

Hydrogen-bonded structures of the 1:1 and 1:2 compounds of chloranilic acid with pyrrolidin-2-one and piperidin-2-one

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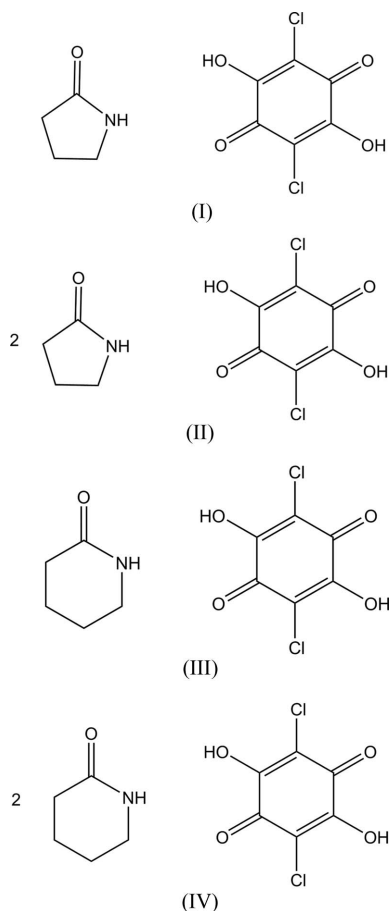
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In the four compounds of chloranilic acid (2,5-dichloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione) with pyrrolidin-2-one and piperidin-2-one, namely, chloranilic acid–pyrrolidin-2-one (1/1), $C_6H_2Cl_2O_4 \cdot C_4H_7NO$, (I), chloranilic acid–pyrrolidin-2-one (1/2), $C_6H_2Cl_2O_4 \cdot 2C_4H_7NO$, (II), chloranilic acid–piperidin-2-one (1/1), $C_6H_2Cl_2O_4 \cdot C_5H_9NO$, (III), and chloranilic acid–piperidin-2-one (1/2), $C_6H_2Cl_2O_4 \cdot 2C_5H_9NO$, (IV), the shortest interactions between the two components are O–H...O hydrogen bonds, which act as the primary intermolecular interaction in the crystal structures. In (II), (III) and (IV), the chloranilic acid molecules lie about inversion centres. For (III), this necessitates the presence of two independent acid molecules. In (I), there are two formula units in the asymmetric unit. The O...O distances are 2.4728 (11) and 2.4978 (11) Å in (I), 2.5845 (11) Å in (II), 2.6223 (11) and 2.5909 (10) Å in (III), and 2.4484 (10) Å in (IV). In the hydrogen bond of (IV), the H atom is disordered over two positions with site occupancies of 0.44 (3) and 0.56 (3). This indicates that proton transfer between the acid and base has partly taken place to form ion pairs. In (I) and (II), N–H...O hydrogen bonds, the secondary intermolecular interactions, connect the pyrrolidin-2-one molecules into a dimer, while in (III) and (IV) these hydrogen bonds link the acid and base to afford three- and two-dimensional hydrogen-bonded networks, respectively.

Comment

Chloranilic acid (2,5-dichloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione), a strong dibasic acid with hydrogen-bond donor and acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with various organic bases (Ishida & Kashino, 1999*a,b*, 2002; Zaman *et al.*, 1999, 2004; Gotoh, Maruyama & Ishida, 2010), and also as a model compound for investigating hydrogen-transfer mechanisms in O–H...N and N–H...O hydrogen-

bond systems (Ikeda *et al.*, 2005; Suzuki *et al.*, 2007; Gotoh *et al.*, 2008; Gotoh, Asaji & Ishida, 2010; Seliger *et al.*, 2009, 2011; Asaji, Hoshino *et al.*, 2010; Asaji, Seliger *et al.*, 2010). Furthermore, salts and cocrystals of chloranilic acid with pyridine derivatives have recently attracted much interest with respect to organic ferroelectrics (Horiuchi, Ishii *et al.*, 2005; Horiuchi, Kumai & Tokura, 2005; Asaji *et al.*, 2007; Gotoh *et al.*, 2007; Horiuchi & Tokura, 2008; Horiuchi *et al.*, 2010).



In the present study, we have prepared four compounds of chloranilic acid with pyrrolidin-2-one and piperidin-2-one,

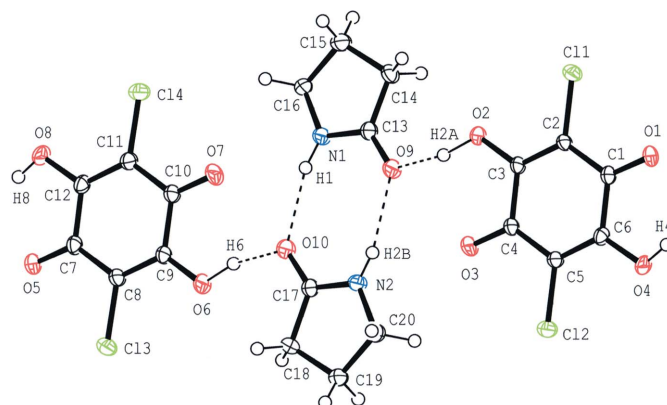
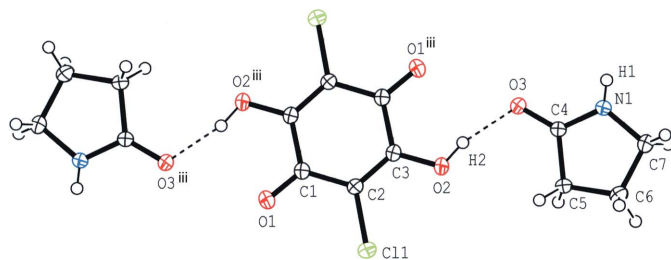
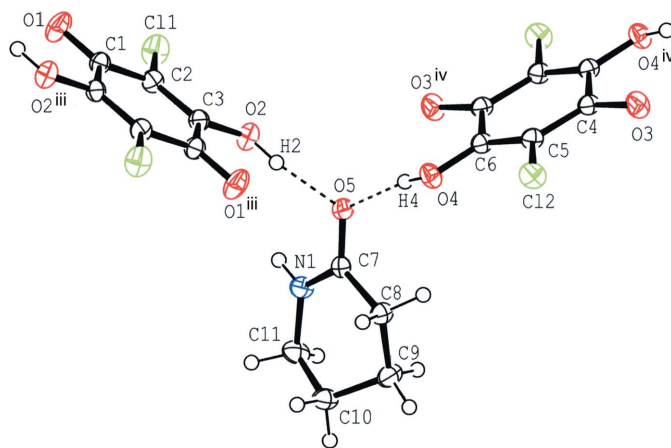


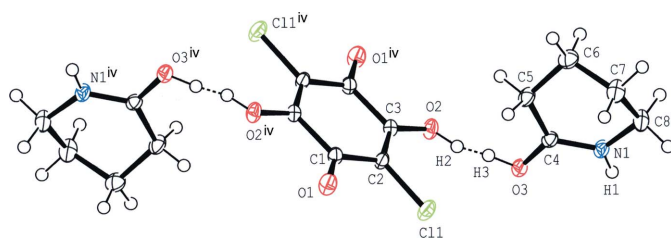
Figure 1
 The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. O–H...O and N–H...O hydrogen bonds are indicated by dashed lines.

**Figure 2**

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. O—H...O hydrogen bonds are indicated by dashed lines. [Symmetry code: (iii) $-x + 1, -y + 1, -z + 2$.]

**Figure 3**

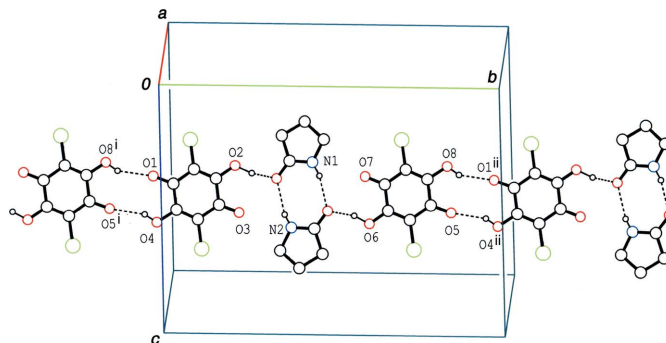
The molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. O—H...O hydrogen bonds are indicated by dashed lines. [Symmetry codes: (iii) $-x, -y, -z$; (iv) $-x + 1, -y, -z + 1$.]

**Figure 4**

The molecular structure of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. O...H...O hydrogen bonds are indicated by dashed lines. [Symmetry code: (iv) $-x + 1, -y + 1, -z + 1$.]

namely, chloranilic acid–pyrrolidin-2-one (1/1), (I), chloranilic acid–pyrrolidin-2-one (1/2), (II), chloranilic acid–piperidin-2-one (1/1), (III), and chloranilic acid–piperidin-2-one (1/2), (IV), and determined their crystal structures at 180 K in order to extend our study of $D-H\cdots A$ hydrogen bonding ($D = N, O$ or C ; $A = N, O$ or Cl) in chloranilic acid–organic base systems (Gotoh *et al.*, 2009; Gotoh & Ishida, 2009).

The molecular structures of (I), (II), (III) and (IV) are shown in Figs. 1, 2, 3 and 4, respectively. The chloranilic acid molecules in all four compounds show a characteristic struc-

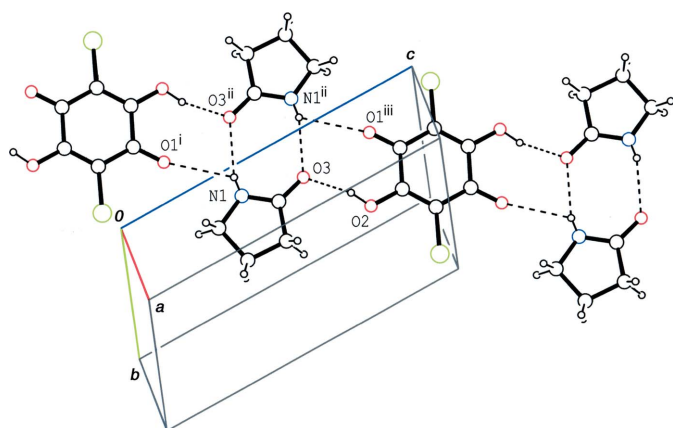
**Figure 5**

A partial packing diagram for (I), showing the hydrogen-bonded tape structure formed by the 2+2 aggregates. Dashed lines show N—H...O and O—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y + 1, z$.]

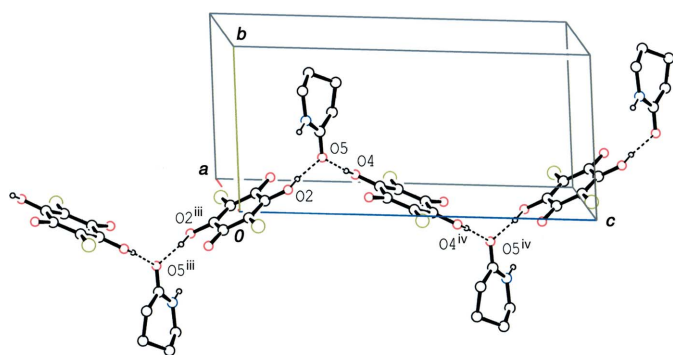
ture with two long and two short C—C bonds, as described by Andersen (1967). The pyrrolidin-2-one molecules in (I) and (II) adopt an approximate envelope conformation, while the piperidin-2-one molecules in (III) and (IV) have half-chair conformations.

The asymmetric unit of (I) contains two crystallographically independent pyrrolidin-2-one molecules and two chloranilic acid molecules (Fig. 1). The acid and base are held together by short O—H...O hydrogen bonds ($O2-H2A\cdots O9$ and $O6-H6\cdots O10$; Table 1), and the two bases are further connected to each other by a pair of N—H...O hydrogen bonds ($N1-H1\cdots O10$ and $N2-H2B\cdots O9$; Table 1), thus forming a quasi-centrosymmetric 2+2 aggregate. These 2+2 aggregates are linked through a pair of O—H...O hydrogen bonds between adjacent chloranilic acid molecules ($O4-H4\cdots O5^i$ and $O8-H8\cdots O1^{ii}$; details and symmetry codes in Table 1), forming an approximately flat tape structure along the b axis (Fig. 5). In this tape, the dihedral angle between the acid C1—C6 and C7—C12 rings is $2.67(5)^\circ$, and those between the least-squares plane of atoms N1/C13—C16/O9/N2/C17—C20/O10 of the hydrogen-bonded pyrrolidin-2-one dimer and the acid C1—C6 and C7—C12 rings are $9.23(4)$ and $6.92(4)^\circ$, respectively. The tapes, related to each other by an inversion centre, are stacked alternately along the a axis, forming a layer parallel to the ab plane.

In compound (II), the acid molecule is located on an inversion centre, so that the asymmetric unit contains one pyrrolidin-2-one molecule and one half-molecule of chloranilic acid (Fig. 2). The acid and the base are connected by a short O—H...O hydrogen bond ($O2-H2\cdots O3$; Table 2) and the two components are further connected by an N—H...O(O,O) bifurcated hydrogen bond [$N1-H1\cdots(O1^i, O3^{ii})$; details and symmetry codes in Table 2], such that the hydrogen-bonded pyrrolidin-2-one dimer and the chloranilic acid molecules are arranged alternately into an essentially planar molecular tape along the [111] direction (Fig. 6). In this tape, the dihedral angle between the acid ring and the least-squares plane of atoms N1/C4—C7/O3 of pyrrolidin-2-one is $8.81(12)^\circ$. The tapes are stacked along the a axis and form a layer parallel to the $(0\bar{1}1)$ plane.


Figure 6

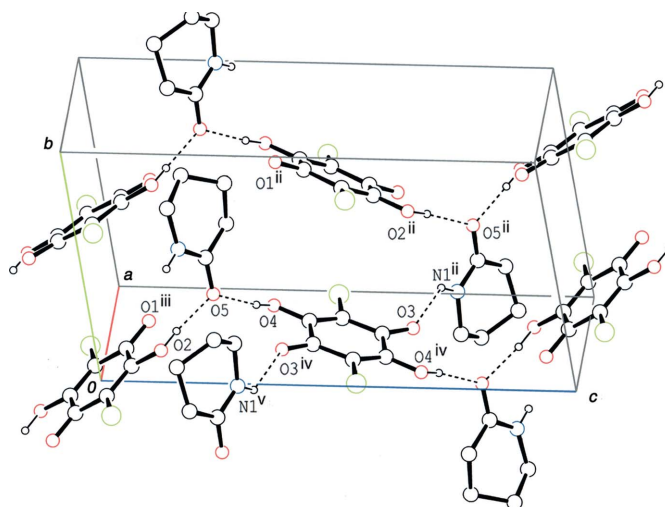
A partial packing diagram for (II), showing the hydrogen-bonded tape structure. Dashed lines show N—H...O and O—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (i) $x - 1, y - 1, z - 1$; (ii) $-x, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z + 2$.]


Figure 7

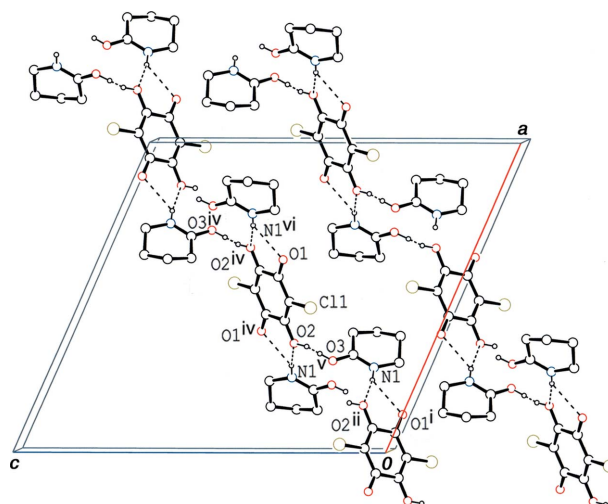
A partial packing diagram for (III), showing the hydrogen-bonded chain structure. Dashed lines show O—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (iii) $-x, -y, -z$; (iv) $-x + 1, -y, -z + 1$.]

In the asymmetric unit of (III), there is one piperidin-2-one molecule and two crystallographically independent half-molecules of chloranilic acid, with each of the acid molecules lying about an inversion centre (Fig. 3). No formation of dimers of piperidin-2-one molecules is observed, while the piperidin-2-one O atom participates in two O—H...O hydrogen bonds as an acceptor for two chloranilic acid O—H groups (O2—H2...O5 and O4—H4...O5; Table 3), forming a zigzag chain along the [101] direction in which the two components are arranged alternately (Fig. 7). An N—H...O hydrogen bond (N1—H1...O3ⁱⁱ; symmetry code in Table 3) formed between the piperidin-2-one and chloranilic acid molecules connects the chains into a three-dimensional network (Fig. 8).

The asymmetric unit of (IV) contains one piperidin-2-one molecule and one half-molecule of chloranilic acid, which is located on an inversion centre (Fig. 4). A short O—H...O hydrogen bond with an O...O distance of 2.4484 (10) Å connects the two components. The H atom in the hydrogen bond is disordered over two positions with refined occupancies of 0.44 (3) and 0.56 (3) at the O2 and O3 sites, respectively, which indicates that proton transfer between the


Figure 8

A partial packing diagram for (III), showing the three-dimensional hydrogen-bonded network. Dashed lines show N—H...O and O—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (ii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x, -y, -z$; (iv) $-x + 1, -y, -z + 1$; (v) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.]


Figure 9

A packing diagram for (IV), viewed along the b axis, showing the hydrogen-bonded layer structure. Dashed lines show N—H...O and O—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

acid and base has partly taken place to form ion pairs. This disordered feature is confirmed in a difference Fourier map (see *Supplementary materials*). The acid and base are further connected by an N—H...O(O,O) bifurcated hydrogen bond [N1—H1...O1ⁱ, O2ⁱⁱⁱ]; details and symmetry codes in Table 4], forming a layer parallel to the (10 $\bar{1}$) plane (Fig. 9).

We have shown that in all compounds the primary intermolecular interactions are O—H...O hydrogen bonds formed between the acid and the base. The secondary interactions are N—H...O hydrogen bonds, which connect the piperidin-2-one molecules into a dimer in (I) and (II), and link the acid and base into three- and two-dimensional hydrogen-bonded networks in (III) and (IV), respectively. Furthermore, in (IV)

it is noteworthy that (a) the orientation of the O—H group of the acid is different from that in (I), (II) and (III), in that the O—H group in (IV) points to the Cl atom due to the N—H...O(O) hydrogen bond; and (b) the O atom of the base acts as a single acceptor only for the O—H group. These may cause the disorder of the H atom in the O...H...O hydrogen bond.

Experimental

Single crystals of the 1:1 compounds (I) and (III) were obtained by slow evaporation from acetonitrile solutions [120 and 200 ml for (I) and (III), respectively] of chloranilic acid with pyrrolidin-2-one or piperidin-2-one in a 1:1 molar ratio [0.475 g of chloranilic acid and 0.194 g of pyrrolidin-2-one for (I), and 1.03 g of chloranilic acid and 0.49 g of piperidin-2-one for (III)] at room temperature. Single crystals of the 1:2 compounds (II) and (IV) were obtained by slow evaporation from acetonitrile solutions [200 and 125 ml for (II) and (IV), respectively] of chloranilic acid with pyrrolidin-2-one or piperidin-2-one in a 1:2.2 molar ratio [0.452 g of chloranilic acid and 0.405 g of pyrrolidin-2-one for (II), and 0.367 g of chloranilic acid and 0.383 g of piperidin-2-one for (IV)] at room temperature. About 10% excess pyrrolidin-2-one or piperidin-2-one was used to avoid contamination by the 1:1 compound.

Compound (I)

Crystal data

$C_6H_7NO \cdot C_6H_2Cl_2O_4$	$V = 2276.2 (2) \text{ \AA}^3$
$M_r = 294.09$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.7256 (4) \text{ \AA}$	$\mu = 0.58 \text{ mm}^{-1}$
$b = 19.3792 (11) \text{ \AA}$	$T = 180 \text{ K}$
$c = 15.2486 (8) \text{ \AA}$	$0.35 \times 0.20 \times 0.15 \text{ mm}$
$\beta = 94.404 (2)^\circ$	

Data collection

Rigaku R-Axis RAPID II diffractometer	47031 measured reflections
Absorption correction: numerical (NUMABS; Higashi, 1999)	6636 independent reflections
$T_{\min} = 0.858, T_{\max} = 0.916$	5477 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.05 \text{ e \AA}^{-3}$
6636 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
349 parameters	

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O10$	0.870 (15)	2.056 (15)	2.9065 (13)	165.5 (14)
$O2-H2A \cdots O9$	1.05 (2)	1.44 (2)	2.4728 (11)	167 (2)
$N2-H2B \cdots O9$	0.839 (15)	2.108 (15)	2.9249 (13)	164.6 (15)
$O4-H4 \cdots O5^i$	0.849 (17)	2.002 (17)	2.7774 (11)	151.6 (15)
$O6-H6 \cdots O10$	0.99 (2)	1.54 (2)	2.4978 (11)	163 (2)
$O8-H8 \cdots O1^{ii}$	0.850 (17)	2.025 (17)	2.7850 (11)	148.5 (15)

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$.

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O1^i$	0.73 (2)	2.537 (19)	3.0036 (12)	123.8 (17)
$N1-H1 \cdots O3^{ii}$	0.73 (2)	2.22 (2)	2.9185 (13)	162.0 (19)
$O2-H2 \cdots O3$	0.84 (2)	1.76 (2)	2.5845 (11)	164 (2)

Symmetry codes: (i) $x-1, y-1, z-1$; (ii) $-x, -y, -z+1$.

Compound (II)

Crystal data

$C_6H_2Cl_2O_4 \cdot 2C_4H_7NO$	$\gamma = 108.734 (2)^\circ$
$M_r = 379.20$	$V = 396.42 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 4.9665 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.4767 (4) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$c = 11.8445 (6) \text{ \AA}$	$T = 180 \text{ K}$
$\alpha = 106.7904 (19)^\circ$	$0.38 \times 0.32 \times 0.25 \text{ mm}$
$\beta = 90.299 (2)^\circ$	

Data collection

Rigaku R-Axis RAPID II diffractometer	9315 measured reflections
Absorption correction: numerical (NUMABS; Higashi, 1999)	2296 independent reflections
$T_{\min} = 0.853, T_{\max} = 0.895$	2156 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
2296 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
117 parameters	

Compound (III)

Crystal data

$C_6H_2Cl_2O_4 \cdot C_5H_9NO$	$V = 1244.42 (7) \text{ \AA}^3$
$M_r = 308.12$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.41079 (17) \text{ \AA}$	$\mu = 0.54 \text{ mm}^{-1}$
$b = 8.0690 (4) \text{ \AA}$	$T = 180 \text{ K}$
$c = 18.1026 (3) \text{ \AA}$	$0.43 \times 0.36 \times 0.26 \text{ mm}$
$\beta = 115.1397 (7)^\circ$	

Data collection

Rigaku R-Axis RAPID II diffractometer	22572 measured reflections
Absorption correction: numerical (NUMABS; Higashi, 1999)	3626 independent reflections
$T_{\min} = 0.793, T_{\max} = 0.870$	3461 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.018$

Table 3

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (III).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O3^i$	0.869 (18)	2.213 (19)	2.8871 (12)	134.2 (14)
$O2-H2 \cdots O5$	0.909 (19)	1.743 (18)	2.6223 (11)	162.1 (18)
$O4-H4 \cdots O5$	0.843 (19)	1.767 (18)	2.5909 (10)	165.1 (19)

Symmetry code: (i) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$.

Table 4

Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 ⁱ	0.845 (18)	2.398 (17)	2.9561 (12)	124.1 (14)
N1—H1...O2 ⁱⁱ	0.845 (18)	2.214 (17)	3.0358 (12)	164.3 (15)
O3—H3...O2	0.84 (2)	1.61 (2)	2.4484 (10)	173 (3)
O2—H2...O3	0.82 (3)	1.66 (3)	2.4484 (10)	161 (4)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	
$S = 1.06$	
3626 reflections	$\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$
184 parameters	$\Delta\rho_{\min} = -0.30 \text{ e } \text{Å}^{-3}$

Compound (IV)

Crystal data

$\text{C}_6\text{H}_{0.88}\text{Cl}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_{9.56}\text{NO}$	$V = 1732.12 (12) \text{ Å}^3$
$M_r = 407.25$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.8438 (5) \text{ Å}$	$\mu = 0.41 \text{ mm}^{-1}$
$b = 5.4253 (3) \text{ Å}$	$T = 180 \text{ K}$
$c = 19.5958 (5) \text{ Å}$	$0.45 \times 0.40 \times 0.15 \text{ mm}$
$\beta = 114.0658 (7)^\circ$	

Data collection

Rigaku R-AXIS RAPID II diffractometer	17611 measured reflections
Absorption correction: numerical (NUMABS; Higashi, 1999)	2524 independent reflections
$T_{\min} = 0.835, T_{\max} = 0.940$	2382 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	
$S = 1.07$	
2524 reflections	$\Delta\rho_{\max} = 0.51 \text{ e } \text{Å}^{-3}$
129 parameters	$\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$
2 restraints	

H atoms attached to O and N atoms were found in difference Fourier maps and refined isotropically (refined O—H and N—H distances are given in Tables 1–4). For compound (IV), the O-bound H atom, which is involved in the O...H...O hydrogen bond, was found to be disordered over two positions in a difference Fourier map. Since the site-occupancy factors and isotropic displacement parameters were strongly correlated, the positional parameters and occupancy factors were refined, with O—H bond-length restraints of 0.84 (2) Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were treated as riding, with C—H = 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. For compound (I), the two highest residual electron-density peaks of 1.05 and 0.90 e Å⁻³ are located 0.60 and 0.63 Å, respectively, from atoms C18 and C16.

For all four compounds, data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008). Molecular graphics: *ORTEP-3* (Farrugia, 1997) for (I), (II) and (III); *ORTEP-3* and *WinGX* (Farrugia, 1999) for (IV). For all compounds, software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3233). Services for accessing these data are described at the back of the journal.

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