

Intermolecular interactions and unexpected isostructurality in the crystal structures of the dichlorobenzaldehyde isomers

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The crystal structures of the six dichlorobenzaldehyde isomers, four of them newly determined, are analyzed in terms of the geometry and energies of their intermolecular interactions, quantified using the semi-classical density sums (SCDS-PIXEL) method. A consistent feature in all six structures is molecular stacks propagating along a short crystallographic axis of *ca* 3.8 Å. The stacks have a closely comparable geometry in each isomer, but the interaction energies between stacked molecules are variable on account of the differing relative positions of the Cl substituents. In the majority of the isomers the stacking interactions are the most stabilizing in the structure. Exceptions are the 2,4- and 3,5-isomers, where more stabilizing interactions are made between stacks. In general, the most stabilizing non-stacking intermolecular interactions in the structures are those involving C—H···O contacts. Observed motifs based on Cl···Cl interactions appear to be largely imposed by the constraints of other more stabilizing intermolecular interactions. The isomeric series displays the following noteworthy features: (i) the 2,3- and 2,6-isomers are isostructural despite having different orientations of the Cl and aldehyde functionalities; (ii) the 2,5-isomer exhibits whole-molecule disorder; (iii) the 2,5- and 3,5-isomers have more than one molecule in the crystallographic asymmetric unit ($Z' > 1$). These features in particular are considered on the basis of the intermolecular interaction energies.

1. Introduction

In the context of developing robust correlations between molecular and crystal structure, molecular isomers provide a valuable opportunity to examine interactions between particular functional groups in different spatial arrangements within molecules of identical molecular weight. Analysis of sets of isomers (*e.g.* Boese *et al.*, 2001; Simperler *et al.*, 2006) or extended homologous series (*e.g.* Boese *et al.*, 1999; Thalladi, Boese & Thalladi, 2000*a,b*; Thalladi, Nüsse & Boese, 2000; Bond, 2003, 2004, 2006) can provide insight into the driving forces behind observed crystal packing arrangements that might not be immediately apparent from isolated crystal structures. With this perspective, we examine in this paper the structures of the six dichlorobenzaldehyde isomers, denoted (1)–(6) for the 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-isomers, respectively. The intermolecular interactions of aldehydes are generally less well studied than other functional groups such as carboxylic acids or amides, and only the structures of (2) and (4) have been reported previously (Cabello *et al.*, 2010; Gawlicka-Chruszcz *et al.*, 2006). We have determined the structures of the four remaining isomers, and describe here the

Table 1

Experimental details.

For all structures: $C_7H_4Cl_2O$, $M_r = 175.00$. Experiments were carried out at 120 K with Mo $K\alpha$ radiation using a Bruker–Nonius X8APEX-II CCD diffractometer. H-atom parameters were constrained. Comparative data for the published structures of (2) and (4): (2) $P2_1/n$, $a = 13.100$ (1), $b = 3.772$ (1), $c = 15.332$ (1) Å, $\alpha = 90$, $\beta = 113.797$ (2), $\gamma = 90^\circ$, $Z = 4$, $T = 100$ K, CSD refcode: HUGQOQ (Cabello *et al.*, 2010); (4) $P2_1/n$, $a = 3.837$ (1), $b = 13.633$ (4), $c = 13.117$ (1) Å, $\alpha = 90$, $\beta = 91.230$ (7), $\gamma = 90^\circ$, $Z = 4$, $T = 103$ K, CSD refcode: QEWXIA (Gawlicka-Chruszcz *et al.*, 2006).

	(1)	(3)	(5)	(6)
Crystal data				
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$	Monoclinic, $P2_1/n$
a, b, c (Å)	3.7888 (3), 13.7784 (15), 13.0368 (15)	3.8150 (5), 7.8290 (11), 17.895 (3)	3.8094 (3), 14.8887 (13), 6.2014 (5)	3.7785 (5), 31.353 (5), 12.058 (2)
α, β, γ ($^\circ$)	90, 90.979 (5), 90	89.091 (5), 85.728 (5), 81.115 (5)	90, 91.849 (4), 90	90, 91.546 (6), 90
V (Å ³)	680.47 (12)	526.60 (13)	351.54 (5)	1428.0 (4)
Z	4	3	2	8
μ (mm ⁻¹)	0.87	0.84	0.84	0.82
Crystal size (mm)	0.30 × 0.05 × 0.05	0.35 × 0.03 × 0.03	0.30 × 0.20 × 0.10	0.30 × 0.15 × 0.01
Data collection				
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{\min}, T_{\max}	0.751, 1.000	0.704, 0.975	0.881, 1.000	0.698, 0.992
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11 531, 1226, 1036	6319, 1827, 1313	6778, 1272, 1220	13 283, 2678, 1731
R_{int}	0.049	0.047	0.026	0.069
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.093, 1.13	0.037, 0.081, 1.04	0.024, 0.055, 1.09	0.046, 0.098, 1.02
No. of reflections	1226	1827	1272	2678
No. of parameters	91	145	91	181
No. of restraints	0	0	1	0
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.63, -0.37	0.41, -0.30	0.24, -0.22	0.38, -0.35
Flack parameter	–	–	-0.03 (7)	–

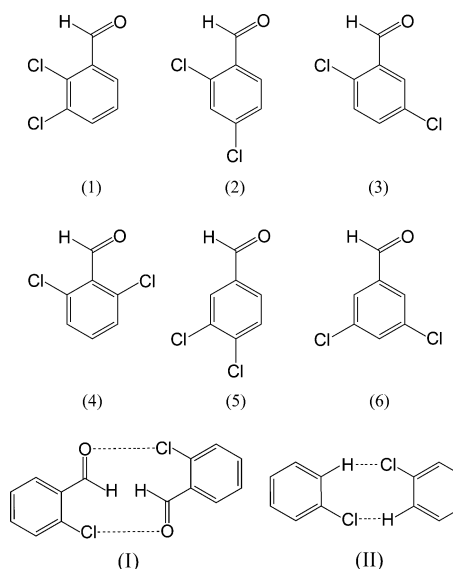
Computer programs used: APEX2 (Bruker, 2004), SAINT (Bruker, 2003), SHELXTL (Sheldrick, 2008).

complete series with a focus on the geometry and energies of the intermolecular interactions.

Previous interest in the structures of halogenated benzaldehydes has concerned principally the orientation of the aldehyde group in *ortho*-halogenated derivatives (Koppenhoefer & Bats, 1986), and the conformational preferences of these compounds have been exploited to achieve control over photocyclization reactions in the solid state (Moorthy, Venkatakrisnan, Mal & Venugopalan, 2003). From the viewpoint of crystal engineering, chloro-substituted aromatic compounds are well known to form ‘short-axis’ structures (Sarma & Desiraju, 1986, and references therein), and this ‘chloro effect’ was exploited by Schmidt and co-workers in the earliest days of the subject to devise novel photochemical reactions (for example, Elgavi *et al.*, 1973). A directly relevant study concerning intermolecular interactions in halogen-substituted aromatic dialdehydes (Moorthy, Venkatakrisnan, Mal, Dixit & Venugopalan, 2003) highlighted a centrosymmetric synthon (I) formed by $C=O \cdots Cl/Br$ ‘halogen bonds’ (Metrangolo & Resnati, 2008; Gavezzotti, 2008a) in the crystal structures of some aromatic aldehydes with Cl or Br substituents. Observation of the same synthon is a possibility for the four dichlorobenzaldehyde isomers with Cl in the *ortho* position, and we consider therefore the frequency of occurrence of (I) within these structures. We also refer here to synthon (II), based on $C-H \cdots Cl$ interactions. The dichlorobenzaldehyde series as a whole exhibits several noteworthy features:

- (i) the 2,3- and 2,6-isomers are isostructural, despite having different orientations of the Cl and aldehyde functionalities;
- (ii) the 2,5-isomer exhibits whole-molecule disorder;
- (iii) the 2,3 and 2,5-isomers have $Z' > 1$.

We examine these features in particular by analysis of the geometry and energies of the intermolecular interactions.



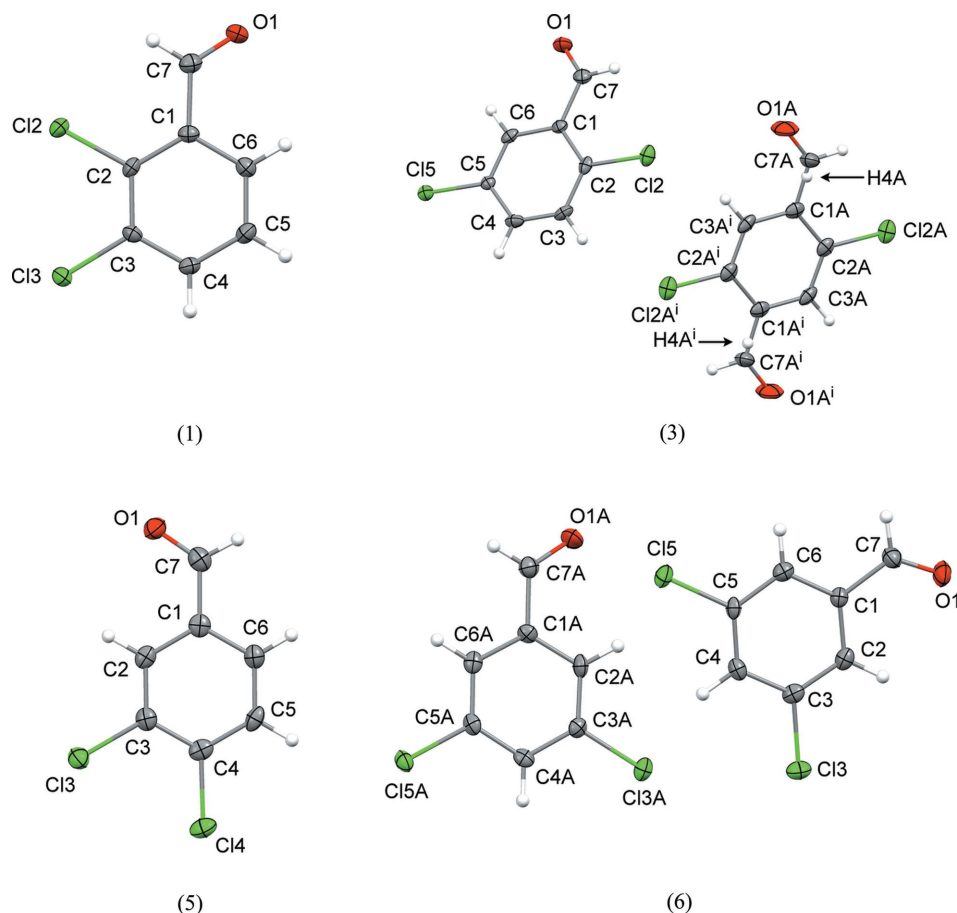


Figure 1
Molecular structures of the new crystal structures, (1), (3), (5) and (6), showing displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary size. For (3) the disorder components C7A/O1A/H7A and H4A have site occupancy 0.5 [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

2. Experimental

The dichlorobenzaldehyde isomers were purchased from Sigma Aldrich and recrystallized from acetone. Crystallographic details are summarized in Table 1, and ellipsoid plots for the four new structures are shown in Fig. 1. All H atoms were placed in calculated positions and refined as riding using the default parameters within *SHELXL* (Sheldrick, 2008). Intermolecular interaction energies were calculated using the SCDS-PIXEL method (Gavezzotti, 2003, 2005) within the 2007 version of the *OPIX* package (Gavezzotti, 2007).¹ Full details of the calculations are provided in the supplementary material.² H-atom positions were re-calculated within *OPIX* with a C–H distance of 1.08 Å, and the values given throughout the discussion refer to the re-calculated structures (provided in CIF format in the supplementary material). The calculated interaction energies are partitioned into coulombic,

¹ The *OPIX* package has been superseded by the *CLP* package (Gavezzotti, 2011).

² Supplementary data for this paper are available from the IUCr electronic archives (Reference: GP5044). Services for accessing these data are described at the back of the journal.

polarization, dispersion and repulsion terms, and they are expected to be accurate within a range of 1–2 kJ mol⁻¹. Molecules are treated as rigid and intramolecular energies are not considered. For (3), where one molecule in the unit cell is disordered about an inversion centre in space group *P* $\bar{1}$, the space-group symmetry was lowered to *P*1 and one orientation of the disordered molecule was retained. This gives a structure with three molecules in the asymmetric unit, which cannot be handled in full by the *OPIX* package since it is limited to structures with no more than two independent molecules. The structure was therefore processed three times, with the three possible pairs of molecules included in the asymmetric unit. This considers all relevant pairwise intermolecular interactions between the molecules, assuming some constraints on the nature of the disorder, as described in §3.

3. Results and discussion

3.1. Crystal structures of the dichlorobenzaldehyde isomers

In the *ortho*-substituted compounds (1)–(4) the aldehyde group is oriented in the expected manner (Koppenhoefer & Bats, 1986) within each molecule so that the H atom points towards the *ortho*-Cl atom. The plane through atoms C7, H7 and O1 of the aldehyde group forms a dihedral angle with the mean plane of the benzene ring of 16.0 (2)° for (1), 8.8 (2)° for (2) and 9.6 (2)/3.4 (4)° for the ordered and disordered molecules in (3). In (4) a much larger angle of 27.6 (2)° is adopted on account of the presence of Cl atoms in both *ortho*-positions. For (5) and (6) the corresponding dihedral angles are 4.7 (2) and 4.9 (3)/10.9 (2)°.

A consistent feature in the structures of (1)–(6) is stacks in which the molecules adopt offset face-to-face arrangements. The planes of the benzene rings are parallel in each case and separated by 3.38–3.45 Å (Table 2, Fig. 2). In each structure, the centroid–centroid distance (Table 2) corresponds to a short crystallographic axis and the lateral shift of adjacent rings in a stack occurs approximately parallel to the C=O bond vector of the aldehyde group (Fig. 2). Although the relative position of the benzene rings within a stack is very closely comparable in all of the structures, the calculated intermolecular interaction energies vary over the range –17.2

Table 2

Geometrical parameters and PIXEL energies for the intermolecular stacking interactions.

	Substituent position	Interplanar distance (Å)	Centroid–centroid distance (Å)	Intermolecular interaction energy (kJ mol ⁻¹)				
				Coulombic	Polarization	Dispersion	Repulsion	Total
(1)	2,3-	3.39	3.789	-10.8	-4.4	-43.2	37.2	-21.2
(2)	2,4-	3.39	3.772	-8.0	-3.4	-41.0	33.6	-18.8
(3) (A: disordered)	2,5-	3.39	3.815	-7.0	-3.9	-42.9	32.0	-21.8
(3) (B: ordered)	2,5-	3.38	3.815	-8.9	-3.5	-41.2	34.4	-19.3
(4)	2,6-	3.43	3.837	-10.8	-5.2	-42.2	37.0	-21.2
(5)	3,4-	3.43	3.809	-4.4	-3.9	-39.4	30.5	-17.2
(6) (A)	3,5-	3.42	3.779	-6.8	-4.0	-39.9	32.5	-18.1
(6) (B)	3,5-	3.45	3.779	-6.8	-4.0	-39.4	31.2	-19.1

Standard uncertainties on the interplanar distances are 0.01 Å or less. The centroid–centroid distances correspond to a crystallographic axis in each structure, so the uncertainties are as reported in Table 1.

to -21.8 kJ mol⁻¹ on account of the differing arrangements of the Cl atoms. The least stabilizing interaction is found for the 3,4-isomer (5), which has a short Cl...Cl contact of 3.8537 (8) Å between the 3-Cl and 4-Cl atoms in adjacent molecules, in addition to the short Cl...Cl contacts that occur in all structures along the stacking vector (Fig. 3). Since the stacks provide a consistent feature in all six structures, the following discussion focuses on a reference molecule (or molecules where *Z'* > 1) within a 'reference stack', labelled **A**

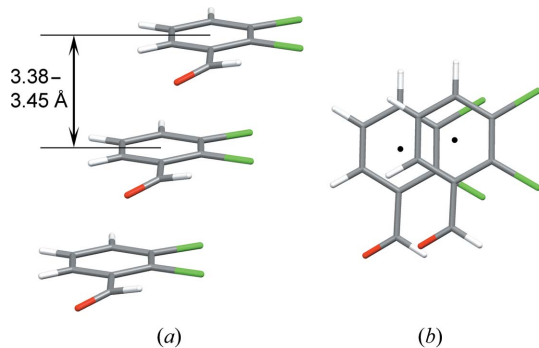


Figure 2

Representative stacking interaction observed in (1)–(6): (a) view approximately perpendicular to the stacking axis; (b) projection onto the molecular plane; the small dots indicate the centroids of the benzene rings.

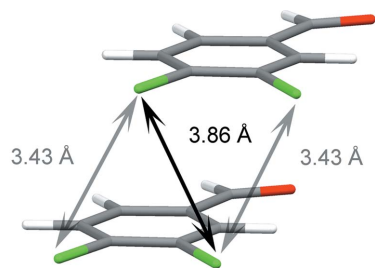


Figure 3

The least stabilizing of the stacking interactions, observed in (5), containing short Cl...Cl contacts (3.86 Å) in addition to the Cl...Cl contacts along the stacking vector (3.43 Å).

or **B**, and its interactions with molecules in neighbouring stacks, labelled **1**, **2**, etc.

3.1.1. 2,3-Dichlorobenzaldehyde (1). In (1) the stacking interactions (Table 2) are the most stabilizing pairwise interactions by some margin. By comparison, the most stabilizing interaction between stacks is -13.7 kJ mol⁻¹. All molecular planes in the structure are approximately parallel. Molecules in two of the neighbouring stacks (**1** and **4** in Fig. 4) are nearly co-planar with the molecules in the reference stack and the O atom of the aldehyde group approaches the Cl atom in the 3-position approximately along the Cl–C bond vector [O...Cl = 3.135 (2) Å]. The geometry of this contact might be expected for the approach of C=O towards the anisotropic charge distribution around halogen atoms: atoms with negative partial charge (nucleophiles) frequently approach along the Cl–C bond vector, while atoms with positive partial charge (electrophiles) frequently approach perpendicular to the Cl–C bond vector (Price *et al.*, 1994). The O...Cl contact is accompanied by C–H...Cl contacts. The interaction with the

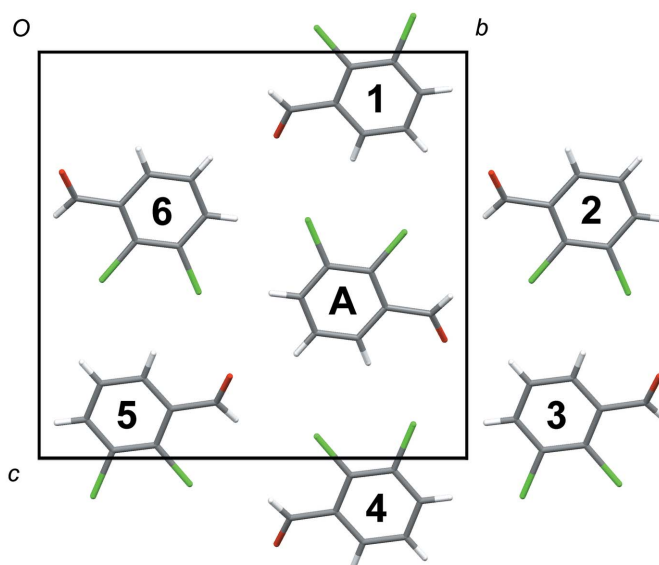


Figure 4

Projection of (1) along the *a* axis, showing the labelling scheme for the central stack (**A**) and neighbouring stacks (**1–6**).

next molecule along stacks **1** or **4** (*i.e.* with interplanar separation *ca* 3.4 Å) is also one of the most stabilizing in the structure. For the remaining four stacks (labelled **2**, **3**, **5** and **6** in Fig. 4), the planes of molecules in the reference stack lie between the planes of the molecules in adjacent stacks so that the arrangements are ‘interdigitated’. The **A** ↔ **2** interactions resemble synthon (I), albeit with the molecules some way from co-planar. The **A** ↔ **6** interactions are calculated to be more stabilizing, whereby the 3-Cl/4-H edges of the molecules meet to form synthon (II). The **A** ↔ **3** and **A** ↔ **5** interactions (equivalent by symmetry) have the C=O group of the aldehyde pointing towards the 3-H/4-H edge of an adjacent molecule, forming C–H···O contacts (Fig. 4).

3.1.2. 2,4-Dichlorobenzaldehyde (2). The structure of (2) (Cabello *et al.*, 2010; Fig. 5) contains some approximately coplanar intermolecular interactions as in (1), but also some edge-to-face type interactions. The **A** ↔ **1** interactions occur between molecules that are close to co-planar, comprising a centrosymmetric arrangement of two C–H···O contacts between the C=O groups of the aldehyde and the 5-H/6-H edges. There is also an accompanying short H···H contact (2.25 Å). This intermolecular interaction is calculated to be the most stabilizing of any in the six structures, with an interaction energy of $-25.3 \text{ kJ mol}^{-1}$, principally due to an especially stabilizing coulombic term. The corresponding interaction between the molecule in the reference stack and the next molecule along stack **1** is also calculated to be significantly stabilizing. The next most stabilizing interactions in the structure are **A** ↔ **4**, comprising an edge-on approach of the 2-Cl/3-H/4-Cl edges, with an angle of $54.0 (3)^\circ$ between the molecular planes. These contain Cl···Cl contacts of 3.728 (1) and 3.827 (1) Å. The **A** ↔ **6** interactions are formed between aldehyde groups and can be considered to define a catemeric motif of C–H···O contacts running along the *b* axis. In the **A** ↔ **2** and **A** ↔ **5** interactions (equivalent by symmetry), the

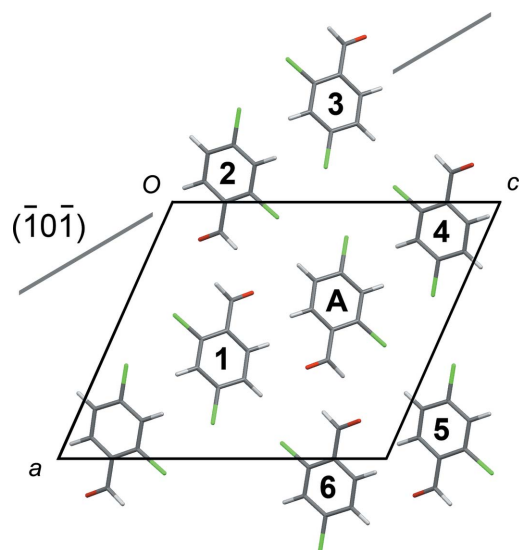


Figure 5
Projection of (2) along the *b* axis, showing the labelling scheme for the central stack (**A**) and neighbouring stacks (**1–6**).

2-Cl atom of one molecule points towards the 4-Cl/5-H edge of an adjacent molecule, with $\text{Cl}\cdots\text{H} = 3.11 \text{ \AA}$ and $\text{Cl}\cdots\text{Cl} = 3.443 (1) \text{ \AA}$. The **A** ↔ **3** interactions comprise relatively long $\text{Cl}\cdots\text{Cl}$ contacts [3.704 (1) Å] and are calculated to be only weakly stabilizing (-2.3 kJ mol^{-1}).

Neither synthon (I) nor synthon (II) is present in this structure, although both could potentially have been formed. The structure contains a centrosymmetric pattern of four $\text{Cl}\cdots\text{Cl}$ contacts [3.443 (1) and 3.827 (1) Å; Fig. 5], which might be highlighted as a notable motif (*e.g.* Banerjee *et al.*, 2003). In terms of the interaction energies, however, it seems that this motif is largely ‘imposed’ by the combination of other more stabilizing pairwise interactions. By far the most stabilizing interactions in the structure are **A** ↔ **A**, **A** ↔ **1** and **A** ↔ **4**, which define two-dimensional sections parallel to the $(\bar{1}01)$ planes, and the most stabilizing interactions between these two-dimensional sections are **A** ↔ **6** (equivalent to **1** ↔ **2** in Fig. 5), defining the catemeric C–H···O motifs. The **A** ↔ **2** (= **A** ↔ **5**) and **A** ↔ **3** interactions are rather weaker (-3.8 and -2.3 kJ mol^{-1}) and could therefore be viewed as a ‘consequence’ of the framework defined by the other more significant interactions. Of course, these interactions are still stabilizing, but it is probably not reasonable to assign any ‘structure-directing’ character to the cyclic Cl_4 motif.

3.1.3. 2,5-Dichlorobenzaldehyde (3). The structure of (3) is disordered (Fig. 1). In space group $P\bar{1}$ the unit cell contains three molecules, two of which (denoted **B**) are ordered and sited on general positions related by an inversion centre, and one of which (denoted **A**) is disordered about an inversion centre. The nature of the disorder is examined further in §3.3. For the present discussion, only one orientation of the **A** molecule needs to be considered, since the other orientation has identical intermolecular interactions. When only one

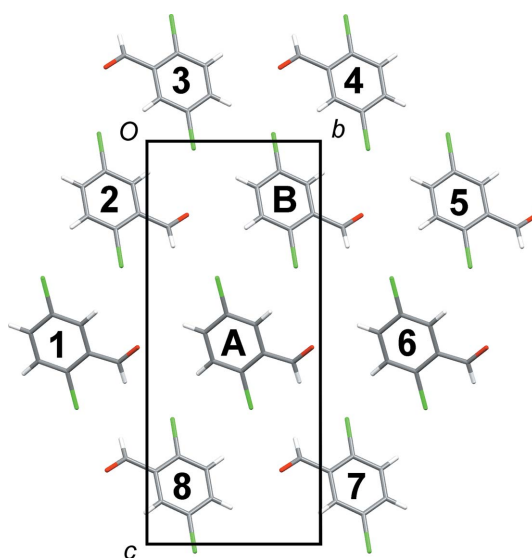


Figure 6
Projection of (3) along the *a* axis, showing the labelling scheme for independent molecules **A** and **B** and neighbouring stacks (**1–8**). Molecule **A** is disordered about a crystallographic inversion centre. The molecular orientation shown here is consistent with the main text.

orientation of molecule **A** is retained, its centroid does not lie exactly at the crystallographic inversion centre.

The ordered part of the structure, consisting of molecule **B** and its symmetry equivalents, comprises sections parallel to the (001) planes in which all molecules in adjacent stacks have approximately parallel planes. After the stacking interactions, the most stabilizing interactions in the structure comprise synthon (II) formed between molecules in stacks **B** and **4**. Interactions between the same molecule in stack **B** and the next molecule in stack **4** are also significantly stabilizing. Closely comparable interactions are formed between stack **B** and stack **3**. Although the **B** ↔ **4** interactions are calculated to be more stabilizing than **B** ↔ **3** (−15.8 and −11.9 kJ mol^{−1}), this is not necessarily representative of the local C—H···Cl contacts involved in synthon (II) since the calculated interaction energies consider the interaction between complete molecules, and the relative molecular orientations differ for **B** ↔ **4** compared with **B** ↔ **3**. The remaining energetically significant interactions in the ordered part of the structure are **B** ↔ **2** and **B** ↔ **5**, in which the aldehyde group of each molecule points between the 3-H/4-H edges of molecules in the adjacent stacks.

The disordered **A** molecules lie in sections parallel to the (001) planes at $z = \frac{1}{2}$ (Fig. 6). The geometry of the **A** ↔ **1** and **A** ↔ **6** interactions resembles that of **B** ↔ **2** and **B** ↔ **5**, except that the **A** molecules in adjacent stacks are co-planar rather than ‘interdigitated’. This co-planar arrangement makes the interactions more stabilizing (−13.0 kJ mol^{−1}) compared with the interdigitated geometry, principally due to a more stabilizing dispersion term. In projection along the *a* axis (Fig. 6), most of the other interactions formed by molecule **A** have clearly similar counterparts formed by molecule **B**: **A** ↔ **2** resembles **B** ↔ **6**, and both **A** ↔ **B** and **A** ↔ **8** resemble **B** ↔ **4**. However, the **A** molecules form interplanar angles of 56.3 (3)° with the **B** molecules, so that all of these interactions are actually formed in an edge-on manner. Interaction **A** ↔ **7** is unique in the structure and resembles synthon (I) when

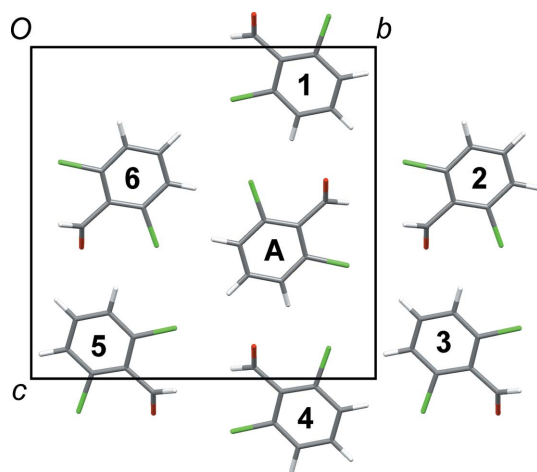


Figure 7
Projection of (4) along the *a* axis, showing the labelling scheme for the central stack (**A**) and neighbouring stacks (**1–6**).

viewed in projection, as in Fig. 6. However, the edge-on arrangement means that the interaction actually comprises one Cl···O contact and one C—H···Cl contact with the next molecule in the stack. Thus, synthon (I) is not present in the structure of (3).

3.1.4. 2,6-Dichlorobenzaldehyde (4). Compound (4) (Gawlicka-Chruszcz *et al.*, 2006; Fig. 7) is isostructural to (1). Although the orientations of the aldehyde and Cl functionalities are obviously different, several directly comparable local intermolecular interactions can be identified. The **A** ↔ **6** interactions [comprising synthon (II)] have essentially identical geometry in the two structures. The **A** ↔ **2** interactions can be considered to comprise synthon (I) in both cases, although they display some minor geometrical differences: the molecules are much closer to co-planar in (4) and the C—H bonds of the aldehyde groups are more clearly twisted away from the Cl atoms compared with (1). The remaining interactions with stacks **1**, **3**, **4** and **5** resemble those in (1) except that the position of the aldehyde group is interchanged with one of the Cl substituents. Thus, the **A** ↔ **1** interactions in (4) comprise one C—H···O and one C—H···Cl contact rather than two C—H···Cl contacts, together with a Cl···Cl contact [3.679 (1) Å] rather than a Cl···O contact. The **A** ↔ **3** and **A** ↔ **5** interactions (equivalent by symmetry) comprise C—H···Cl contacts rather than the C—H···O contacts in (1), and the **A** ↔ **4** interactions comprise one C—H···O and one C—H···Cl contact rather than two C—H···Cl contacts. Further comparison of (1) and (4) is made in §3.2.

3.1.5. 3,4-Dichlorobenzaldehyde (5). In (5) (Fig. 8) all molecular planes are close to parallel. After the stacking interactions, the most stabilizing interactions are **A** ↔ **1** and **A** ↔ **4** (−15.2 kJ mol^{−1}, equivalent by translation), comprising approximately co-planar molecules forming C—H···O and C—H···Cl contacts. The interactions with the next molecules in stacks **1** and **4** are also calculated to be significantly stabilizing. Interactions with stacks **2** and **6** (equivalent by symmetry) comprise the H atom of the aldehyde group and the 6-H atom interdigitated between the 3-Cl/4-Cl edges of

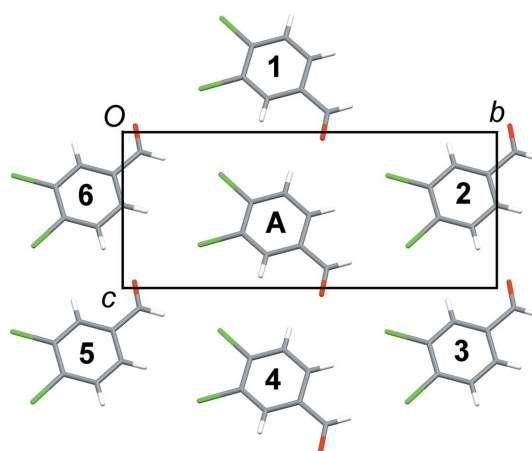


Figure 8
Projection of (5) along the *a* axis, showing the labelling scheme for the central stack (**A**) and neighbouring stacks (**1–6**).

molecules in the adjacent stack. The interaction can be considered as ‘bifurcated’ since the interactions with both molecules adjacent in the stack are calculated to be equally stabilizing, although with slightly different partitioning for the various energy terms. The interactions with stacks **3** and **5** (related by symmetry) comprise essentially a single O···Cl contact and are calculated to be only weakly stabilizing (-3.0 kJ mol^{-1}). The structure of (5) is unique amongst the isomers in that it is non-centrosymmetric.

3.1.6. 3,5-Dichlorobenzaldehyde (6). The structure of (6) (Fig. 9) contains two crystallographically distinct molecules ($Z' = 2$). All molecular planes are approximately parallel. The structure as a whole can be viewed in terms of ‘bilayers’, where the aldehyde groups are gathered at the centre of each bilayer and the interactions between bilayers comprise C—H···Cl and Cl···Cl contacts. The aldehyde groups form an undulating catemeric C—H···O motif running through the centre of each bilayer. The bilayer description is supported to a large extent by the intermolecular interaction energies, since almost all of the most stabilizing interactions in the structure occur within these defined bilayers. The most stabilizing interactions of all ($-20.2 \text{ kJ mol}^{-1}$), calculated to be marginally more stabilizing than the stacking interactions (Table 2), are the **A** ↔ **1** and **B** ↔ **6** interactions (equivalent by translation), comprising two

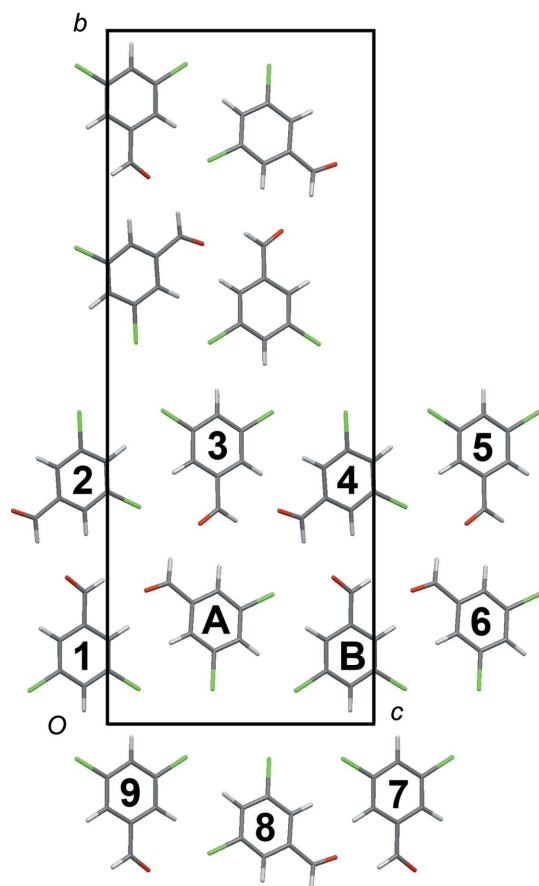


Figure 9
Projection of (6) along the *a* axis, showing the labelling scheme for the crystallographically distinct stacks **A** and **B** and neighbouring stacks (**1**–**9**).

C—H···O contacts and one C—H···Cl contact. As observed for the **A** ↔ **1** interactions in (2), the stability is largely due to a highly stabilizing coulombic term. The **A** ↔ **B** interactions are close to co-planar and comprise synthon (II), while the **A** ↔ **3** and **B** ↔ **4** interactions (equivalent by symmetry) include the C—H···O contacts between aldehyde groups, supported by a C—H···O contact involving the 2-H atom. The other interactions within the bilayer are significantly less stabilizing. Between the defined bilayers, the only significantly stabilizing interactions are **B** ↔ **7** ($-11.1 \text{ kJ mol}^{-1}$), which amount to an ‘interdigitated’ version of synthon (II). All other intermolecular interactions are considerably weaker (-2.4 kJ mol^{-1} or less). Notably in this region the structure contains a centrosymmetric cyclic motif of four Cl···Cl contacts comparable to that in (2) [comprising stacks **A**, **B**, **9** and **8**, Cl···Cl = 3.5511 (13) and 3.8215 (14) Å]. Again, however, this motif seems to be imposed by the combination of the other more stabilizing interactions in the structure.

3.2. Isostructurality of (1) and (4)

An overlay of the structures of (1) and (4) is given in Fig. 10. According to the PIXEL calculations, the total dispersion and repulsion terms are very closely comparable in the two structures, as should be expected for isostructural molecular isomers. The difference arises principally in the coulombic term and to a lesser extent in the polarization term. Considering the geometries of the intermolecular contacts, the structures exhibit two-dimensional similarity in planes parallel to (001) (highlighted in Fig. 10), which can be viewed as ‘corrugated sheets’. The exchange of Cl and aldehyde groups between the two molecules does not affect the nature of the interactions within each sheet, comprising essentially synthons (I) and (II), but it does affect the distribution of functional groups exposed on the surfaces of the sheets. The convex sections of the surfaces do not change: they comprise the H/H edges of molecules in both structures. In the concave sections,

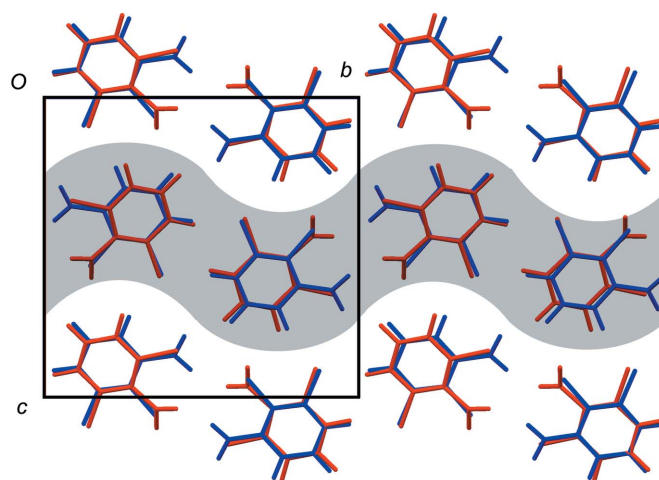


Figure 10
Overlay of the structures of (1) (blue) and (4) (red). The shaded section highlights ‘corrugated sheets’ with planes parallel to (001).

however, (1) exposes two Cl atoms on the surface while (4) exposes one Cl atom and the O atom of the aldehyde group. The corrugated sheets are arranged so that ‘bumps fit into hollows’. In (1) this gives an interaction between Cl/Cl and H/H edges where the convex section of the surface protrudes into the concave section of the neighbouring surface ($\mathbf{A} \leftrightarrow \mathbf{1}$ and $\mathbf{A} \leftrightarrow \mathbf{4}$ in Fig. 4), while (4) includes an interaction between the Cl/CHO and H/H edges in the same region ($\mathbf{A} \leftrightarrow \mathbf{1}$ and $\mathbf{A} \leftrightarrow \mathbf{4}$ in Fig. 7). The latter is far more stabilizing [$-12.1 \text{ kJ mol}^{-1}$ in (1) *cf.* $-20.1 \text{ kJ mol}^{-1}$ in (4)], principally due to a significantly more stabilizing coulombic term associated with the C–H \cdots O contacts.

3.3. Disorder in (3)

Since we have examined the complete set of dichlorobenzaldehyde isomers and observed comparable molecular stacks within all of them, it seems reasonable to assume that the stacks along the *a* axis in (3) resemble those in all of the other structures — that is, adjacent **A** molecules are related by translation rather than inversion. With this assumption, adjacent stacks (**1** and **6** in Fig. 6) must also be related by translation rather than inversion, since the latter introduces unreasonably short O \cdots O contacts between molecules (*ca* 1.06 Å). Thus, the arrangement within each **A** layer [parallel to the (001) planes] is closely comparable to that within each **B** layer (which also seems reasonable), and the observed disorder must arise from alternative inversion-related orientations of *complete* **A** layers. Although our analysis does not provide any means to predict this disorder *a priori*, the energetic feasibility of the disorder, and the fact that it occurs only for the **A** layers, is corroborated by the PIXEL calculations. The total interaction energy between adjacent **B** layers (comprising interactions $\mathbf{B} \leftrightarrow \mathbf{3}$ and $\mathbf{B} \leftrightarrow \mathbf{4} = -47.1 \text{ kJ mol}^{-1}$) is significantly more stabilizing than the interaction between adjacent **A** and **B** layers (either $\mathbf{A} \leftrightarrow \mathbf{B}$ and $\mathbf{A} \leftrightarrow \mathbf{2} = -31.8 \text{ kJ mol}^{-1}$ or $\mathbf{A} \leftrightarrow \mathbf{7}$ and $\mathbf{A} \leftrightarrow \mathbf{8} = -33.3 \text{ kJ mol}^{-1}$), and the two possible arrangements for the **A** layers with respect to the **B** layers are calculated to have closely comparable energies.

3.4. $Z' > 1$ structures for (3) and (6)

Gavezzotti (2008*b*) has previously made a general survey of a subset of structures in the CSD with $Z' > 1$. It was found that the interaction between symmetry-independent molecules was the most stabilizing in the structure for 55–60% of cases. In (6) it is the case that the molecules not related by any symmetry element form the most stabilizing interactions, specifically $\mathbf{A} \leftrightarrow \mathbf{1}$ and $\mathbf{B} \leftrightarrow \mathbf{6} = -20.2 \text{ kJ mol}^{-1}$ (Fig. 9). These interactions are calculated to be marginally more stabilizing than even the stacking interactions in (6), and they are therefore consistent with a view of ‘tightly bound molecular pairs’ that are not formed about any symmetry element. The principal contributor to the stabilizing energy of the $\mathbf{A} \leftrightarrow \mathbf{1}$ and $\mathbf{B} \leftrightarrow \mathbf{6}$ interactions is the coulombic term, which is the second largest seen for all pairwise interactions in the series [after the $\mathbf{A} \leftrightarrow \mathbf{1}$ interaction within structure (2)]. The existence of this highly

stabilizing but asymmetric pairwise interaction can be viewed as the probable origin of the $Z' > 1$ structure for (6).

In (3) the crystallographically distinct molecules arise at the interface between the **A** and **B** layers, where the molecular planes in adjacent layers are inclined and there are no symmetry elements between them. The distinction between ‘aldehyde up’ and ‘aldehyde down’ arrangements [with reference to a particular stacking direction normal to (001), *e.g.* upwards in Fig. 6] gives two possibilities for this interface that differ marginally in their intermolecular interaction energies, but are essentially equivalent in terms of the Cl \cdots Cl contacts at the layer surfaces. This means that the observation of $Z' > 1$ is not intimately linked to the disorder — in other words, if this structure were to have fully ordered **A** layers it would still have $Z' > 1$. In this structure, pairwise intermolecular interaction energies between molecules not related by any symmetry operation are of average magnitude, and the notion of tightly bound asymmetric molecular pairs therefore cannot rationalize the observation of $Z' > 1$. Instead, it seems that the observed asymmetric arrangement is optimal for pairs of two-dimensional layers, rather than isolated pairs of molecules. Thus, $Z' > 1$ in this case is an emergent property of the crystal structure that is difficult to rationalize on the basis of the molecular structure alone.

4. Conclusions

Analysis and comparison of the intermolecular interaction energies in the complete series of dichlorobenzaldehyde isomers provides some insight into the driving forces that lead to the observed packing arrangements. Stacking interactions along a short crystallographic axis provide some of the most stabilizing interactions, and stacks are a consistent feature in all six of the structures. In general, the most stabilizing non-stacking intermolecular interactions are those involving C–H \cdots O and/or C–H \cdots Cl contacts. Thus, synthon (II), comprising a planar centrosymmetric pair of C–H \cdots Cl contacts, is observed in four of the six structures, and an edge-on variant is observed in one of the other structures. The previously reported synthon (I) can be identified in two of the four structures where it could potentially be formed, although the relative energies of the intermolecular interactions observed throughout the series suggests that it is probably the Cl \cdots H contacts that should be emphasized rather than the Cl \cdots O contacts. Instances of motifs based on Cl \cdots Cl contacts [for example, the Cl₄ motifs in (2) and (6)] are calculated to be only marginally stabilizing, and they appear in these structures to be ‘imposed’ within the constraints of other significantly more stabilizing interactions. The isostructurality of the 2,3- and 2,6-isomers seems surprising considering the different distribution of functional groups and expected supramolecular synthons. The closely comparable total dispersion and repulsion terms reflect a comparable drive towards ‘close packing’ in these structures, and the exchange of chloro and aldehyde functionalities within the isostructural arrangements appears to be tolerated within the close-packing constraints. The $Z' > 1$ structures observed for (3) and (6) arise for different reasons:

(6) contains a tightly bound asymmetric molecular pair that is retained in the crystal structure, while the asymmetric regions in (3) are found at the interface between complete layers of molecules. The former condition might be predictable *a priori* from analysis of an isolated molecular pair, while the latter is an emergent feature of the crystal structure in the sense that the layered pattern must be established for the asymmetry to be realised.

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