Supplementary Material (ESI) for CrystEngComm

Supplementary Information
Molecular association in low-temperature and high-pressure polymorphs of 1,1,1,2-tetrachloroethane

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Table S1 The 1112TCE crystal data and structure determination summary

temperature, K	100.0(1)	195.0(1)	295(2)	295(2)	295(2)
pressure	0.1 MPa	0.1 MPa	1.05(5) GPa	1.65(5) GPa	2.55(5) GPa
formula	$C_2H_2Cl_4$	$C_2H_2Cl_4$	$C_2H_2Cl_4$	$C_2H_2Cl_4$	$C_2H_2Cl_4$
fw, g/mol	167.84	167.84	167.84	167.84	167.84
crystal size, mm^3	0.30 x 0.20 x 0.20	0.30 x 0.20 x 0.20	0.44 x 0.43 x 0.25	0.44 x 0.44 x 0.25	0.43 x 0.43 x 0.25
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group, Z	$C2/c$, 8	$C2/c$, 8	$P2_1/c$, 4	$P2_1/c$, 4	$P2_1/c$, 4
a, Å	22.1891(15)	22.2760(8)	5.7549(14)	5.6957(14)	5.5937(14)
b, Å	5.4975(2)	5.59764(17)	11.979(7)	11.850(7)	11.586(6)
c, Å	10.2493(6)	10.3599(4)	8.734(5)	8.610(5)	8.336(5)
β, º	110.055(7)	109.912(4)	110.32(4)	110.35(4)	110.60(4)
V, $Å^3$	1174.45(11)	1214.58(7)	564.6(5)	544.9(5)	505.7(4)
ρ, g/cm^3	1.898	1.836	1.974	2.046	2.204
μ, mm^{-1}	1.864	1.802	1.938	2.009	2.164
θ range, º	3.83 – 25.00	3.77 – 25.00	3.01 – 24.96	3.05 – 25.00	3.15 – 24.90
index ranges	$-26 \le h \le 26$	$-26 \le h \le 26$	$-6 \le h \le 6$	$-6 \le h \le 6$	$-6 \le h \le 6$
	$-4 \le k \le 6$	$-4 \le k \le 6$	$-11 \le k \le 11$	$-11 \le k \le 11$	$-11 \le k \le 11$
	$-12 \le l \le 12$	$-12 \le l \le 12$	$-8 \le l \le 8$	$-8 \le l \le 8$	$-8 \le l \le 8$
reflns collected	4398	4591	3635	3565	3193
R_{int}	0.0172	0.0200	0.2175	0.1536	0.2712
data [$I > 2\sigma(I)$]	944	927	488	478	404
data/parameters	1034/75	1076/75	515/55	500/55	443/55
GOF on F^2	1.084	1.104	1.155	1.180	1.154
R_1 [$I > 2\sigma(I)$]	0.0261	0.0383	0.0861	0.0691	0.0901
R_1 (all data)[a]	0.0294	0.0441	0.1269	0.0713	0.0973
wR_2 (all data)[a]	0.0543	0.0940	0.2024	0.1729	0.2365
lrgst diff peak, $e/Å^3$	0.616	0.578	0.471	0.434	0.746
lrgst diff hole, $e/Å^3$	–0.592	–0.362	–0.423	–0.428	–0.541

[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 S2a Molecular dimensions (Å, º) for 1112TCE

Atoms; Pressure/Temperature (K)		0.1 MPa/100.0(1)	0.1 MPa/195.0(1)	1.05(5) GPa/295(2)	1.65(5) GPa/295(2)	2.55(5) GPa/295(2)
C11–Cl1/C12–Cl4	C1–Cl1	1.787(6)/1.884(18)	1.797(11)/1.90(3)	1.774(10)	1.779(8)	1.739(11)
C11–Cl2/C12–Cl3	C1–Cl2	1.775(4)/1.796(11)	1.776(7)/1.787(16)	1.780(8)	1.777(7)	1.764(9)
C11–Cl3/C12–Cl2	C1–Cl3	1.788(4)/1.849(10)	1.788(7)/1.830(15)	1.749(9)	1.759(7)	1.770(10)
C11–C21/C12–C22	C1–C2	1.527(9)/1.42(3)	1.519(16)/1.45(4)	1.527(13)	1.510(10)	1.537(15)
C21–Cl4/C22–Cl1	C2–Cl4	1.753(6)/1.768(18)	1.747(11)/1.74(3)	1.778(10)	1.766(8)	1.741(11)
C11–C21–Cl4/C12–C22–Cl1	C1–C2–Cl4	110.4(4)/108.4(11)	110.2(7)/108.0(17)	111.5(7)	111.9(5)	113.4(8)
C21–C11–Cl1/C22–C12–Cl4	C2–C1–Cl1	106.0(3)/103.8(10)	105.8(6)/103.7(15)	106.3(6)	106.9(5)	108.5(8)
C21–C11–Cl2/C22–C12–Cl3	C2–C1–Cl2	109.0(4)/108.1(12)	108.8(7)/108.5(18)	110.5(6)	110.5(4)	109.5(6)
C21–C11–Cl3/C22–C12–Cl2	C2–C1–Cl3	108.8(4)/105.2(11)	109.2(7)/105.7(17)	111.2(6)	111.8(5)	109.7(7)
Cl1–C11–Cl2/Cl4–C12–Cl3	Cl1–C1–Cl2	113.2(3)/118.1(8)	113.4(5)/117.5(12)	109.4(5)	109.0(4)	110.6(5)
Cl1–C11–Cl3/Cl4–C12–Cl2	Cl1–C1–Cl3	112.0(3)/116.5(8)	112.0(5)/115.6(12)	109.2(4)	108.3(3)	108.9(4)
Cl2–C11–Cl3/Cl3–C12–Cl2	Cl2–C1–Cl3	107.7(2)/104.2(6)	107.5(4)/105.2(9)	110.2(5)	110.1(4)	109.6(6)
Cl1–C11–C21–Cl4/Cl4–C12–C22–Cl1	Cl1–C1–C2–Cl4	–178.4(2)/179.9(5)	–178.5(3)/179.8(7)	–175.8(4)	–174.6(3)	–173.4(5)
Cl2–C11–C21–Cl4/Cl3–C12–C22–Cl1	Cl2–C1–C2–Cl4	59.4(4)/53.6(10)	59.2(7)/54.1(15)	65.6(7)	66.8(5)	65.7(8)
Cl3–C11–C21–Cl4/Cl2–C12–C22–Cl1	Cl3–C1–C2–Cl4	–57.8(4)/–57.3(9)	–57.8(7)/–58.3(14)	–57.0(8)	–56.2(6)	–54.6(8)

Table S2b The shortest intermolecular distances and angles (Å, º) for 1112TCE

Atoms; Pressure/Temperature (K)		0.1 MPa/100.0(1)	0.1 MPa/195.0(1)	1.05(5) GPa/295(2)	1.65(5) GPa/295(2)	2.55(5) GPa/295(2)
	$Cl1\cdots Cl2^{IV}$	–	–	3.481(4)	3.408(3)	3.271(4)
	$C1–Cl1\cdots Cl2^{IV}$	–	–	129.6(3)	129.7(2)	129.8(3)
	$Cl1\cdots Cl2^{IV}–C1^{IV}$	–	–	164.0(3)	163.5(3)	161.9(4)
	$C1–Cl1\cdots Cl2^{IV}–C1^{IV}$	–	–	–68(1)	–71.0(8)	–73(1)
	$Cl1\cdots Cl3^{V}$	–	–	3.445(4)	3.383(3)	3.262(4)
	$C1–Cl1\cdots Cl3^{V}$	–	–	158.8(3)	158.2(2)	156.5(3)
	$Cl1\cdots Cl3^{V}–C1^{V}$	–	–	131.6(3)	130.6(3)	130.8(4)
	$C1–Cl1\cdots Cl3^{V}–C1^{V}$	–	–	–103.0(8)	–105.4(6)	–106.4(7)
	$Cl1\cdots Cl4^{VI}$	–	–	–	–	3.436(3)
	$C1–Cl1\cdots Cl4^{VI}$	–	–	–	–	98.6(3)
	$Cl1\cdots Cl4^{VI}–C2^{VI}$	–	–	–	–	143.5(3)
	$C1–Cl1\cdots Cl4^{VI}–C2^{VI}$	–	–	–	–	–164.7(8)
	$Cl2\cdots Cl4^{VII}$	–	–	–	–	3.405(5)
	$C1–Cl2\cdots Cl4^{VII}$	–	–	–	–	128.6(4)
	$Cl2\cdots Cl4^{VII}–C2^{VII}$	–	–	–	–	118.7(5)
	$C1–Cl2\cdots Cl4^{VII}–C2^{VII}$	–	–	–	–	83.5(6)
	$Cl3\cdots Cl3^{VIII}$	–	–	–	–	3.404(6)
	$C1–Cl3\cdots Cl3^{VIII}$	–	–	–	–	130.5(4)
	$Cl3\cdots Cl3^{VIII}–C1^{VIII}$	–	–	–	–	130.5(4)
	$C1–Cl3\cdots Cl3^{VIII}–$	–	–	–	–	180.00
$Cl3\cdots Cl4^{I}$	$Cl3\cdots Cl4^{IX}$	3.424(1)	3.484(2)	–	3.490(3)	3.413(3)
$C11–Cl3\cdots Cl4^{I}/C12–Cl3\cdots Cl4^{I}$	$C1–Cl3\cdots Cl4^{IX}$	160.8(2)/160.9(6)	161.3(4)/161.2(8)	–	144.2(3)	144.6(4)
$Cl3\cdots Cl4^{I}–C21^{I}/Cl3\cdots Cl4^{I}–C22^{I}$	$Cl3\cdots Cl4^{IX}–C2^{IX}$	125.0(2)/–	125.2(2)/–	–	88.0(2)	86.6(3)
$C11–Cl3\cdots Cl4^{I}–C21^{I}$	$C1–Cl3\cdots Cl4^{IX}–C2^{IX}$	5.2(6)	4(1)	–	–57.6(5)	–56.5(8)
$C12–Cl3\cdots Cl4^{I}–C22^{I}$	–	–	–	–	–	–
$C11–Cl3\cdots Cl4^{I}–C22^{I}$	–	–	–	–	–	–
$C12–Cl3\cdots Cl4^{I}–C21^{I}$	–	98(1)	96(2)	–	–	–
$Cl4\cdots Cl4^{II}$	–	3.428(2)	3.474(3)	–	–	–
$C21–Cl4\cdots Cl4^{II}/C22–Cl4\cdots Cl4^{II}$	–	144.6(2)/–	143.9(3)/–	–	–	–
$Cl4\cdots Cl4^{II}–C21^{II}/Cl4\cdots Cl4^{II}–C22^{II}$	–	144.6(2)/–	143.9(3)/–	–	–	–
$C21–Cl4\cdots Cl4^{II}–C21^{II}$	–	–35.3(5)	–35.8(8)	–	–	–
$C22–Cl4\cdots Cl4^{II}–C22^{II}$	–	–	–	–	–	–

C21–Cl4···Cl4^{I}–C22^{II}	–	–	–	–	–	–
C22–Cl4···Cl4^{II}–C21^{II}	–	–	–	–	–	–
	Cl4···C2^{X}	–	–	–	–	3.412(11) (Table S3)
	C2–Cl4···C2^{X}	–	–	–	–	100.3(4)
	Cl4···C2^{X}–C1^{X}	–	–	–	–	154.7(7)
	Cl4···C2^{X}–Cl4^{X}	–	–	–	–	79.7(4)
	C2–Cl4···C2^{X}–C1^{X}	–	–	–	–	–124(2)
	C2–Cl4···C2^{X}–Cl4^{X}	–	–	–	–	0.00
	Cl2···H21^{XI}	–	–	–	2.94	2.85
	C1–Cl2···H21^{XI}	–	–	–	105.2	103.8
	Cl2···H21^{XI}–C2^{XI}	–	–	–	144.1	142.5
	C1–Cl2···H21^{XI}–C2^{XI}	–	–	–	32.1	37.1
	Cl4···H21^{X}	–	–	–	–	2.82 (Table S3)
	C2–Cl4···H21^{X}	–	–	–	–	109.2
	Cl4···H21^{X}–C2^{X}	–	–	–	–	119.9
	C2–Cl4···H21^{X}–C2^{X}	–	–	–	–	53.5
Cl4···H212^{III}	Cl4···H22^{XII}	2.83 (Table S3)	2.87	2.87	2.84	2.74 (Table S3)
C21–Cl4···H212^{III}/C22–Cl4···H212^{III}	C2–Cl4···H22^{XII}	107.7/–	106.2/–	79.1	79.3	77.9
Cl4···H212^{III}–C21^{III}/Cl4···H212^{III}–C22^{III}	Cl4···H22^{XII}–C2^{XII}	142.5/–	144.0/–	154.7	153.0	150.9
C21–Cl4···H212^{III}–C21^{III}	C2–Cl4···H22^{XII}–C2^{XII}	6.5	5.0	67.5	68.5	72.7
C22–Cl4···H212^{III}–C22^{III}	–	–	–	–	–	–
C21–Cl4···H212^{III}–C22^{III}	–	–	–	–	–	–
C22–Cl4···H212^{III}–C21^{III}	–	–	–	–	–	–

Symmetry codes: (I) x, 1 – y, –1/2 + z; (II) 1 – x, y, 3/2 – z; (III) 1 – x, –y, 1 – z; (IV) 1 + x, 3/2 – y, 1/2 + z; (V) 1 – x, 1/2 + y, 1/2 – z; (VI) –x, 1/2 + y, 1/2 – z; (VII) –x, 1 – y, –z; (VIII) 1 – x, 1 – y, –z; (IX) 1 + x, y, z; (X) –x, 1 – y, 1 – z; (XI) x, 3/2 – y, –1/2 + z; (XII) 1 – x, 1 – y, 1 – z.

Table S3 Hydrogen bonds (Å, º) for 1112TCE

Atoms	D–H	H···A	D···A	D–H···A
0.1 MPa/100.0(1) K				
C21–H212···Cl4^{I}	0.97	2.83	3.647(5)	142.5
2.55(5) GPa/295(2) K				
C2–H21···Cl4^{II}	0.97	2.82	3.412(11)	119.9
C2–H22···Cl4^{III}	0.97	2.74	3.620(10)	150.9

Symmetry codes: (I) 1 – x, –y, 1 – z; (II) –x, 1 – y, 1 – z; (III) 1 – x, 1 – y, 1 – z.