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Supporting information for article:

**Melting point, molecular symmetry and aggregation of tetrachloro-
benzene isomers: the role of halogen bonding**

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Table S1 Molecular dimensions (Å, °) for 1234TCB.

	270 K	90 K
C1–C11	1.724(6)	1.729(6)
C2–C12	1.720(6)	1.718(6)
C3–C13	1.725(6)	1.732(6)
C4–C14	1.725(6)	1.732(6)
C1–C2	1.380(8)	1.395(8)
C1–C6	1.378(8)	1.382(8)
C2–C3	1.393(8)	1.399(8)
C3–C4	1.384(8)	1.385(8)
C4–C5	1.387(8)	1.398(8)
C5–C6	1.384(9)	1.386(8)
C5–H5	0.93	0.93
C6–H6	0.93	0.93
C11–C1–C2	120.8(5)	120.5(4)
C11–C1–C6	119.1(5)	118.9(4)
C12–C2–C1	120.4(4)	120.9(4)
C12–C2–C3	120.1(4)	120.3(4)
C13–C3–C2	119.6(4)	119.4(4)
C13–C3–C4	120.2(4)	120.2(4)
C14–C4–C3	120.4(5)	120.3(4)
C14–C4–C5	119.5(4)	119.4(4)
C1–C2–C3	119.5(5)	118.8(5)
C1–C6–C5	120.9(5)	120.7(5)
C2–C1–C6	120.1(5)	120.6(5)
C2–C3–C4	120.2(5)	120.4(5)
C3–C4–C5	120.1(5)	120.3(5)
C4–C5–C6	119.2(5)	119.2(5)

C1–C6–H6	119.6	119.7
C4–C5–H5	120.4	120.4
C5–C6–H6	119.6	119.7
C6–C5–H5	120.4	120.4
Cl1–C1–C2–Cl2	0.6(7)	0.8(7)
Cl1–C1–C2–C3	–179.0(4)	–179.5(4)
Cl1–C1–C6–C5	–179.9(5)	179.7(4)
Cl2–C2–C3–Cl3	0.0(7)	–1.1(7)
Cl2–C2–C3–C4	178.8(4)	179.0(4)
Cl3–C3–C4–Cl4	–0.1(7)	0.5(7)
Cl3–C3–C4–C5	–179.4(5)	–179.3(4)
Cl4–C4–C5–C6	179.9(5)	179.9(4)
C1–C2–C3–Cl3	179.6(4)	179.2(4)
C1–C2–C3–C4	–1.7(8)	–0.7(8)
C2–C1–C6–C5	0.7(9)	–0.5(8)
C2–C3–C4–Cl4	–178.9(4)	–179.7(4)
C2–C3–C4–C5	1.8(9)	0.5(8)
C3–C4–C5–C6	–0.7(9)	–0.3(8)
C4–C5–C6–C1	–0.5(10)	0.3(8)
C6–C1–C2–Cl2	180.0(5)	–179.0(4)
C6–C1–C2–C3	0.4(8)	0.7(8)

Table S2 Molecular dimensions (Å, °) for 1235TCB.

	270 K	90 K		270 K	90 K
C1–C11	1.7314(17)	1.7355(14)	C7–C17	1.7263(17)	1.7307(14)
C2–C12	1.7179(17)	1.7229(14)	C8–C18	1.7153(18)	1.7219(15)
C3–C13	1.7248(17)	1.7275(14)	C9–C19	1.7291(18)	1.7304(15)
C5–C15	1.7374(18)	1.7392(15)	C11–C111	1.7286(18)	1.7330(15)
C1–C2	1.387(2)	1.393(2)	C7–C8	1.393(2)	1.398(2)
C1–C6	1.380(2)	1.387(2)	C7–C12	1.380(2)	1.385(2)
C2–C3	1.393(2)	1.3967(19)	C8–C9	1.387(2)	1.394(2)
C3–C4	1.378(2)	1.388(2)	C9–C10	1.372(3)	1.382(2)
C4–C5	1.374(2)	1.384(2)	C10–C11	1.383(3)	1.388(2)
C5–C6	1.376(2)	1.383(2)	C11–C12	1.378(2)	1.386(2)
C4–H4	0.93	0.93	C10–H10	0.93	0.93
C6–H6	0.93	0.93	C12–H12	0.93	0.93
C11–C1–C2	120.02(13)	120.07(11)	C17–C7–C8	120.41(14)	120.25(11)
C11–C1–C6	118.68(14)	118.46(11)	C17–C7–C12	118.31(13)	118.53(11)
C12–C2–C1	120.87(13)	120.95(11)	C18–C8–C7	121.00(14)	121.03(11)
C12–C2–C3	121.02(13)	120.82(11)	C18–C8–C9	120.81(14)	120.63(11)
C13–C3–C2	120.05(13)	120.14(11)	C19–C9–C8	120.15(15)	120.15(11)
C13–C3–C4	118.61(14)	118.51(11)	C19–C9–C10	118.43(14)	118.49(11)
C15–C5–C4	118.95(14)	118.79(11)	C111–C11–C10	119.39(14)	119.19(11)
C15–C5–C6	119.31(14)	119.24(11)	C111–C11–C12	119.34(14)	119.33(11)
C1–C2–C3	118.11(15)	118.23(13)	C7–C8–C9	118.19(16)	118.34(13)
C1–C6–C5	118.77(17)	118.50(13)	C7–C12–C11	118.79(16)	118.79(13)
C2–C1–C6	121.30(16)	121.47(13)	C8–C7–C12	121.28(16)	121.22(13)
C2–C3–C4	121.34(16)	121.35(13)	C8–C9–C10	121.42(17)	121.36(13)
C3–C4–C5	118.73(16)	118.48(13)	C9–C10–C11	119.05(17)	118.81(13)
C4–C5–C6	121.74(16)	121.97(13)	C10–C11–C12	121.26(17)	121.47(14)
C1–C6–H6	120.6	120.8	C7–C12–H12	120.6	120.6

C3–C4–H4	120.6	120.8	C9–C10–H10	120.5	120.6
C5–C4–H4	120.6	120.8	C11–C10–H10	120.5	120.6
C5–C6–H6	120.6	120.8	C11–C12–H12	120.6	120.6
C11–C1–C2–C12	–0.3(2)	0.16(17)	C17–C7–C8–C18	0.0(2)	0.00(17)
C11–C1–C2–C3	179.83(12)	–179.83(11)	C17–C7–C8–C9	–179.55(14)	–179.36(11)
C11–C1–C6–C5	–179.54(13)	–179.76(11)	C17–C7–C12–C11	179.45(14)	179.03(11)
C12–C2–C3–C13	–0.5(2)	–0.96(17)	C18–C8–C9–C19	0.6(2)	0.61(18)
C12–C2–C3–C4	179.96(14)	179.75(11)	C18–C8–C9–C10	–179.35(15)	–179.08(11)
C13–C3–C4–C5	–179.51(13)	–179.05(11)	C19–C9–C10–C11	179.71(15)	179.81(11)
C15–C5–C6–C1	179.84(13)	179.97(11)	C111–C11–C12–C7	–179.39(14)	–179.10(11)
C1–C2–C3–C13	179.36(13)	179.03(11)	C7–C8–C9–C19	–179.89(13)	179.97(11)
C1–C2–C3–C4	–0.2(2)	–0.3(2)	C7–C8–C9–C10	0.2(3)	0.3(2)
C2–C1–C6–C5	0.3(3)	0.5(2)	C8–C7–C12–C11	–0.2(3)	–0.6(2)
C2–C3–C4–C5	0.0(3)	0.3(2)	C8–C9–C10–C11	–0.4(3)	–0.5(2)
C3–C4–C5–C15	–179.99(13)	179.64(11)	C9–C10–C11–C111	179.69(15)	179.65(11)
C3–C4–C5–C6	0.3(3)	0.2(2)	C9–C10–C11–C12	0.2(3)	0.1(2)
C4–C5–C6–C1	–0.5(3)	–0.6(2)	C10–C11–C12–C7	0.0(3)	0.4(2)
C6–C1–C2–C12	179.89(13)	179.85(11)	C12–C7–C8–C18	179.66(14)	179.65(11)
C6–C1–C2–C3	0.0(3)	–0.1(2)	C12–C7–C8–C9	0.1(3)	0.3(2)

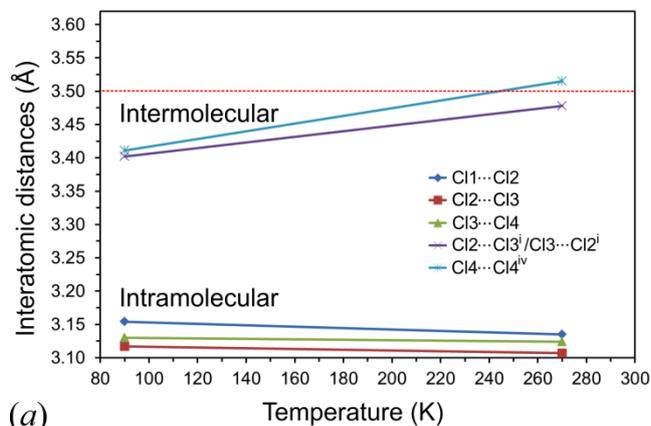
Table S3 Shortest intramolecular and intermolecular contacts (Å), along with the corresponding angles (°), for 1234TCB and 1235TCB. Interatomic distances commensurate with the sums of van der Waals radii of the respective atoms at 90 K (Bondi, 1964; Nyburg & Faerman, 1985; Batsanov, 2001; Hu *et al.*, 2014).

	1234TCB		1235TCB		
	270 K	90 K	270 K	90 K	
Intramolecular					
C11...C12	3.135(3)	3.154(2)	C11...C12	3.1347(7)	3.1492(5)
C1–C11...C12	59.2(2)	59.2(2)	C1–C11...C12	59.53(6)	59.49(5)
C11...C12–C2	59.5(2)	59.4(2)	C11...C12–C2	59.58(6)	59.49(5)
C1–C11...C12–C2	0.2(3)	0.4(3)	C1–C11...C12–C2	–0.12(9)	0.07(8)
C12...C13	3.107(3)	3.117(2)	C12...C13	3.1422(7)	3.1469(5)
C2–C12...C13	60.1(2)	60.2(2)	C2–C12...C13	59.36(6)	59.44(5)
C12...C13–C3	60.2(2)	60.1(2)	C12...C13–C3	59.57(6)	59.60(5)
C2–C12...C13–C3	0.0(3)	–0.5(3)	C2–C12...C13–C3	–0.24(9)	–0.42(8)
C13...C14	3.124(3)	3.130(2)	C17...C18	3.1500(7)	3.1571(5)
C3–C13...C14	59.8(2)	59.8(2)	C7–C17...C18	59.25(6)	59.40(5)
C13...C14–C4	59.7(2)	59.8(2)	C17...C18–C8	59.34(6)	59.33(5)
C3–C13...C14–C4	–0.0(3)	0.2(3)	C7–C17...C18–C8	–0.01(10)	0.00(8)
			C18...C19	3.1342(8)	3.1410(5)
			C8–C18...C19	59.59(6)	59.63(5)
			C18...C19–C9	59.45(7)	59.58(5)
			C8–C18...C19–C9	0.25(10)	0.27(8)
Intermolecular					
C12...C13 ⁱ	3.478(2)	3.402(2)	C12...C19 ^v	3.5490(7)	3.4737(5)
C2–C12...C13 ⁱ	163.1(2)	164.4(2)	C2–C12...C19 ^v	108.08(6)	107.04(5)
C12...C13 ⁱ –C3 ⁱ	129.0(2)	127.7(2)	C12...C19 ^v –C9 ^v	174.03(7)	173.74(5)
C2–C12...C13 ⁱ –C3 ⁱ	64.7(8)	66.7(8)	C2–C12...C19 ^v –C9 ^v	–99.9(7)	–94.3(5)
C13...C12 ⁱ	3.478(2)	3.402(2)	C12...C11 ^{vi}	3.5337(7)	3.4868(5)
C3–C13...C12 ⁱ	129.0(2)	127.7(2)	C2–C12...C11 ^{vi}	167.89(6)	167.82(5)

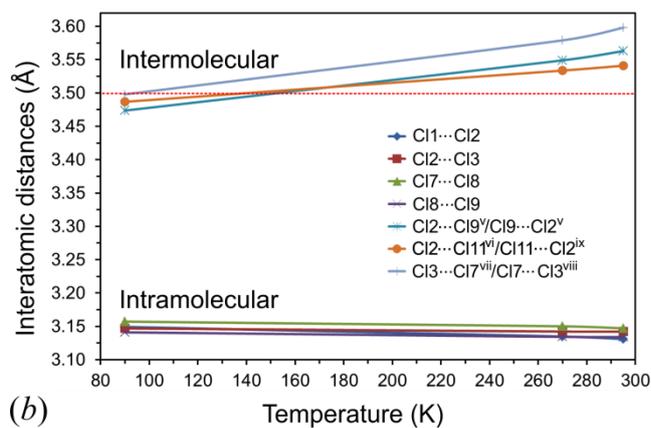
C13...C12 ⁱ -C2 ⁱ	163.1(2)	164.4(2)	C12...C11 ^{vi} -C11 ^{vi}	101.82(7)	101.30(5)
C3-C13...C12 ⁱ -C2 ⁱ	-64.7(8)	-66.7(8)	C2-C12...C11 ^{vi} -C11 ^{vi}	5.0(3)	4.9(2)
C13...H6 ⁱⁱ	2.94	2.89	C13...C17 ^{vii}	3.5790(7)	3.4980(5)
C3-C13...H6 ⁱⁱ	139.2	138.8	C3-C13...C17 ^{vii}	101.74(6)	101.70(5)
C13...H6 ⁱⁱ -C6 ⁱⁱ	139.1	136.4	C13...C17 ^{vii} -C7 ^{vii}	161.69(6)	162.67(5)
C3-C13...H6 ⁱⁱ -C6 ⁱⁱ	-126.6	-128.1	C3-C13...C17 ^{vii} -C7 ^{vii}	45.0(2)	40.9(2)
H6...C13 ⁱⁱⁱ	2.94	2.89	C17...C13 ^{viii}	3.5790(7)	3.4980(5)
C6-H6...C13 ⁱⁱⁱ	139.1	136.4	C7-C17...C13 ^{viii}	161.69(6)	162.67(5)
H6...C13 ⁱⁱⁱ -C3 ⁱⁱⁱ	139.2	138.8	C17...C13 ^{viii} -C3 ^{viii}	101.74(6)	101.70(5)
C6-H6...C13 ⁱⁱⁱ -C3 ⁱⁱⁱ	-126.6	-128.1	C7-C17...C13 ^{viii} -C3 ^{viii}	-45.0(2)	-40.9(2)
C14...C14 ^{iv}	3.515(3)	3.411(3)	C19...C12 ^v	3.5490(7)	3.4737(5)
C4-C14...C14 ^{iv}	141.7(2)	142.2(2)	C9-C19...C12 ^v	174.03(7)	173.74(5)
C14...C14 ^{iv} -C4 ^{iv}	141.7(2)	142.2(2)	C19...C12 ^v -C2 ^v	108.08(6)	107.04(5)
C4-C14...C14 ^{iv} -C4 ^{iv}	180.0	180.0	C9-C19...C12 ^v -C2 ^v	99.9(7)	94.3(5)
			C11...C12 ^{ix}	3.5337(7)	3.4868(5)
			C11-C11...C12 ^{ix}	101.82(7)	101.30(5)
			C11...C12 ^{ix} -C2 ^{ix}	167.89(6)	167.82(5)
			C11-C11...C12 ^{ix} -C2 ^{ix}	5.0(3)	4.9(2)

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, y + 1/2, -z + 1/2$; (iii) $-x + 1, y - 1/2, -z + 1/2$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x, -y, -z + 1$; (vi) $-x + 1, y - 1/2, -z + 1/2$; (vii) $x - 1, -y + 1/2, z - 1/2$; (viii) $x + 1, -y + 1/2, z + 1/2$; (ix) $-x + 1, y + 1/2, -z + 1/2$.

Figure S1 Evolution of the shortest intramolecular and intermolecular Cl...Cl contacts with temperature for 1234TCB (*a*) and 1235TCB (*b*, see Tables 2 and S3 for details; Marsh & Williams, 1981). The red dotted horizontal lines mark the sum of van der Waals radii for two Cl atoms of 3.50 Å (Bondi, 1964; Nyburg & Faerman, 1985; Batsanov, 2001; Hu *et al.*, 2014).



(a)



(b)

Figure S2 Hirshfeld surfaces for: 1234TCB (*a*) and 1235TCB (*b*, surfaces generated separately, the upper surface corresponds to the C1-C6 molecule, whereas the lower one to the C7-C12 molecule) both at 90 K, as well as α -phase 1245TCB at 150 K (*c*, surfaces generated separately, the upper surface corresponds to the C1-C3ⁱ molecule, whereas the lower one to the C4-C6ⁱⁱ molecule, (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z$; Barnett *et al.*, 2006) and β -phase 1245TCB at 173 K (*d*, Anderson *et al.*, 1991) along with the cluster-generated molecules within radius of 4.5 Å. The overlapped surfaces are marked in red, the touching surfaces in white and the separated surfaces in blue (Wolff *et al.*, 2007; McKinnon *et al.*, 2004; Spackman *et al.*, 2008; Spackman & Jayatilaka, 2009).

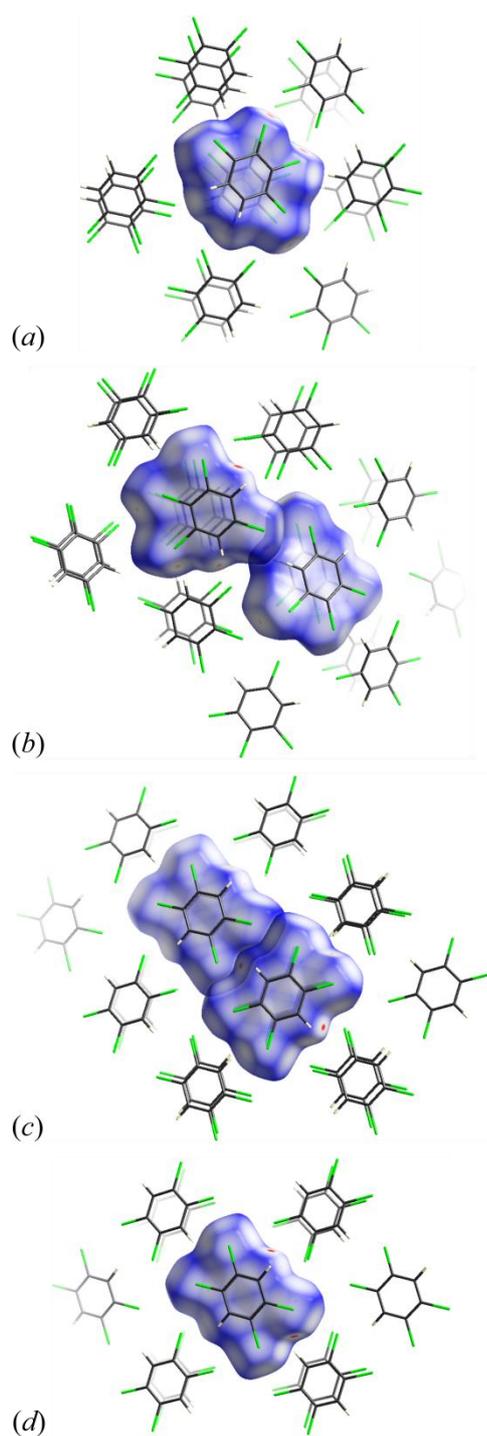


Figure S3 Molecular isodensity surfaces along with the calculated partial atomic charges (NBO, for Cl and H atoms) for tetrachlorobenzene isomers: 1234TCB (*a*), 1235TCB (*b*) and 1245TCB (*c*) mapped with their electrostatic potential. The colours show positive from 0.01 a.u. (blue) to negative -0.001 a.u. (red) and intermediate degrees (orange-green) of electrostatic potential (Frisch *et al.*, 2009; Dennington *et al.*, 2009).

