. Bujak, A. Budzianowski and A. Katrusiak, *Z. Kristallogr.*, 2004, **63**, 573–579]. The ruby-fluorescence line shift measured with BETSA PRL spectrometer was used for measuring the pressure in the DAC [Barnett, J. D.; Block, S.; Piermarini, G. J. *Rev. Sci. Instrum.* **1973**, *44*, 1–9; Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A. *J. Appl. Phys.* **1975**, *46*, 2774–2780] with the accuracy of *ca.* 0.05 GPa.
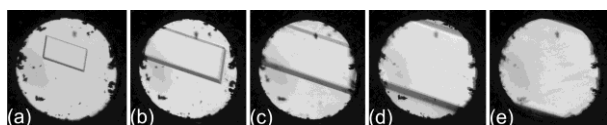

Fig. S1. The isochoric single-crystal growth stages (a → e) of 1122TCE in a diamond-anvil cell at 0.65 GPa. The pressure chamber is 0.48 mm in diameter and ruby chips for the pressure calibration are scattered close to the gasket edges.

The analysis of intermolecular interactions was performed with program CrystalExplorer [Wolff, S. K.; Grimwood, D. J.; McKinnon, J. J.; Jayatilaka, D.; Spackman, N. A. *CrystalExplorer* 2.0 (r 313). University of Western Australia, Perth, Australia, 2007; http://hirshfeldsurface.net/CrystalExplorer/; McKinnon, J. J.; Spackman, M. A.; Mitchell, A. S. *Acta Cryst*. **2004**, *B60*, 627–668].

The compressibility measurement, between ambient pressure and *ca.* 1 GPa, was performed in the cylinder-and-piston apparatus [Baranowski, B.; Moroz, A. *Polish J. Chem.* **1982**, *56*, 379–391]. The pressure was changed at the rate of *ca.* 0.02 GPa. The initial volume of the reaction chamber was 9.8 cm^3.

**Table S1.** The 1122TCE crystal data and structure determination summary.

	phase α	phase β
pressure	0.65(5) GPa	0.1 MPa
temperature, K	295(2)	215(1)
formula	$C_2H_2Cl_4$	$C_2H_2Cl_4$
fw, g/mol	167.84	167.84
crystal size, mm	0.48 x 0.48 x 0.22	0.3 x 0.3 x 0.3
crystal system	monoclinic	orthorhombic
space group, Z	$P2_1/c$, 2	$P2_12_12_1$, 8
a, Å	6.1941(9)	8.8687(19)
b, Å	6.186(2)	10.501(2)
c, Å	7.361(3)	12.835(3)
β, °	104.90(2)	90.0
V, Å^3	272.57(15)	1195.3(4)
ρ, g/cm^3	2.045	1.865
μ, mm^{-1}	2.008	1.831
θ range, °	3.40–25.34	2.51–28.42
index ranges	$-7 \leq h \leq 7$	$-8 \leq h \leq 7$
	$-5 \leq k \leq 5$	$-8 \leq k \leq 14$
	$-7 \leq l \leq 7$	$-17 \leq l \leq 17$
reflns collected	1157	4746
R_{int}	0.1028	0.0159
data [$I > 2\sigma(I)$]	191	2243
data/parameters	198/31	2372/111
GOF on F^2	1.174	1.039
R_1 [$I > 2\sigma(I)$]	0.0598	0.0273
R_1 (all data)[a]	0.0620	0.0298
wR_2 (all data)[a]	0.1469	0.0656
lrgst diff peak, e/Å^3	0.280	0.386
lrgst diff hole, e/Å^3	−0.245	−0.260

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$

Table S2. Molecular dimensions (Å, º) and intermolecular Cl···Cl distances (Å, º) for 1122TCE

Pressure/Temperature(K)		0.65(5) GPa/295(2)	0.1 MPa/215(1)
Cl1–C1	Cl1–C1/Cl3–C2	1.751(11)	1.771(3)/1.774(3)
	Cl5–C3/Cl7–C4		1.775(3)/1.763(3)
C1–C1^I	C1–C2/C3–C4	1.531(17)	1.504(4)/1.508(4)
Cl2–C1	Cl2–C1/Cl4–C2	1.792(10)	1.777(3)/1.774(3)
	Cl6–C3/Cl8–C4		1.780(3)/1.782(3)
Cl1–C1–Cl2	Cl1–C1–Cl2/Cl5–C3–Cl6	110.0(6)	111.14(16)/111.12(15)
	Cl3–C2–Cl4/Cl7–C4–Cl8		109.76(16)/110.23(17)
Cl1–C1–C1^I	Cl1–C1–C2/Cl5–C3–C4	111.5(9)	109.02(19)/112.5(2)
	Cl3–C2–C1/Cl7–C4–C3		109.59(19)/112.8(2)
Cl2–C1–C1^I	Cl2–C1–C2/Cl6–C3–C4	108.2(9)	111.9(2)/108.88(19)
	Cl4–C2–C1/Cl8–C4–C3		112.8(2)/108.23(19)
Cl1–C1–C1^I–Cl1^I	Cl1–C1–C2–Cl3/Cl5–C3–C4–Cl7	−180.0(5)	−175.19(18)/−58.1(3)
Cl1–C1–C1^I–Cl2^I	Cl1–C1–C2–Cl4/Cl5–C3–C4–Cl8	−58.9(8)	62.2(3)/64.2(3)
Cl2–C1–C1^I–Cl1^I	Cl2–C1–C2–Cl3/Cl6–C3–C4–Cl7	58.9(8)	61.5(3)/65.5(3)
Cl2–C1–C1^I–Cl2^I	Cl2–C1–C2–Cl4/Cl6–C3–C4–Cl8	180.0(5)	−61.2(2)/−172.22(17)
Cl1···Cl1^{II}	Cl1···Cl2^{IV}	3.453(3)	3.434(2)
Cl1···Cl1^{II}–C1^{II}	Cl1···Cl2^{IV}–C1^{IV}	123	174
C1–Cl1···Cl1^{II}	C1–Cl1···Cl2^{IV}	123	91
Cl1···Cl2^{III}	Cl3···Cl6^V	3.453(3)	3.437(1)
Cl1···Cl2^{III}–C1^{III}	Cl3···Cl6^V–C3^V	152	131
C1–Cl1···Cl2^{III}	C2–Cl3···Cl6^V	111	144

Symmetry codes: (^{I}) −x+2, −y+1, −z+2; (^{II}) −x+2, −y, −z+2; (^{III}) −x+1, y−1/2, −z+3/2; (^{IV}) x−1/2, −y+1/2, −z; (^{V}) x+1/2, −y+1/2, −z+1.
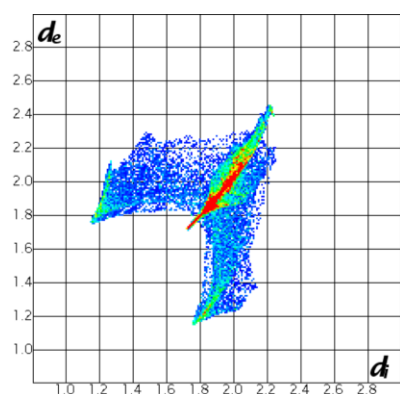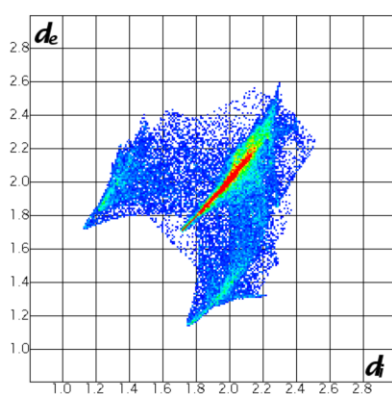
(a) (b)

Fig. S2 Two-dimensional fingerprint plots for the structures of 1122TCE at (a) 0.65 GPa/295 K, and (b) 215 K/0.1 MPa (note two crystallographically independent 1122TCE molecules).