Supplementary Information

Halogen and hydrogen bonds in compressed pentachloroethane

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In-situ low-temperature and high-pressure crystal growth

The commercially available pentachloroethane (95%, Sigma-Aldrich), was used in the lowtemperature and high-pressure single-crystal X-ray diffraction and compressibility experiments. PCE was isobarically frozen in a glass capillary (the internal diameter of 0.3 mm and the wall 0.01 mm thick). The liquid sample, filling *ca*. 0.4 mm of the sealed capillary, was cooled in a nitrogen gas stream from an Oxford Cryosystems attachment. At *ca*. 230 K the PCE sample froze as a polycrystal and it was warmed to *ca*. 240 K, and then the temperature was cycled at a rate of 1-2 K ·min⁻¹ till the sample was partly melting at 244 K [D. R. Lide, ed., *CRC Handbook of Chemistry and Physics, Internet Version 2007*, Taylor and Francis, Boca Raton, FL, 87th edn, 2007]. This resulted in reduction of the number of smaller grains and the growth of the larger crystals. The single-crystal X-ray intensity data were collected at 230.0(1) K, and then again at 85.0(5) K.

A modified Merrill-Bassett diamond-anvil cell, DAC [L. Merrill and W. A. Bassett, Rev. Sci. Instrum., 1974, 45, 290–294; W. A. Bassett, High Press. Res., 2009, 29, 163–186] was used for the high-pressure freezing of PCE. A general experimental procedure for the high-pressure crystallization 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, 219, 573–579]. The diameter of the diamond culets was 0.8 mm. The gasket was made of 0.3 mm thick steel foil with spark-eroded 0.52/0.30 mm in diameter hole [A. Katrusiak, J. Appl. Crystallogr., 1999, 32, 1021–1023]. The first data set was collected at 0.36(2) GPa. Then the pressure was increased and the second data set was collected at 0.45(2) GPa in an analogous way. During the course of high-pressure crystallization we found that PCE undergoes a reversible phase transition above ca. 0.62 GPa, but it was extremely difficult to grow a good-quality single crystal at those conditions. Therefore the mixture of PCE and propan-2-ol (pure p.a., POCh) was squeezed in a DAC for growing a single crystal of PCE [R. J. Angel, M. Bujak, J. Zhao, G. D. Gatta and S. D. Jacobsen, J. Appl. Cryst., 2007, 40, 26-32]. Two single crystals of PCE at two different pressure points were grown independently and the room-temperature X-ray intensity data were collected at 0.76(2) and 1.00(2) GPa.

The ruby-fluorescence method, using a BETSA PRL spectrometer, was utilized to measure the pressure in the DAC [J. D. Barnett, S. Block and G. J. Piermarini, *Rev. Sci. Instrum.*, 1973, 44, 1–9; G. J. Piermarini, S. Block, J. D. Barnett and R. A. Forman, *J. Appl. Phys.*, 1975, 46, 2774–2780] with the accuracy of *ca.* 0.02 GPa.

In order to comply with the conversion, we have assigned the monoclinic angle to β , however the group-subgroup relation proceeds from class *mmm* to 2/*m*, and for space groups from *Pnma* for phase I to $P2_1/n11$ for phase II (although space group $P12_1/n1$ has been used, as explained above).

Data collection, data reduction, structure solution and refinement

The low-temperature ambient-pressure (0.1 MPa) and room-temperature (295 K) high-pressure diffraction data were collected on Xcalibur and KUMA KM4-CCD diffractometers, both with the graphite-monochromated MoK α radiation. At 230.0(1) and 85.0(5) K the reflections were measured using ω -scan technique with $\Delta \omega = 0.8^{\circ}$ and the 35 and 25 s exposure time, respectively. The pressurefrozen single crystals of PCE were centred on a diffractometer using the shadow method [A. Budzianowski and A. Katrusiak, in High-Pressure Crystallography, eds. A. Katrusiak, P. F. McMillan, Dordrecht: Kluwer Academic Publishers, 2004, pp. 101-112]. The room-temperature high-pressure intensity data, at 0.36(2), 0.45(2), 0.76(2) and 1.00(2) GPa, were collected using the ω - and φ -scan techniques with $\Delta \omega / \Delta \varphi = 0.75 - 1^{\circ}$ and 32 - 38 s exposures. All data were accounted for the Lorentz, polarization and sample absorption effects [CrysAlis CCD and CrysAlis Pro, Oxford Diffraction Ltd., version 1.171.33.57, 2010; CrysAlis Pro, Agilent Technologies version 171.36.28, 2012] and the highpressure data additionally for the absorption of X-rays by the DAC and shadowing of the single crystals by the gasket edges [CrysAlis Pro, Agilent Technologies version 171.36.28, 2012]. The structures were solved by direct methods and refined with SHELX [G. M. Sheldrick, Acta Crystallogr. Sect. A: Found. Crystallogr., 2008, 64, 112–122; G. M. Sheldrick, Acta Crystallogr. Sect. C: Structural Chemistry, 2015, 71, 3–8]. The Cl- and C-atoms were refined with anisotropic displacement parameters. The H-atoms were isotropically refined using the riding model with constrained C-H distances and U_{eq} 's equal to 1.2 times U_{eq}'s of the corresponding C-atoms. The CrysAlis CCD and CrysAlisPro programs [CrysAlis CCD and CrysAlis Pro, Oxford Diffraction Ltd., version 1.171.33.57, 2010; CrysAlis Pro, Agilent Technologies version 171.36.28, 2012] were used for the data collection, unit-cell refinement and data reductions.

The PCE crystal data and structure determination summary are listed in Tables 1 and S1. The bond lengths, angles and the shortest intermolecular distances are gathered in Tables 2, 3, S2 and S3. The intermolecular contacts have been compared using the Hirshfeld surface analysis together with the two-dimensional fingerprint plots, provided by *Crystal Explorer* [S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka and M. A. Spackman, 2007, *CrystalExplorer 2.0*. University of Western Australia, Crowley, Australia; J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Crystallogr., Sect. B: Struct. Sci.,* 2004, **60**, 627–668; M. A. Spackman, J. J. McKinnon and D. Jayatilaka,

CrystEngComm, 2008, **10**, 377–388; M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, **11**, 19–32]. The structure drawings were prepared using *Mercury* [C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466–470].

PCE-I			PCE-II				
temperature, K	295(2)	295(2)	85.0(5)	230.0(1)	295(2)	295(2)	
pressure	0.36(2) GPa	0.45(2) GPa	0.1 MPa	0.1 MPa	0.76(2) GPa	1.00(2) GPa	
formula	C ₂ HCl ₅						
fw, g/mol	202.28	202.28	202.28	202.28	202.28	202.28	
crystal size, mm	0.50 x 0.50 x 0.25	0.50 x 0.50 x 0.25	0.3 x 0.25 x 0.2	0.3 x 0.25 x 0.2	0.25 x 0.21 x 0.15	0.18 x 0.18 x 0.15	
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	
space group, Z, Z'	<i>Pnma</i> , 4, 0.5	<i>Pnma</i> , 4, 0.5	$P2_1/n$, 4, 1				
a, Å	10.325(8)	10.210(7)	9.5458(6)	9.7420(9)	9.5190(17)	9.4194(9)	
<i>b</i> , Å	11.063(3)	11.039(3)	11.3671(6)	11.5821(8)	11.3199(4)	11.2200(3)	
<i>c</i> , Å	6.0870(10)	6.0415(9)	6.4745(4)	6.5192(6)	6.393(3)	6.379(4)	
<i>β</i> , °	90	90	111.126(7)	111.347(10)	111.78(3)	111.75(3)	
<i>V</i> , Å ³	695.3(6)	680.9(5)	655.32(7)	685.11(11)	639.7(3)	626.2(4)	
ρ , g/cm ³	1.932	1.973	2.050	1.961	2.100	2.146	
μ , mm ⁻¹	1.964	2.005	2.084	1.993	2.135	2.181	
θ range, °	4.30-27.61	3.85-27.02	3.32-25.00	3.29-24.93	4.79-26.79	5.00-27.40	
index ranges	$-6 \le h \le 6$	$-6 \le h \le 6$	$-10 \le h \le 11$	$-11 \leq h \leq 11$	$-9 \le h \le 9$	$-11 \le h \le 11$	
	$-12 \le k \le 12$	$-12 \le k \le 12$	$-13 \le k \le 13$	$-13 \le k \le 13$	$-14 \le k \le 14$	$-14 \le k \le 14$	
	$-7 \le l \le 7$	$-7 \le l \le 7$	$-7 \le l \le 4$	$-7 \le l \le 4$	$-3 \le l \le 4$	$-1 \le l \le 1$	
reflns collected	2436	2374	3347	3775	3612	3483	
R _{int}	0.035	0.021	0.025	0.024	0.045	0.045	
data $[I > 2\sigma(I)]$	145	157	1109	1037	342	324	
data/parameters	202/37	208/37	1158/64	1200/64	370/64	350/65	
GOF on F^2	1.175	1.095	1.032	1.076	1.163	1.097	
$R_I [I > 2\sigma(I)]$	0.1066	0.0997	0.0275	0.0393	0.0409	0.0282	
R_1 (all data) ^a	0.1260	0.1147	0.0295	0.0441	0.0501	0.0305	
wR_2 (all data) ^a	0.3494	0.3193	0.0739	0.1114	0.1152	0.0745	
lrgst diff peak, e/Å3	0.304	0.327	0.503	0.475	0.253	0.165	
lrgst diff hole, e/Å3	-0.263	-0.300	-0.395	-0.333	-0.245	-0.156	
${}^{a}R_{I} = \Sigma F_{o} - F_{c} /\Sigma F_{o} ; wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}]\}^{1/2}; w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP], \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3$							

 Table S1. The room-temperature/high-pressure and low-temperature/ambient pressure PCE-I and PCE-II crystal data and structure determination summary.

Compressibility measurement

The room-temperature, at 295(2) K, compressibility measurement, between ambient pressure and *ca*. 1.9 GPa, was performed in the piston-and-cylinder apparatus [B. Baranowski and A. Moroz, *Polish J*. *Chem.*, 1982, **56**, 379–391; K. Dziubek and A. Katrusiak, *Z. Kristallogr.*, 2014, **229**, 129–134]. The pressure was increased in *ca*. 20 MPa steps.

Table S2. The molecular dimensions (Å, °) of PCE-I at 295 K/0.36 GPa and 295 K/0.45 GPa.

temperature, K	295(2)	295(2)			
pressure, GPa/atoms	0.36(2)	0.45(2)			
C1–C2	1.47(8)	1.53(7)			
C1C11	1.82(3)	1.87(3)			
C1C12	1.70(6)	1.65(6)			
C2C13	1.80(3)	1.85(2)			
C1C2C13	111(3)	104(3)			
C2C1Cl1	101(3)	97(3)			
C2C1Cl2	103(4)	114(4)			
Cl1-C1-Cl1 ^I	110(2)	106(2)			
Cl1-C1-Cl2	119(2)	119(2)			
Cl3-C2-Cl3 ^I	116(3)	112(2)			
Cl1-C1-C2-Cl3	-171(2)	-175.3(14)			
Cl1-C1-C2-Cl3 ^I	58(4)	68(3)			
Cl1 ^I C1C2Cl3	-58(4)	-68(3)			
Cl1 ^I -C1-C2-Cl3 ^I	171(2)	175.3(14)			
Cl2ClCl3	65(3)	58.4(17)			
Cl2-Cl-C2-Cl3I	-65(3)	-58.4(17)			
Symmetry code: (I) x , $1/2 - y$, z					

Table S3. The molecular dimensions (Å, °) of PCE-II at 295 K/0.76 GPa, 295 K/1.00 GPa, 230 K/0.1 MPa and 85 K/0.1 MPa.

temperature, K	295(2)	295(2)	230.0(1)	85.0(5)
pressure/atoms	0.76(2) GPa	1.00(2) GPa	0.1 MPa	0.1 MPa
C1–C2	1.45(3)	1.61(2)	1.517(5)	1.539(2)
C1–Cl1	1.788(7)	1.748(6)	1.779(3)	1.7732(18)
C1C12	1.761(6)	1.759(6)	1.780(3)	1.7601(17)
C1C13	1.770(17)	1.741(12)	1.764(3)	1.7675(17)
C2–Cl4	1.82(2)	1.743(12)	1.759(4)	1.7654(17)
C2C15	1.790(8)	1.755(7)	1.768(3)	1.7648(18)
C1C2Cl4	111.2(6)	111.4(5)	110.9(2)	110.79(12)
C1C2C15	112.0(8)	110.2(8)	110.3(2)	111.08(13)
C2C1C11	107.7(7)	107.1(8)	107.9(2)	108.32(12)
C2C1Cl2	113.0(12)	108.3(9)	111.0(2)	111.77(12)
C2C1C13	108.5(6)	109.3(5)	109.5(2)	108.89(12)
Cl1-C1-Cl2	110.0(3)	111.1(4)	110.05(17)	109.82(9)
Cl1-C1-Cl3	107.5(9)	110.4(7)	108.77(18)	108.40(9)
Cl2ClCl3	109.9(7)	110.6(7)	109.63(18)	109.58(9)
Cl4-C2-Cl5	106.2(11)	110.9(8)	110.0(2)	109.76(9)
Cl1-C1-C2-Cl4	64.3(9)	61.0(5)	61.5(3)	61.86(14)
Cl1-C1-C2-Cl5	-177.0(6)	-175.51(19)	-176.40(16)	-175.87(8)
Cl2ClClCl4	-57.4(6)	-58.9(5)	-59.1(3)	-59.26(15)
Cl2ClC2Cl5	61.2(11)	64.6(6)	63.0(3)	63.01(14)
Cl3-C1-C2-Cl4	-179.5(3)	-179.40(16)	179.71(16)	179.55(8)
Cl3-Cl-C2-Cl5	-60.9(10)	-56.0(6)	-58.2(3)	-58.18(14)



Fig. S1. The phase diagram of PCE. The boiling point at 0.1 MPa (435.15 K; b.p.), melting point at 0.1 MPa (244.37 K; m.p.) and the critical point (3.65 MPa/663.15 K; c.p.) after [D. R. Lide, ed., *CRC Handbook of Chemistry and Physics, Internet Version 2007*, Taylor and Francis, Boca Raton, FL, 87th edn, 2007]; the triple point (t.p.) at *ca.* 260 K/100 MPa deduced from a DSC diagram (Fig. S2); the freezing point (f.p.) at 295 K from this work; the freezing line obtained from the m.p. at 0.1 MPa, f.p. at 295 K/0.22 GPa and from melting point at 0.45 GPa (our optical observations of PCE melting in the DAC – spectroscopic pressure calibration and temperature measured by a thermocouple – red squares); diffractometric determinations of PCE-I (green circles) and PCE-II (blue circles); the PCE-I/PCE-II boundary line from optical observations of the phase transition during high-pressure experiments at 295 K/0.62 GPa and 355 K/1.00 GPa; the inset magnifies the gas-liquid region: the experimental vapour-pressure data (red triangles after [R. H. Perry and D. W. Green, *Perry's Chemical Engineers' Handbook*, 7th Edition, The McGraw Hill Companies, Inc, 1999]) and the gas-liquid boundary extrapolation (red line).



Fig. S2. The DSC cooling and heating (bottom) runs of PCE, measured at rate of 5 °C/min, with a DSC 2010 TA Instruments Differential Scanning Calorimeter.



Fig. S3. The molecular volume of PCE at room temperature as a function of pressure measured in the piston-andcylinder press (green diamonds). Red triangles and blue circles indicate the molecular volume obtained from the highpressure and low-temperature single-crystal X-ray diffraction experiments, respectively.



Fig. S4. The shortest H…H, H…Cl and Cl…Cl intermolecular distances (Å) in phases I and II of PCE. The horizontal lines mark the sums of van der Waals radii for relevant atoms [A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451; S. C. Nyburg, C. H. Faerman, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 274–279; S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871–885].



2.8 de

2.

2

2.2

Н∙∙∙Н

2

CI---H/H--CI

2.8 de

2.

2

2.

CI···CI

2.8 de

Fig. S5. The two-dimensional fingerprint plots of PCE-I molecules at: 295 K/0.36 GPa (a) and 295 K/0.45 GPa (b), and PCE-II molecules at: 295 K/0.76 GPa (c), 295 K/1.00 GPa (d), 230 K/0.1 MPa (e) and 85 K/0.1 MPa (f).



Fig. S6. Temperature- and pressure dependence of unit-cell parameters a, b, c, monoclinic β angle and unit-cell volume of PCE.