Supplementary information for:

Polymorphism and phase transformations in 2,6-disubstituted N-phenylformamides: the influence of hydrogen bonding, chloro-methyl exchange, intermolecular interactions and disorder
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Results from lattice energy calculations

As described in the main text, the molecule-molecule interactions which contribute most to the stability of the crystal lattice were identified using ZipOpec.[1] The following SCHAKAL[2] diagrams show the arrangement of the three most stabilizing molecules around a central molecule (shown with individual atom colors). It is important to note that the energy values given are for the whole molecule interacting with the central molecule and not for individual atom-atom interactions. When a hydrogen bond or weak interaction coincides with one of these molecule-molecule arrangements then it has been highlighted. However, the contribution of the interaction only makes up part of the total energy for that molecule-molecule interaction.

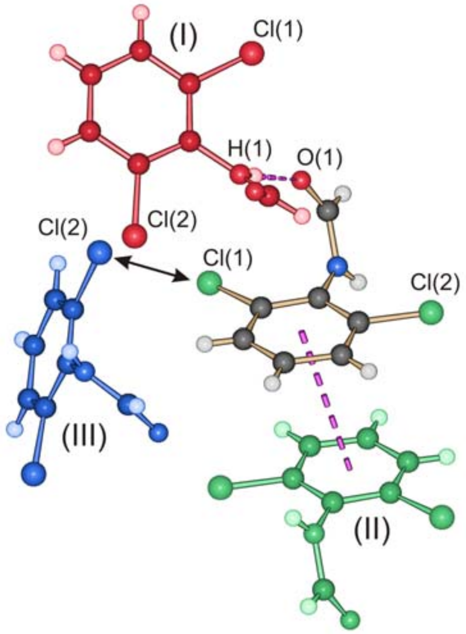

Figure S1 The arrangement of the three molecules contributing most to the stability of structure **1a**; (I) molecules involved in hydrogen bonding (-0.5+x, y, 0.5-z; -39.8 kJ/mol); (II) molecules involved in the π···π interaction (-x, 1-y, -z; -29.8 kJ/mol); (III) molecules involved in the Cl···Cl interaction (-x, 0.5+y, 0.5-z; -8.9 kJ/mol).

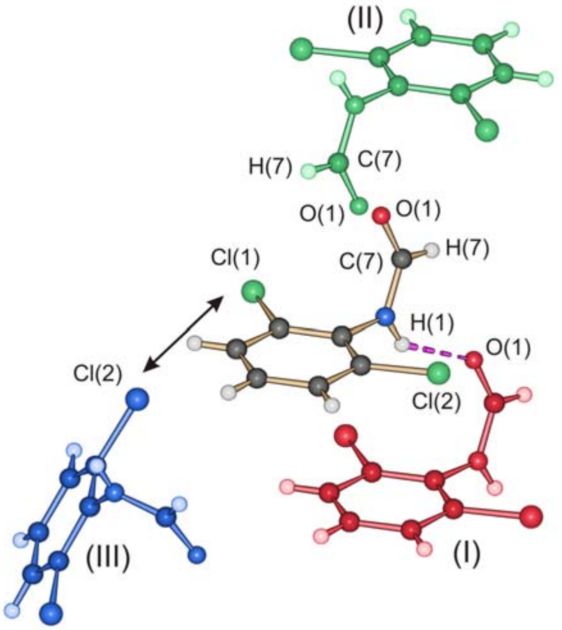

Figure S2 The arrangement of the three molecules contributing most to the stability of structure **1b**; (I) molecules involved in hydrogen bonding (-1+x, y, z; -42.1 kJ/mol); (II) molecules related by a centre of inversion (2-x, 2-y, 2-z; -11.7 kJ/mol); (III) molecules involved in the Cl···Cl interaction (-x, 0.5+y, 0.5-z; -8.9 kJ/mol).

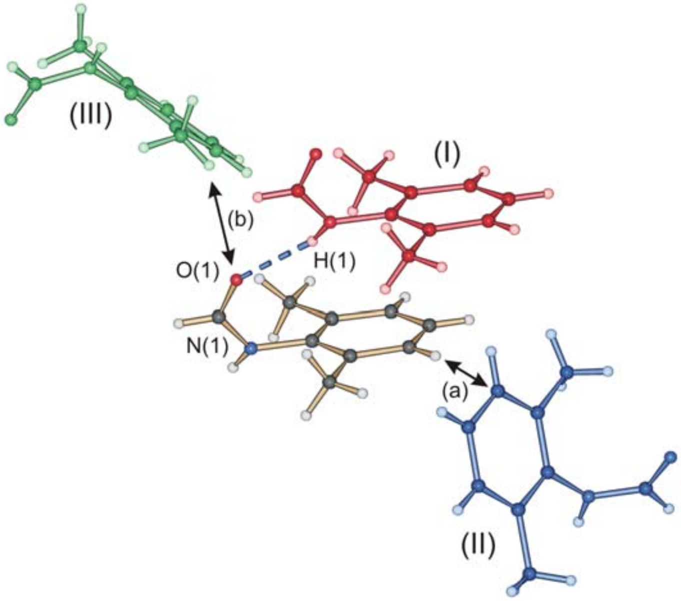

Figure S3 The arrangement of the three molecules contributing most to the stability of structure **3**; (I) molecules involved in hydrogen bonding (-1+x, y, z; -44.0 kJ/mol); (II) molecules possibly involved in a edge-to-face C-H···π interaction as indicated with arrow (a) (-0.5+x, 1.5-y, z; -10.0 kJ/mol); (III) molecules orientated such that the methyl group of one molecule is pointing towards the carbonyl oxygen [indicated by arrow (b)] of the central molecule (-x, 0.5+y, 0.5-z; -10.1 kJ/mol).

Unit cell parameters and diagrams of the previously reported low and high temperature structures of 2,6-dichloroacetanilide provided for comparison with the structures of compound 1

Table S1 Unit cell parameters for the low temperature form (Phase II) of 2,6-dichloroacetanilide

a/Å	b/Å	c/Å	β/º	Volume/Å^3	Space group	Density/g cm^{-3}
7.834(2)	15.319(4)	8.975(2)	121.45(1)	918.9	$P2_1/c$	1.475

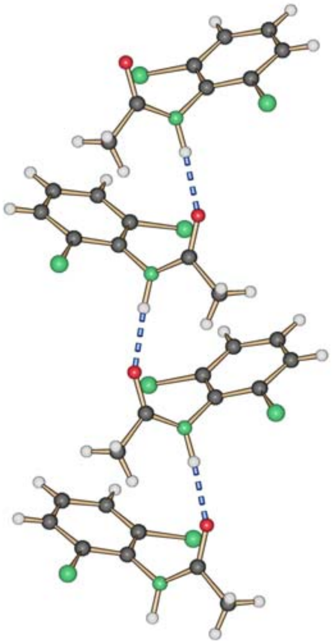

Figure S4 N-H···O hydrogen bonded chain of molecules from the low temperature form (Phase II) of 2,6-dichloroacetanilide (Refcode FEFSAK[3]).

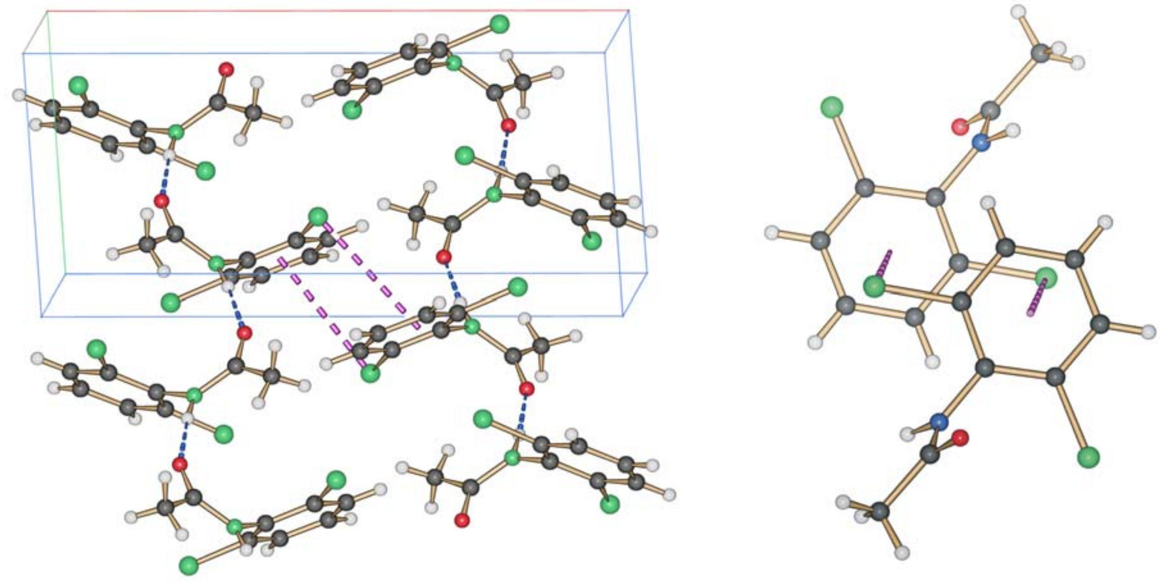
(a) (b)

Figure S5 A sheet of molecules from the low temperature form (Phase II) of 2,6-dichloroacetanilide showing (a) the N-H···O hydrogen bonded chain of molecules, and the Cl atoms interacting with the phenyl ring of a molecule on a neighbouring N-H···O chain. The distance between Cl(2) and the ring centroid (b) of the molecule from the neighbouring chain is 3.85 Å.

Table S2 Unit cell parameters for the high temperature form (Phase I) of 2,6-dichloroacetanilide

a/Å	b/Å	c/Å	Volume/Å^3	Space group	Density/g cm^{-3}
17.268(4)	11.674(3)	4.749(2)	957.3	$P2_12_12_1$	1.416

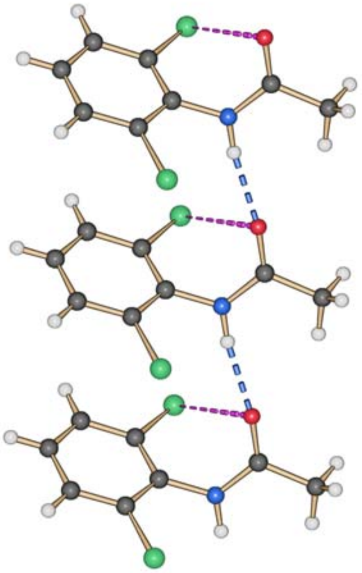

Figure S6 N-H···O hydrogen bonded chain of molecules from the high temperature form (Phase I) of 2,6-dichloroacetanilide (Refcode FEFSAK01[3]). Indicated in purple are intramolecular Cl···O interactions.

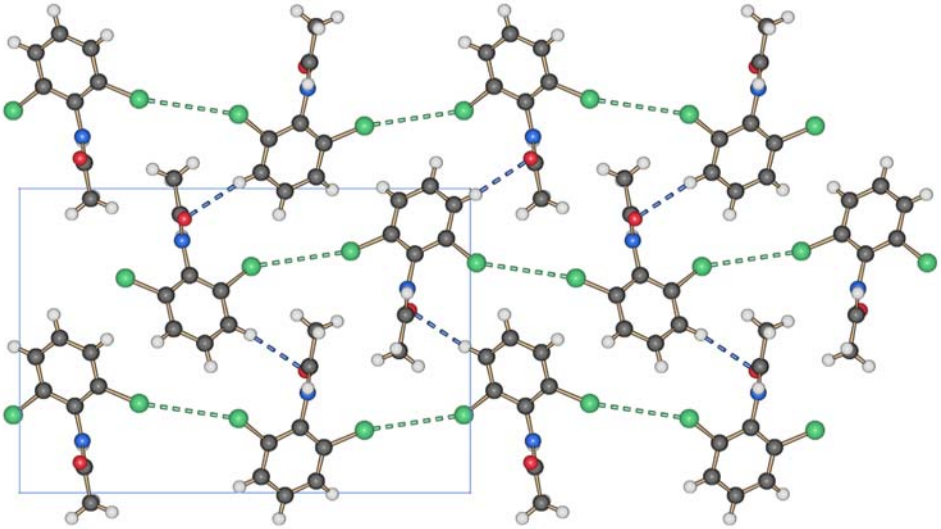

Figure S7 Packing diagram drawn as a projection down the *c* axis of the high temperature form (Phase I) of 2,6-dichloroacetanilide (Refcode FEFSAK01[3]). Indicated in green are intermolecular Cl···Cl interactions and in blue intermolecular C-H···O interactions.

Results from lattice energy calculations for the previously reported low and high temperature structures of 2,6-dichloroacetanilide

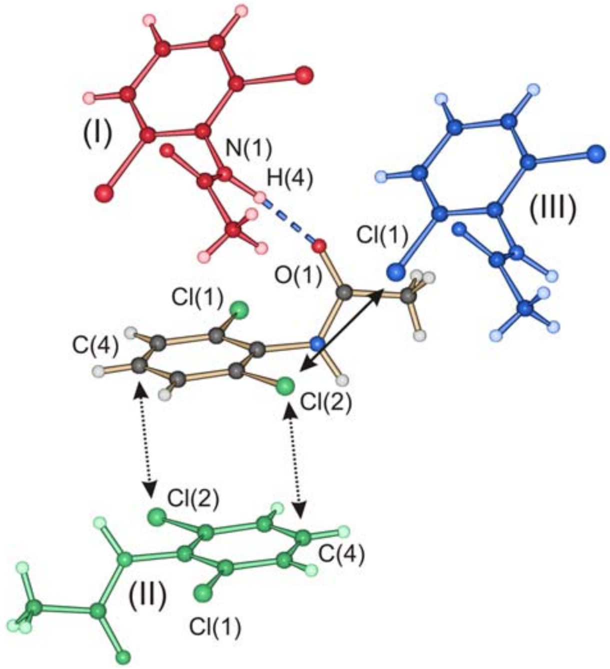

Figure S8 The arrangement of the three molecules contributing most to the stability of low temperature form (Phase II) of 2,6-dichloroacetanilide; (I) molecules involved in hydrogen bonding (x, 0.5-y, -0.5+z; -40.6 kJ/mol); (II) molecules involved in the Cl···π interaction (1-x, -y, 1-z; -21.9 kJ/mol; see also Fig. S5b); (III) molecules involved in a Cl···Cl interaction (indicated by the solid arrow; -1+x, 0.5-y, -0.5+z; -14.8 kJ/mol). The distance between C(4) and Cl(2) [shown with dashed arrows] is 3.74 Å.

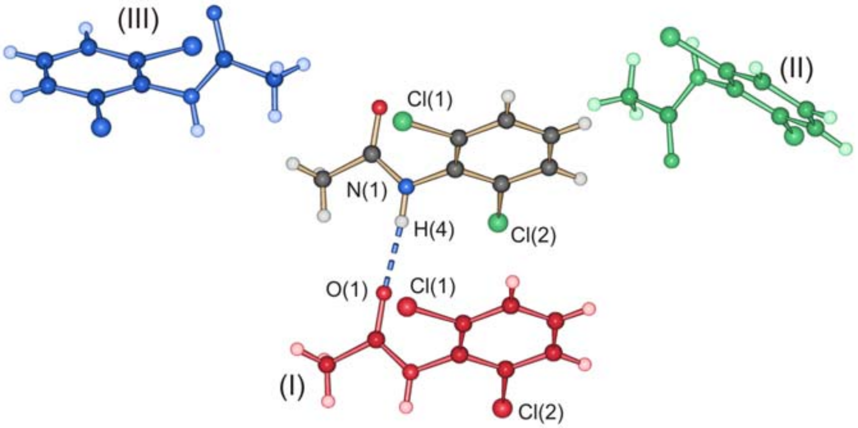

Figure S9 The arrangement of the three molecules contributing most to the stability of the high temperature form (Phase I) of 2,6-dichloroacetanilide; (I) molecules involved in hydrogen bonding (x, y, 1+z; -42.7 kJ/mol); (II) molecules involved a C-H···O and C-H···Cl interaction (2-x, 0.5+y, 0.5-z; -12.5 kJ/mol); (III) molecules involved in a C-H···O interaction (1.5-x, 1-y, -0.5+z; -11.4 kJ/mol).

Table S3 Summary of the most stabilizing molecule-molecule interactions in all the structures discussed in this paper, including the previously reported low and high temperature forms of 2,6-dichloroacetanilide. Separate calculations have been done for the two conformations of **2** and have been indicated by whether the calculation was done on the conformation allowing the Cl···O interaction or on the one allowing the C-H···O interaction. Note the similarities in the sequence of interaction energies for the low temperature structures (big···big···small) versus those of the high temperature forms (big···small···small). Structure **3** also behaves like a high temperature form in this comparison.

Structure	**Symmetry operator between molecules**	**Energy/kJmol^{-1}**
1a	-0.5+x, y, 0.5-z	-39.8
	-x, 1-y, -z	-29.8
	-x, 0.5+y, 0.5-z	-8.9
	-0.5-x, 1-y, -0.5+z	-8.3
1b	-1+x, y, z	-42.1
	2-x, 2-y, 2-z	-11.7
	1.5-x, -0.5+y, 1.5-z	-11.0
	2.5-x, -0.5+y, 1.5-z	-9.1
2a (Cl···O)	0.5+x, y, 0.5-z	-41.5
	-x, 1-y, -z	-28.5
	-x, -0.5+y, 0.5-z	-8.7
2a (C-H···O)	0.5+x, y, 0.5-z	-39.8
	-x, 1-y, -z	-30.1
	0.5-x, -0.5+y, z	-8.2
2b (Cl···O)	x, -1+y, z	-43.6
	x, 1+y, z	-9.8
	0.5+x, 1.5-y, z	-9.2
2b (C-H···O)	x, -1+y, z	-43.7
	-0.5+x, 0.5-y, z	-11.5
	0.5-x, -0.5+y, 1-z	-9.9
3	-1+x, y, z	-44.0
	-x, 0.5+y, 0.5-z	-10.1
	-0.5+x, 1.5-y, -z	-10.0
FEFSAK	x, 0.5-y, -0.5+z	-40.6
	1-x, -y, 1-z	-21.9
	-1+x, 0.5-y, -0.5+z	-14.8
	-1+x, y, z	-9.5
FEFSAK01	x, y, 1+z	-42.7
	2-x, 0.5+y, 0.5-z	-12.5
	1.5-x, 1-y, -0.5+z	-11.4
	1.5-x, 2-y, -0.5+z	-10.6

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[1] OPiX, *A computer program package for the calculation of intermolecular interactions and crystal energies,* A.Gavezzotti, , University of Milano, 2003.

[2] E. Keller, *SCHAKAL*-99, University of Freiberg, Germany.

[3] V. Nagarajan, H. Paulus, N. Weiden and A. Weiss, *J. Chem. Soc., Faraday Trans.2*, **82,** 1986, 1499-1520.