Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information: Electrostatic matching in phase IV of chloroiodomethane: a new aggregation pattern in the isostructural classes of dihalomethanes

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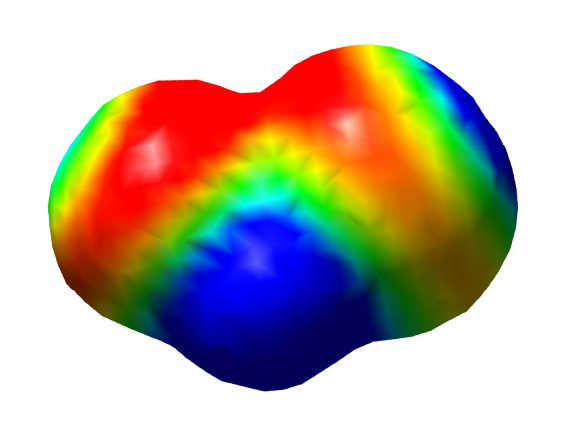

Figure S1. The electrostatic potential mapped on the molecular surface of CH_2ClI: the red-to-blue colour scale ranges from −58.66 to 118.56 kJ/mol, respectively.

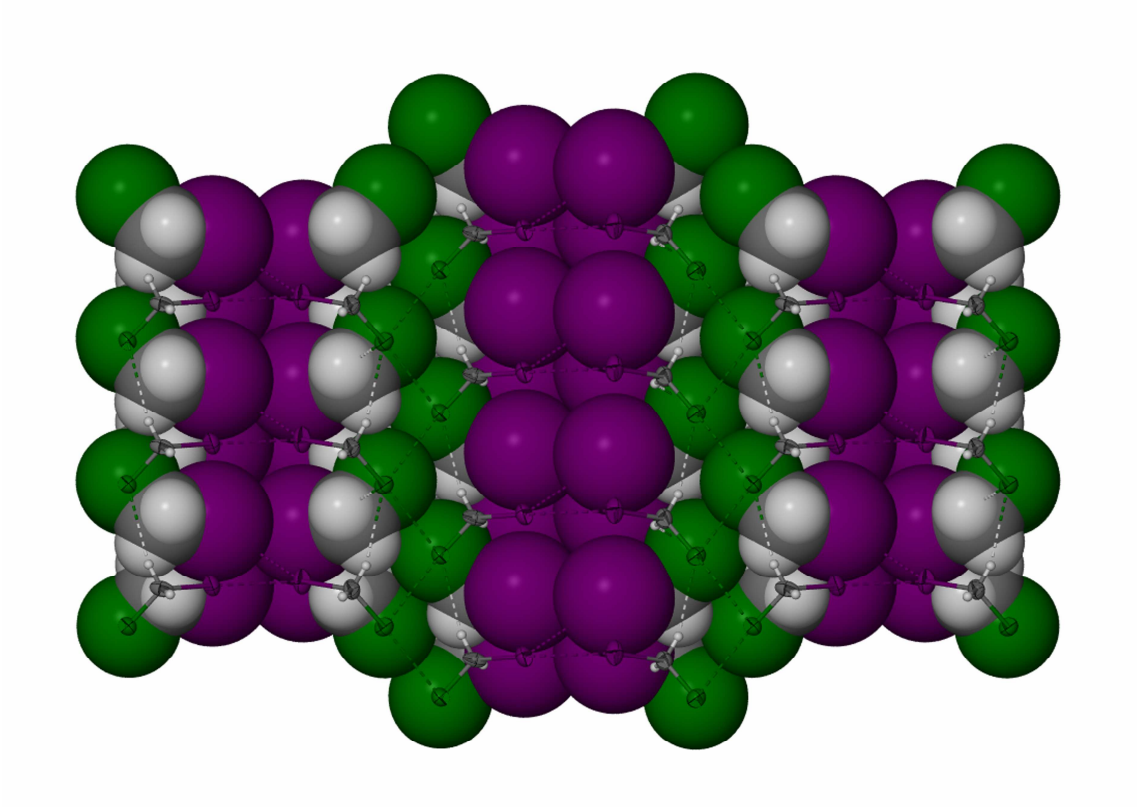

Figure S2. Four layers of CH_2ClI phase IV molecules viewed along ***a***. In the lower three layers molecules are presented as a van der Waals spheres while in the upper layer molecules are shown as a ellipsoid-and-stick models with short halogen···halogen and H···halogen intermolecular interactions indicated with dashed lines. The displacement ellipsoids are shown at the 50% probability level.

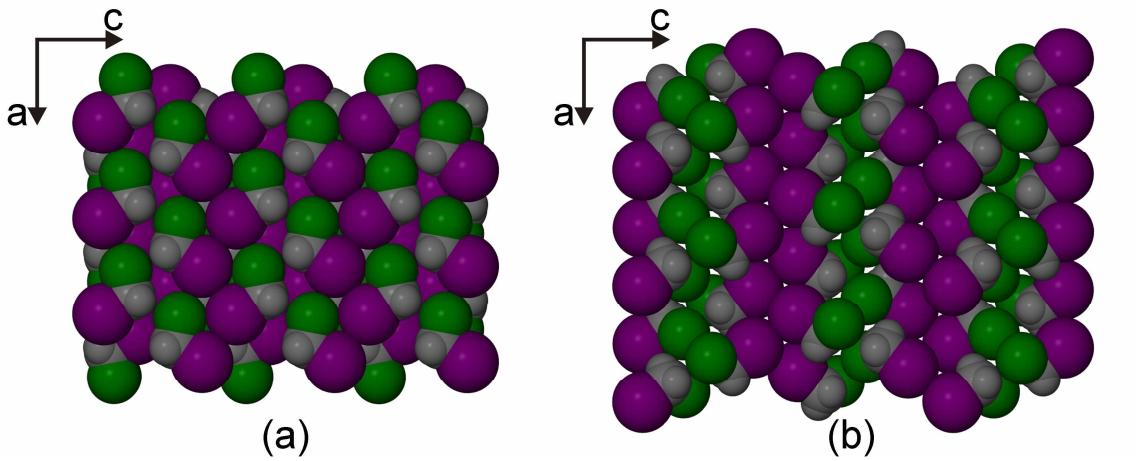

Figure S3. Comparison of CH_2ClI phase III (a) and IV (b) packing viewed along ***b***. Six layers of CH_2ClI molecules perpendicular to ***b*** are represented as a van der Waals spheres models. The gaps present in molecular arrangement in less dense packed CH_2ClI phase IV are clearly visible in (b).

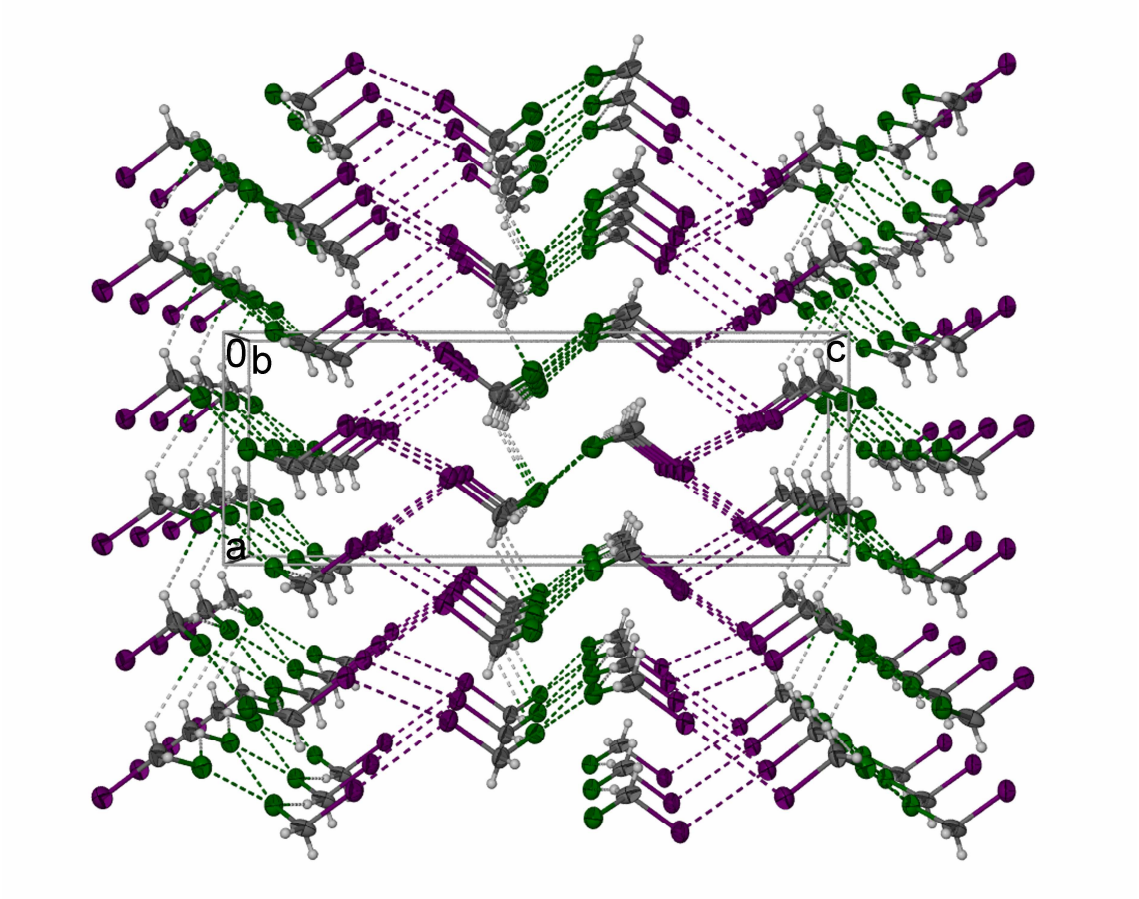

Figure S4. The crystal structure of CH_2ClI phase IV measured at 180 K/0.10 MPa viewed along ***b***. Shortest intermolecular halogen···halogen and H···halogen distances are indicated as dashed lines. The displacement ellipsoids are shown at the 50% probability level.

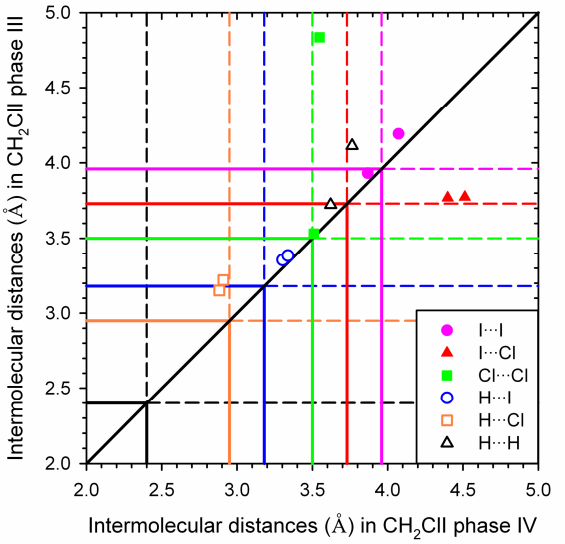

Figure S5. Distance-distance plot of shortest intermolecular distances (Å) present in the structures of CH_2ClI phases III (13 K/0.10 MPa; B. H. Torrie, O. S. Binbrek and R. von Dreele, *Mol. Phys.*, 1993, **79**, 869) and IV (180 K/0.10 MPa; this work). Black, orange, blue, green, red and purple lines represent the sums of van der Waals radii of two H, H and Cl, H and I, two Cl, I and Cl, two I atoms, respectively.

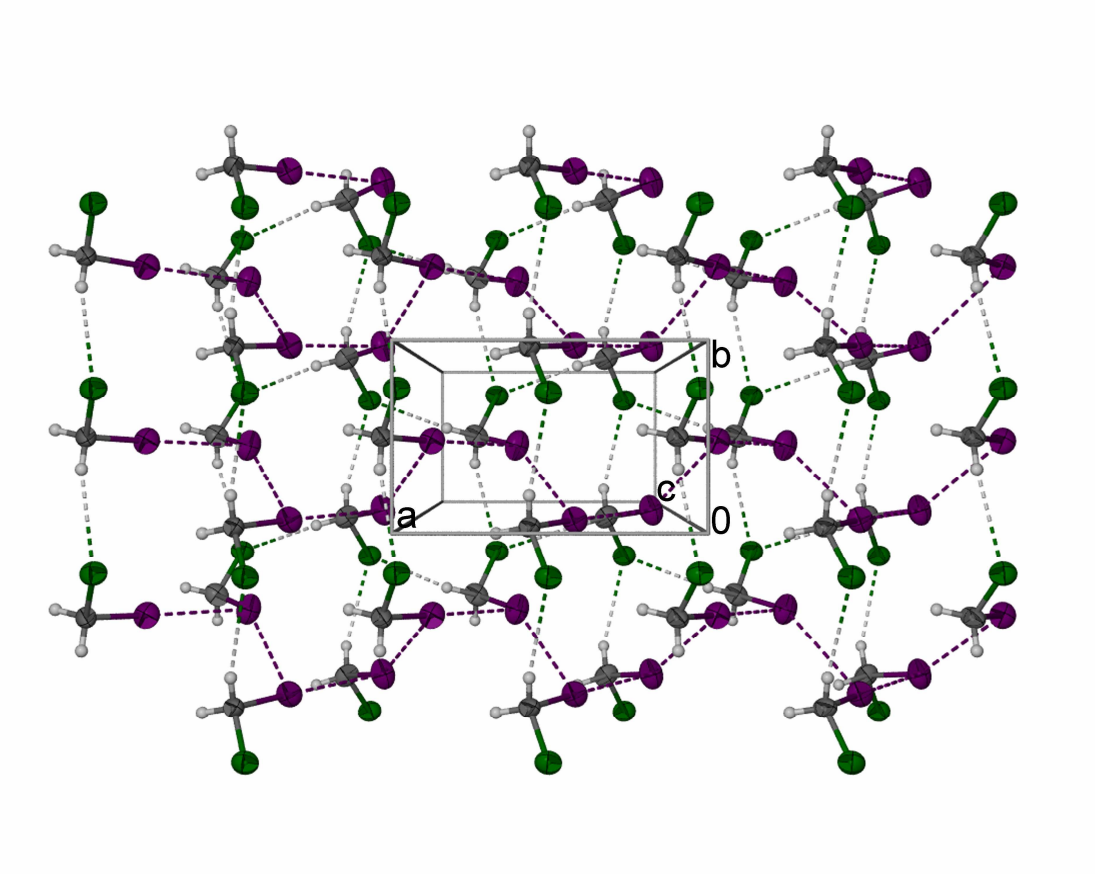

Figure S6. Two layers of CH_2ClI molecules with the same polarization viewed along ***c***. Shortest intermolecular halogen···halogen and H···halogen distances are indicated as dashed lines. The displacement ellipsoids are shown at the 50% probability level.

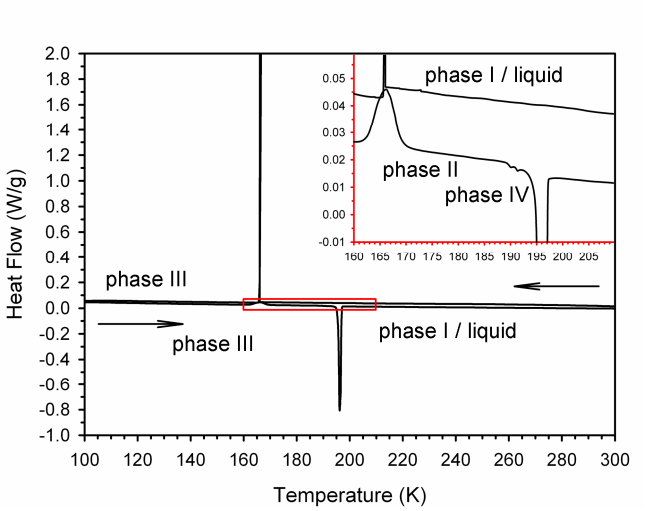

Figure S7. Differential scanning calorimetry (DSC) thermograph for CH_2ClI (9.05 mg) performed in the 300–100 K range with a rate of 1 $K \cdot min^{-1}$. The arrows indicate the directions of temperature changes, and the inset expands the indicated signal range.

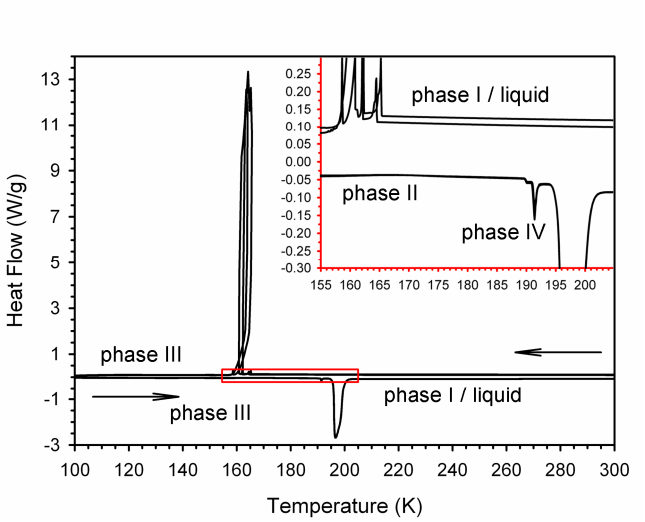

Figure S8. Differential scanning calorimetry (DSC) thermograph for CH_2ClI (9.05 mg) performed in the 300–100 K range with a rate of 10 $K \cdot min^{-1}$. The arrows indicate the directions of temperature changes, and the inset expands the indicated signal range.

Table S1. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^4$) for CH_2ClI in phase IV at 0.10 MPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
0.10 MPa/180 K				
I1	6209(1)	4482(2)	3684(1)	612(3)
Cl1	7054(4)	7656(6)	4995(1)	491(6)
C1	7805(18)	5049(24)	4478(5)	487(26)
H11	7889	3331	4706	585
H12	8922	5537	4336	585
I2	9123(1)	4762(2)	2236(1)	510(3)
Cl2	10054(3)	7600(5)	895(1)	465(6)
C2	10690(15)	4998(21)	1444(8)	491(29)
H21	11828	5376	1580	589
H22	10692	3231	1235	589

Table S2. Lattice parameters, calculated densities and the shortest of I···I and Cl···Cl intermolecular interactions compared for CH_2ClI phases III and IV.

	CD_2ClI phase III at 13 K[a]	CH_2ClI phase III at 1.10 GPa[b]	CH_2ClI phase IV at 180 K[c]
Lattice parameters (Å)			
a	6.383(4)	6.315(1)	7.967(2)
b	6.706(1)	6.562(1)	4.870(1)
c	8.867(4)	8.693(2)	21.351(4)
Cell volume ($Å^3$)	379.55	360.2(1)	828.4(3)
Molecular volume ($Å^3$)	94.89	90.05	103.55
D_x ($g\ cm^{-3}$)	3.086	3.252	2.828
I···I	3.931(2)	3.852(1)	3.867(1)
Cl···Cl	3.531(1)	3.482(1)	3.510(4)

[a] B. H. Torrie, O. S. Binbrek and R. von Dreele, *Mol. Phys.*, 1993, **79**, 869;
[b] M. Podsiadło and A. Katrusiak, *J. Phys. Chem. B*, 2008, **112**, 5355;
[c] This work.

Table S3. Selected bond lengths (Å), angles (º) and intermolecular contacts (Å) for the structure of CH_2ClI phase IV determined at 0.10 MPa/180 K.

molecular dimensions		intermolecular contacts	
		I1···I2^{i} (Å)	3.8672(14)
C1–H11(12) (Å)	0.97	∠C1–I1···I2^{i} (º)	105.8(4)
C1–Cl1 (Å)	1.784(12)	∠I1···I2^{i}–C2^{i} (º)	178.8(3)
C1–I1 (Å)	2.139(12)	I1···I2^{j} (Å)	4.0722(12)
∠Cl1–C1–I1 (º)	112.5(6)	∠C1–I1···I2^{j} (º)	155.6(3)
∠H11–C1–H12 (º)	107.84	∠I1···I2^{j}–C2^{j} (º)	113.3(4)
Cl1···I1 (Å)	3.268(3)	Cl1···Cl2^{k} (Å)	3.510(4)
		∠C1–Cl1···Cl2^{k} (º)	170.8(5)
C2–H21(22) (Å)	0.97	∠Cl1···Cl2^{k}–C2^{k} (º)	90.5(5)
C2–Cl2 (Å)	1.799(13)	Cl1···Cl2^{l} (Å)	3.547(4)
C2–I2 (Å)	2.104(13)	∠C1–Cl1···Cl2^{l} (º)	90.0(4)
∠Cl2–C2–I2 (º)	113.3(5)	∠Cl1···Cl2^{l}–C2^{l} (º)	167.3(4)
∠H21–C2–H22 (º)	107.74	I1···Cl1^{m} (Å)	4.398(3)
Cl2···I2 (Å)	3.264(3)	I2···Cl2^{n} (Å)	4.512(3)
		H11···I1^{o} (Å)	3.6937
		H12···I1^{p} (Å)	3.3379
		H21···I2^{p} (Å)	3.3030
		H22···I2^{o} (Å)	3.7643
		H11···Cl1^{m} (Å)	2.9084
		H12···Cl1^{p} (Å)	2.9969
		H21···Cl2^{p} (Å)	3.1168
		H22···Cl2^{m} (Å)	2.8817

Symmetry codes: (^{i}) *x*, *y*, *z*; (^{j}) –0.5+*x*, 0.5–*y*, *z*; (^{k}) 1.5–*x*, 0.5+*y*, 0.5+*z*; (^{l}) 1.5–*x*, –0.5+*y*, 0.5+*z*; (^{m}) *x*, *y*–1, *z*; (^{n}) –0.5+*x*, 1.5–*y*, *z*; (^{o}) 0.5+*x*, 0.5–*y*, *z*; (^{p}) 0.5+*x*, 1.5–*y*, *z*.