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# 3,5-Dichloro-4-cyanobenzoic acid: two polymorphs and the 0.25-hydrate, exhibiting two-dimensional ribbons and nets involving hydrogen-bonding and intermolecular Cl···N interactions

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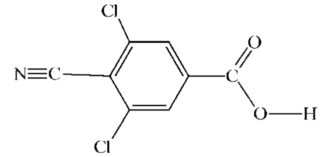
Two polymorphs of 3,5-dichloro-4-cyanobenzoic acid, $C_8H_3Cl_2NO_2$, *viz.* triclinic and monoclinic, and its 0.25-hydrate, $C_8H_3Cl_2NO_2 \cdot 0.25H_2O$, form crystals in which hydrogen bonding and Cl···N interactions appear to be equally important to the structures. In all three structures, there are hydrogen-bonded (COOH) dimers of the well known cyclic type, but in the hydrate there are also dimers in which the two opposing COOH groups are separated by a water molecule. In the monoclinic polymorph and in the hydrate, the intermolecular interactions form two-dimensional nets interwoven three at a time. For both the triclinic and monoclinic polymorphs, $Z' = 2$.

## Comment

In 2,3,5,6-tetrachloro-1,4-dicyanobenzene (Britton, 1981) and its charge-transfer complexes with hexamethylbenzene (Britton, 2002), clearly recognizable Cl···N interactions occur. Reddy *et al.* (1993) have pointed out the usefulness of Cl···N interactions in the construction of molecular tapes. In the title compound, it was expected that the molecules would form dimers through co-operative cyclic hydrogen bonds between the carboxylic acid groups of pairs of molecules to give the graph set $R_2^2(8)$ (Etter, 1990). The question of interest was how important the Cl···N interactions would be. When the crystals were grown, two polymorphs of the pure acid, (I) (triclinic) and (II) (monoclinic), and a 0.25-hydrate, (III), were obtained. The structures of all three are reported here.

In the structure of the triclinic polymorph, (I), $Z' = 2$, and a view of the asymmetric unit showing the atom labelling and anisotropic displacement parameters for both crystallographically independent molecules is given in Fig. 1. The bond lengths and angles are normal. The expected dimers formed by the cyclic co-operative hydrogen bonds between carboxylic acid groups are present and the dimers occur around centres of symmetry such that each molecule *A* dimerizes with a second molecule *A* and pairs of *B* molecules dimerize likewise. The carboxylic acid H atoms are disordered across the two carboxylic acid O atoms in each molecule, with site-occupancy factors of 0.71 (10) and 0.69 (9) for the H atoms on atoms O1*A* and O1*B*, respectively.



(I) triclinic polymorph
(II) monoclinic polymorph
(III) 0.25-hydrate

One layer of the packing in (I) is shown in Fig. 2. The *A* and *B* molecules form similar but crystallographically independent ribbons, which run parallel to the $[3\bar{1}0]$ direction. In each ribbon, the molecules are held together, alternately, by the cyclic hydrogen-bonded dimeric interactions between the carboxylic acid groups, and by pairs of Cl···N interactions. These Cl···N interactions are such that two *A* molecules interact across one centre of symmetry and two *B* molecules interact across another. Bernstein *et al.* (1995) have suggested that graph-set analysis might be extended to systems other than hydrogen bonding. In this spirit, the cyclic Cl···N interactions can be described by the graph set $R_2^2(10)$, with the electron-acceptor Cl replacing H. These ribbons are close to planar, with the *A* molecules tilted by 2.2 (1)° with respect to the mean plane of the ribbon and the *B* molecules tilted by 2.7 (1)°. The ribbons come together to form sheets normal to (131), held together by Cl···O interactions The ribbons deviate from coplanarity with the sheet, *i.e.* by 4.0 (1)° for the *A* ribbons and by 10.4 (1)° for the *B* ribbons. The geometric data for the H···O and Cl···*X* interactions are given in Tables 1 and 2, respectively.

The molecular structure of the monoclinic polymorph, (II), showing the atom labelling and anisotropic displacement parameters, is presented in Fig. 3. The bond lengths and angles

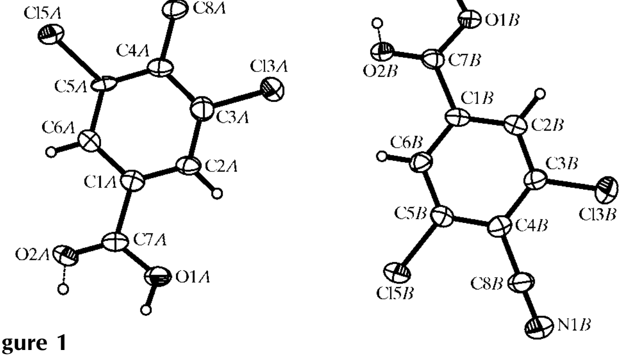


**Figure 1**
The asymmetric unit of (I), showing the two symmetry-independent molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Both partially occupied carboxylic acid H-atom positions are shown on each molecule; site occupancies are 0.71 (10) for O1*A* and 0.69 (9) for O1*B*.

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are normal. The carboxylic acid H atom is disordered across the two carboxylic acid O atoms, with a site-occupancy factor of 0.67 (3) for the H atom on atom O1.

The atom labelling and anisotropic displacement parameters for both crystallographically independent molecules and one orientation of the disordered water molecule of (III) are shown in Fig. 4. Bond lengths and angles are normal. The carboxylic acid H atoms in molecule *A* are disordered in the same way as in (I), with a site-occupancy factor of 0.66 (3) for the H atom on atom O1*A*. The site-occupancy factors for the H atoms on atoms O1*B* and O2*B* are exactly 0.5, as a consequence of the disordered arrangement of the bridging water molecules around centres of inversion.

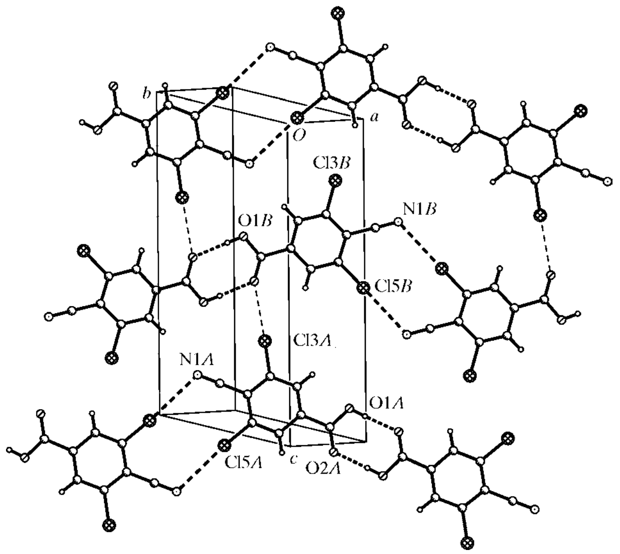

**Figure 2**
One layer of (I), viewed normal to (131). The top and bottom ribbons are composed of *A* molecules, and the central ribbon is composed of *B* molecules. The heavy dashed lines show the H$\cdots$O and Cl$\cdots$N interactions within the ribbons and the light dashed lines show the Cl$\cdots$O interactions between the ribbons. The symmetry operations for the symmetry-related molecules involved in the cyclic interactions are $(2 - x, -y, 2 - z)$ for atoms O1*A* and O2*A*, $(-x, 1 - y, 1 - z)$ for O1*B* and O2*B*, $(-1 - x, 1 - y, 2 - z)$ for Cl5*A* and N1*A*, and $(3 - x, -y, 1 - z)$ for Cl5*B* and N1*B*.

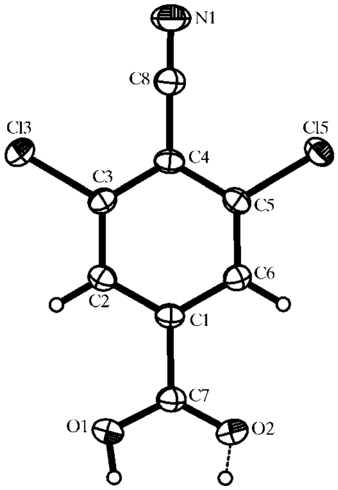

**Figure 3**
A molecule of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The carboxylic acid H atoms are disordered with an occupancy on O1 of 0.67 (3).

The crystal packing in (II) and (III) is very similar (Figs. 5 and 6). The molecules in (II) and the *A* and *B* molecules in (III) dimerize with themselves through hydrogen bonding, which will be discussed further below, and then the dimers associate through Cl$\cdots$N interactions, between the dimers in (II) and between the crystallographically independent dimers in (III), to form a 'chicken-wire' or two-dimensional (6,3)-net. The Cl$\cdots$N interactions are the same cyclic $R_2^2(10)$ interactions found in (I), except that now each N atom is involved in two such interactions, giving a second-level graph set $R_2^2(10)R_2^2(10)$. Both the interactions in (I) and those in (II) and (III) are known in other structures. The distances and angles about the atoms involved in these interactions (Table 2) are similar to those found previously (Britton, 2002). It should also be noted that there are compounds containing *ortho* Cl and CN groups in which there are no Cl$\cdots$N contacts, for

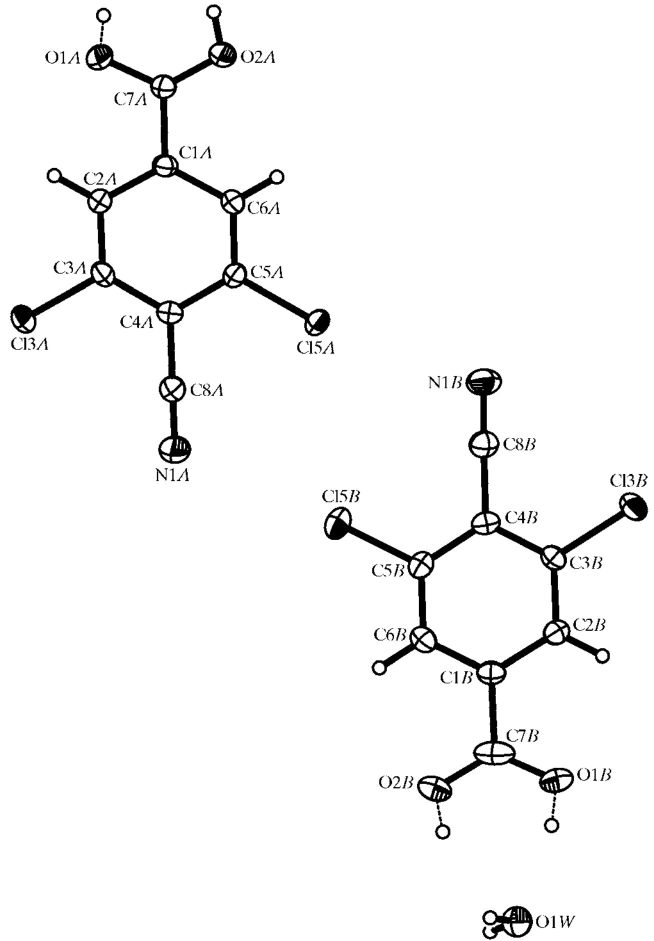

**Figure 4**
The asymmetric unit of (III), showing the two symmetry-independent molecules and the water molecule. Displacement ellipsoids are drawn at the 50% probability level. The water molecule is disordered across a centre of symmetry. Both partially occupied carboxylic acid H-atom positions are shown on each molecule, with occupancies of 0.69 (3) for O1*A* and 0.5 for O1*B* (fixed by the disorder).

example, 2,6-dichlorobenzonitrile (Britton *et al.*, 2000). In order to fill the empty space in these nets, three of them form interpenetrating triple layers, as shown in Fig. 7. For an extensive discussion of such nets and further examples of similar triple layers, see Batten & Robson (1998).

The hydrogen bonds that form the dimers in (II) and the dimers involving *A* molecules in (III) are the familiar cyclic sort already seen in (I). Pairs of *B* molecules in (III) also form dimers, but in a less common way. One water molecule, disordered across a centre of symmetry, lies between the two carboxylic acid groups of opposing *B* molecules in such a way that both carboxylic acid groups are hydrogen-bond donors to the bridging water molecule (Fig. 6). These interactions are not cyclic, but the directionality is disordered because of the inversion symmetry (see Fig. 6 for the two orientations of the disorder). Whether the disorder is completely random or only varies from net to net cannot be determined. The water H atoms point towards and form hydrogen bonds with N atoms in adjacent nets. For this arrangement, the first level graph set is *DD* and the second level is $D_2^2(5)$ [for a description of graph-set levels, see Bernstein *et al.* (1995)]. The $D_2^2(5)$ arrangement is rare but not unknown. In the form found here, where the bridging water molecule acts twice as a hydrogen-bond acceptor, there are 34 examples in the November 2005 release of the Cambridge Structural Database (Allen, 2002).

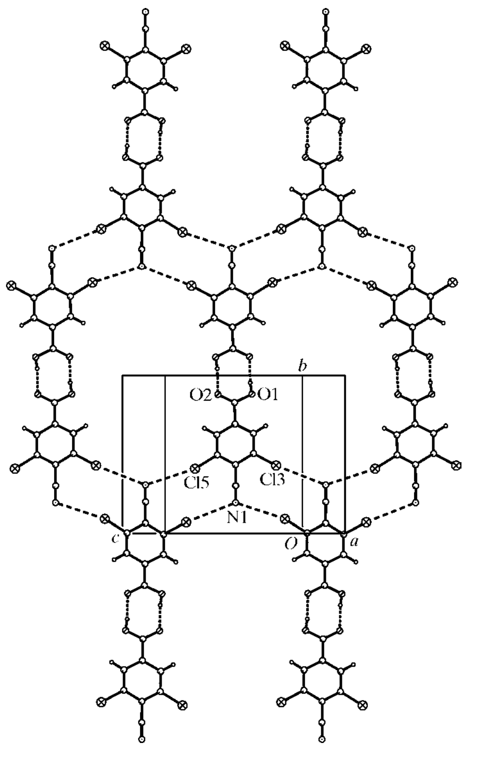

**Figure 5**
A layer of (II), viewed normal to (001). Only the predominant carboxylic acid H atoms are shown. The heavy dashed lines show the H···O and Cl···N interactions. The symmetry operations for the symmetry-related molecules involved in the cyclic interactions are $(1-x, 2-y, 1-z)$ for O1 and O2, $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$ for Cl3 and N1, and $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ for Cl5 and N1.

In Table 2, short Cl···O distances are also given. These refer to interactions between atoms in different nets in the same triple layer. These are comparable in length with the longer Cl···N contacts discussed above, but have no special directional properties. They appear to be ordinary van der Waals contacts.

It is somewhat surprising that the triple layers in (II) and (III) are so similar, given that there are extra water molecules in each net in (III). The repeat distances in the nets for the vertical directions in Figs. 5 and 6 are 3*b* = 31.134 Å in (II) and 3*b* = 34.230 Å in (III); the additional 3.096 Å is approximately what would be expected from the extra water molecule. The repeat distances in the nets for the horizontal directions in Figs. 5 and 6 are *c* = 11.826 Å in (II) and *a* = 11.327 Å in (III). The difference in these latter distances leads to the Cl···N distances generally being longer in (II) than in (III) by about 0.2 Å. This increase in length means that the Cl···N distances in (II) are not shorter than the usual van der Waals distances. However, the similarity in geometries between the Cl···N cyclic dimers in (II) and those in (III) suggests that the same interaction takes place in both, but the tighter overall packing

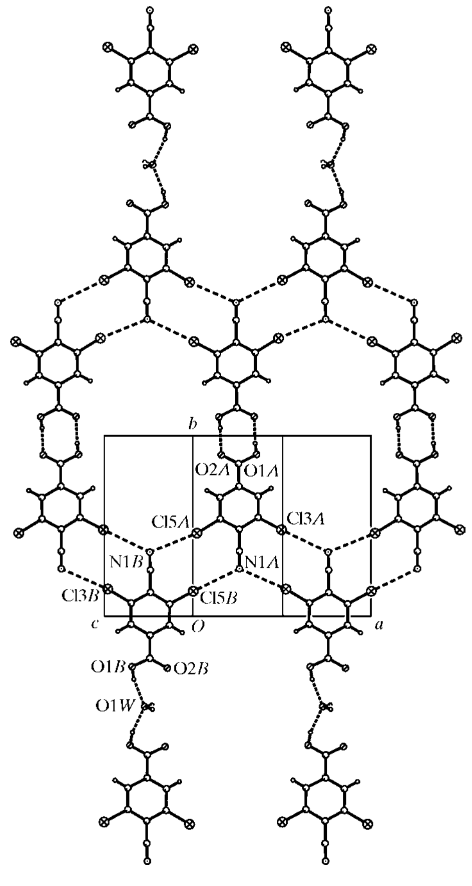

**Figure 6**
A layer of (III), viewed normal to (100). Only the predominant carboxylic acid H atoms are shown. Only one orientation of O1*W* is shown at each position. The heavy dashed lines show the H···O and Cl···N interactions. The symmetry operations for the symmetry-related molecules involved in the cyclic interactions are $(1-x, 2-y, 1-z)$ for O1*A* and O2*A*, $(1+x, y, z)$ for Cl3*A* and N1*B*, and $(-1+x, y, z)$ for Cl3*B* and N1*A*. Atom O2*B*, connected to O1*W*, is at $(-x, -1-y, 1-z)$.

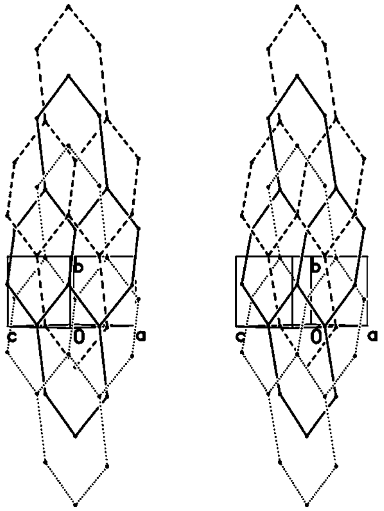

**Figure 7**
A stereoview of a triple layer of three interwoven nets of (II). For clarity, the view is tilted 30° away from the view in Fig. 5. The vertices connected by heavy lines correspond to the centres of the benzene rings in Fig. 5; the lines join rings connected through intermolecular interactions. The dashed and dotted patterns correspond to moving the original pattern one unit-cell length in either direction along the *b* axis. The corresponding view for (III) would be virtually identical.

in (II) forces the molecules apart. The molecules are tilted with respect to the layers, by 14.8 (1)° in (II), and by 16.4 (1) (*A*) and 13.7 (1)° (*B*) in (III).

## Experimental

The title compound was obtained from the chemical collection of the Chemistry Department of the University of Minnesota. Triclinic polymorph (I) was obtained by recrystallization from methanol, benzene or chloroform. Monoclinic polymorph (II) and the 0.25-hydrate (III) were obtained simultaneously by recrystallization from acetone or propan-2-ol. Both (II) and (III) were obtained simultaneously by recrystallization from acetonitrile. In the original crystallizations that produced crystals of (III), the solvents must have contained small amounts of water as none was added. When (III) was deliberately sought, it was necessary to add a small amount of water to the acetone used as solvent.

### Polymorph (I)

*Crystal data*

$C_8H_3Cl_2NO_2$
$M_r = 216.01$
Triclinic, $P\bar{1}$
$a = 4.8859\ (17)$ Å
$b = 11.658\ (4)$ Å
$c = 15.891\ (6)$ Å
$\alpha = 88.39\ (1)^\circ$
$\beta = 84.79\ (1)^\circ$
$\gamma = 81.23\ (1)^\circ$
$V = 890.8\ (6)$ Å$^3$
$Z = 4$
$D_x = 1.611$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 0.69$ mm$^{-1}$
$T = 174\ (2)$ K
Prism, pale yellow
0.25 × 0.20 × 0.10 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2003; Blessing, 1995)
$T_{\min} = 0.85$, $T_{\max} = 0.93$
11344 measured reflections
3178 independent reflections
2660 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.059$
$\theta_{\max} = 25.1^\circ$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.136$
$S = 1.15$
3178 reflections
242 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 1.6P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.46$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.34$ e Å$^{-3}$

### Polymorph (II)

*Crystal data*

$C_8H_3Cl_2NO_2$
$M_r = 216.01$
Monoclinic, $P2_1/c$
$a = 7.3429\ (18)$ Å
$b = 10.378\ (3)$ Å
$c = 11.826\ (3)$ Å
$\beta = 112.22\ (1)^\circ$
$V = 834.3\ (4)$ Å$^3$
$Z = 4$
$D_x = 1.720$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 0.74$ mm$^{-1}$
$T = 174\ (2)$ K
Plate, colorless
0.50 × 0.50 × 0.05 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{\min} = 0.70$, $T_{\max} = 0.96$
9369 measured reflections
1915 independent reflections
1754 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.6^\circ$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.075$
$S = 1.05$
1915 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.30$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.30$ e Å$^{-3}$

### Polymorph (III)

*Crystal data*

$C_8H_3Cl_2NO_2\cdot 0.25H_2O$
$M_r = 220.52$
Monoclinic, $P2_1/n$
$a = 11.237\ (3)$ Å
$b = 11.410\ (3)$ Å
$c = 14.566\ (4)$ Å
$\beta = 112.50\ (1)^\circ$
$V = 1725.4\ (8)$ Å$^3$
$Z = 8$
$D_x = 1.698$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 0.72$ mm$^{-1}$
$T = 174\ (2)$ K
Prism, colorless
0.35 × 0.25 × 0.25 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{\min} = 0.76$, $T_{\max} = 0.84$
19254 measured reflections
3893 independent reflections
3265 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.5^\circ$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.076$
$S = 1.04$
3893 reflections
251 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.92P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.41$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.46$ e Å$^{-3}$

**Table 1**
Comparison of the geometry of the hydrogen bonds (Å, °) in compounds (I), (II) and (III).

All O—H distances are 0.84 Å.

| | $O-H\cdots X-Y$ | $O-H\cdots X$ | $H\cdots X$ | $H\cdots X-Y$ | $O\cdots X$ |
|---|---|---|---|---|---|
| (I) | $\mathrm{O1}A-\mathrm{H1}A\cdots\mathrm{O2}A^{\mathrm{i}}-\mathrm{C7}A^{\mathrm{i}}$ | 178 | 1.80 | 123 | 2.641 (7) |
| | $\mathrm{O2}A-\mathrm{H2}A\cdots\mathrm{O1}A^{\mathrm{i}}-\mathrm{C7}A^{\mathrm{i}}$ | 153 | 1.87 | 105 | 2.641 (7) |
| | $\mathrm{O1}B-\mathrm{H1}B\cdots\mathrm{O2}B^{\mathrm{ii}}-\mathrm{C7}B^{\mathrm{ii}}$ | 175 | 1.81 | 128 | 2.648 (7) |
| | $\mathrm{O2}B-\mathrm{H2}B\cdots\mathrm{O2}A^{\mathrm{ii}}-\mathrm{C7}B^{\mathrm{ii}}$ | 123 | 2.09 | 103 | 2.648 (7) |
| (II) | $\mathrm{O1}-\mathrm{H1}\cdots\mathrm{O2}^{\mathrm{iii}}-\mathrm{C7}^{\mathrm{iii}}$ | 174 | 1.86 | 119 | 2.700 (2) |
| | $\mathrm{O2}-\mathrm{H2}\cdots\mathrm{O1}^{\mathrm{iii}}-\mathrm{C7}^{\mathrm{iii}}$ | 162 | 1.89 | 108 | 2.700 (2) |
| (III) | $\mathrm{O1}A-\mathrm{H1}A\cdots\mathrm{O2}A^{\mathrm{iii}}-\mathrm{C7}A^{\mathrm{iii}}$ | 173 | 1.83 | 120 | 2.669 (2) |
| | $\mathrm{O2}A-\mathrm{H2}A\cdots\mathrm{O1}A^{\mathrm{iii}}-\mathrm{C7}A^{\mathrm{iii}}$ | 159 | 1.87 | 107 | 2.669 (2) |
| | $\mathrm{O1}B-\mathrm{H1}B\cdots\mathrm{O1}W\cdots\mathrm{O2}B^{\mathrm{iv}}$ | 166 | 1.92 | 136 | 2.746 (4) |
| | $\mathrm{O2}B-\mathrm{H2}B\cdots\mathrm{O1}W^{\mathrm{iv}}\cdots\mathrm{O1}B^{\mathrm{iv}}$ | 165 | 2.02 | 136 | 2.843 (4) |
| † | $\mathrm{O1}W-\mathrm{H1}W\cdots\mathrm{N1}B^{\mathrm{v}}-\mathrm{C8}B^{\mathrm{v}}$ | 130 | 2.45 | 122 | 3.056 (4) |
| † | $\mathrm{O1}W-\mathrm{H2}W\cdots\mathrm{N1}B^{\mathrm{vi}}-\mathrm{C8}B^{\mathrm{v}}$ | 133 | 2.30 | 123 | 2.943 (4) |

† These entries describe contacts between layers and are not shown in any of the figures. Symmetry codes: (i) $2-x, -y, 2-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 2-y, 1-z$; (iv) $-x, -1-y, 1-z$; (v) $-x, -y, 1-z$; (vi) $x, -1+y, z$.

**Table 2**
Comparison of geometry (Å, °) of the $Cl\cdots X$ contacts in compounds (I), (II) and (III).

For comparison, the van der Waals contact distances (Bondi, 1964; Rowland & Taylor, 1996) are $Cl\cdots N$ = 3.30 Å and $Cl\cdots O$ = 3.27 Å.

| | $Cl\cdots X$ | $C-Cl\cdots X$ | $Cl\cdots X$ | $Cl\cdots X-C$ |
|---|---|---|---|---|
| (I) | $\mathrm{Cl5}A\cdots\mathrm{N1}A^{\mathrm{i}}$ | 174.7 (6) | 3.195 (6) | 115.0 (4) |
| | $\mathrm{Cl5}B\cdots\mathrm{N1}B^{\mathrm{ii}}$ | 176.2 (6) | 3.128 (6) | 116.4 (4) |
| | $\mathrm{Cl3}A\cdots\mathrm{O2}B$ | 167.1 (3) | 2.989 (6) | 148.3 (4) |
| (II) | $\mathrm{Cl3}\cdots\mathrm{N1}^{\mathrm{iii}}$ | 170.1 (2) | 3.503 (2) | 110.2 (1) |
| | $\mathrm{Cl5}\cdots\mathrm{N1}^{\mathrm{iv}}$ | 162.0 (2) | 3.512 (2) | 104.2 (1) |
| † | $\mathrm{Cl3}\cdots\mathrm{N1}^{\mathrm{v}}$ | 78.8 (1) | 3.374 (2) | 155.9 (1) |
| † | $\mathrm{Cl5}\cdots\mathrm{O1}^{\mathrm{vi}}$ | 101.9 (1) | 3.257 (2) | 147.0 (2) |
| † | $\mathrm{Cl5}\cdots\mathrm{O2}^{\mathrm{vii}}$ | 129.0 (1) | 3.259 (2) | 143.0 (2) |
| (III) | $\mathrm{Cl3}A\cdots\mathrm{N1}B^{\mathrm{viii}}$ | 169.7 (2) | 3.263 (2) | 116.6 (1) |
| | $\mathrm{Cl5}A\cdots\mathrm{N1}B$ | 163.3 (2) | 3.322 (2) | 107.5 (1) |
| | $\mathrm{Cl3}B\cdots\mathrm{N1}A^{\mathrm{ix}}$ | 169.7 (2) | 3.257 (2) | 110.1 (1) |
| | $\mathrm{Cl5}B\cdots\mathrm{N1}A$ | 171.9 (2) | 3.252 (2) | 114.5 (1) |
| † | $\mathrm{Cl3}A\cdots\mathrm{O1}W^{\mathrm{x}}$ | 117.8 (1) | 3.396 (3) | |
| † | $\mathrm{Cl3}A\cdots\mathrm{O1}B^{\mathrm{x}}$ | 89.3 (1) | 3.594 (2) | 133.1 (1) |
| † | $\mathrm{Cl5}A\cdots\mathrm{O1}W^{\mathrm{xi}}$ | 129.6 (1) | 3.282 (3) | |
| † | $\mathrm{Cl5}A\cdots\mathrm{O2}B^{\mathrm{xii}}$ | 91.0 (1) | 3.485 (2) | 149.4 (2) |
| † | $\mathrm{Cl3}B\cdots\mathrm{O2}A^{\mathrm{xiii}}$ | 115.0 (1) | 3.214 (2) | 127.3 (1) |
| † | $\mathrm{Cl5}B\cdots\mathrm{O1}A^{\mathrm{xiv}}$ | 101.6 (1) | 3.402 (2) | 116.9 (1) |

† These entries describe bonds between layers and are not shown in any of the figures. Symmetry codes: (i) $-1-x, 1-y, 2-z$; (ii) $3-x, -y, 1-z$; (iii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (vii) $1-x, -\frac{1}{2}+y, \frac{3}{2}$; (viii) $1+x, y, z$; (ix) $-1+x, y, z$; (x) $1+x, 1+y, z$; (xi) $-x, -y, 1-z$; (xii) $x, 1+y, z$; (xiii) $-x, 1-y, 1-z$; (xiv) $1-x, 1-y, 1-z$.

12 crystals of (I) were examined and all were twinned. Data were collected on a non-merohedrally twinned crystal grown from methanol. The crystal used was indexed using *GEMINI* (Sparks, 2000). The major twin component fitted 112 reflections, while the minor twin component fitted 90 of the overall 138 reflections used. The twin law was determined to be [$\bar{1}00/0\bar{1}0/-0.551, -0.039, 1$], which corresponds to a 180° rotation around the $c^*$ axis. The data were integrated with *SAINT* (Bruker, 2003) and corrected for absorption and scaling with *TWINABS* (Sheldrick, 2003; Blessing, 1995). 28 redundant reflections were eliminated from the final data file with *STRIP REDUNDANT* (Brennessel & Young, 2003). The ratio of the major and minor twin components was 0.570 (2):0.430 (2) based on refinement using *SHELXTL* (Sheldrick, 1997); the twinning necessitated the inclusion of the intensity data for both twin fractions in one file in the HKLF5 format (Sheldrick, 1997).

In each compound, the carboxylic acid H atoms were constrained to an ideal geometry, with O—H = 0.84 Å, but were allowed to rotate freely about the C—O bonds, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$ for (I) and (III) or $1.2U_{\mathrm{eq}}(\mathrm{O})$ for (II). In each case, these H atoms were disordered between the two carboxylic acid O atoms and the site-occupancy factors of the two positions for each H atom were constrained to sum to 1.00. H atoms attached to C atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. In (III), there is a water molecule located near a centre of symmetry, with two half-occupancy O atoms and four half-occupancy H atoms expected within the solvent cavity. The water O atom was refined with an isotropic displacement parameter. Only one independent peak that seemed to correspond to a H atom was found in the difference map. When this peak was assumed to represent hydrogen, the site-occupancy factor refined to 0.95 (3) rather than 0.50. This suggested that two pairs of H-atom positions were too near each other to be separated in the difference Fourier map. The initial model for the refinement had one H atom on a particular O atom located near each of the two disordered H-atom peaks. The final refinement had the O—H distances in the water molecule restrained tightly to 0.840 (1) Å and the H—O—H angle restrained to 109.5 (2)°, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$. In view of the expected uncertainty of the H-atom positions, these are effectively constraints.

For all compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3011). Services for accessing these data are described at the back of the journal.

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