

## Diels–Alder adducts of maleic anhydride and dienes: new compounds by crystallization

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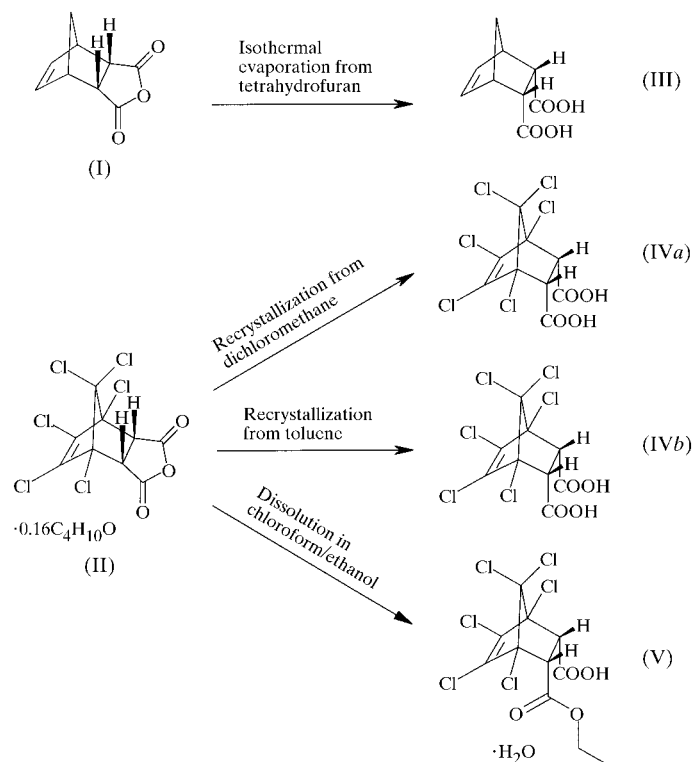
We have determined the crystal structures of bicyclo[2.2.1]hept-2-ene-*endo-cis*-5,6-dicarboxylic anhydride,  $C_9H_8O_3$ , (I), 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene-*endo-cis*-5,6-dicarboxylic anhydride diethyl ether solvate,  $C_9H_2Cl_6O_3 \cdot 0.16 C_4H_{10}O$ , (II), bicyclo[2.2.1]hept-2-ene-*endo-cis*-5,6-dicarboxylic acid,  $C_9H_{10}O_4$ , (III), 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene-*endo-cis*-5,6-dicarboxylic acid,  $C_9H_4Cl_6O_4$ , (IVa) and (IVb), and ethyl 1,2,3,4,7,7-hexachloro-6-carboxybicyclo[2.2.1]hept-2-ene-*endo-cis*-5-carboxylate monohydrate,  $C_{11}H_8Cl_6O_4 \cdot H_2O$ , (V). Compounds (I) and (II) were prepared by a standard Diels–Alder reaction from maleic anhydride and cyclopentadiene or hexachlorocyclopentadiene, respectively. The crystal-growing processes of these compounds led to surprising results: rapid recrystallization of (I) from diethyl ether and (II) from petroleum ether gave crystals of these compounds, however, crystallization by slow evaporation techniques using common solvents yielded new compounds in which the five-membered heterocycle has been cleaved.

### Comment

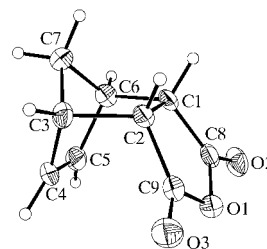
Recrystallization is a standard technique for purifying a reaction product and obtaining crystals suitable for X-ray structure analysis. In most cases, the chemist already knows the constitution of the new compound. If one is not sure of it, an X-ray structure analysis is often the only way to determine the structure unambiguously. Normally, crystals of the compound in question can be obtained by standard crystallization techniques, but sometimes the results of the structure determination are surprising.

We have prepared compounds (I) and (II) by a standard Diels–Alder reaction (Diels & Alder, 1928) from maleic anhydride and cyclopentadiene or hexachlorocyclopentadiene, respectively. Whereas rapid recrystallization (over just a few days) of (I) from diethyl ether and (II) from petroleum ether led to crystals of the desired and expected compounds,

recrystallization by slow evaporation techniques (over several weeks) yielded new compounds, *i.e.* (III), (IVa), (IVb) and (V).



Crystals of (I) (Fig. 1) were obtained by isothermal evaporation from a diethyl ether solution at room temperature. It is essential to avoid any contact of the compound with water, because it is susceptible to hydrolysis. Compound (I) has a rigid molecule, comprising a 2-norbornene skeleton and an anhydride ring. The two planes in the norbornene skeleton (plane 1: C3/C4/C5/C6, r.m.s. deviation = 0.002 Å; plane 2: C1/C2/C3/C6, r.m.s. deviation = 0.012 Å) form an angle of 113.16 (8)°. The anhydride ring is also nearly planar (r.m.s. deviation = 0.016 Å) and both carbonyl O atoms deviate only slightly from this plane [O2 0.074 (2) Å and O3 −0.026 (2) Å]. The dihedral angle between the anhydride ring and the adjacent plane of the norbornene skeleton is 119.09 (7)°. The plane formed by the methylene bridge (C3/C7/C6) encloses a dihedral angle of 128.5 (1)° with plane 1 and 118.4 (1)° with plane 2 of the norbornene skeleton. These results agree well

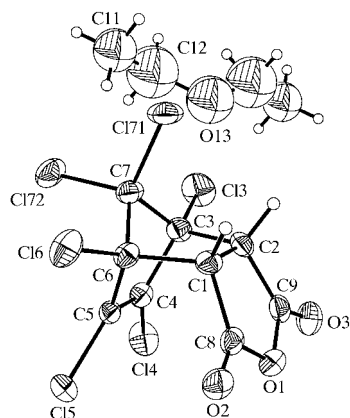


**Figure 1**  
A perspective view of (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

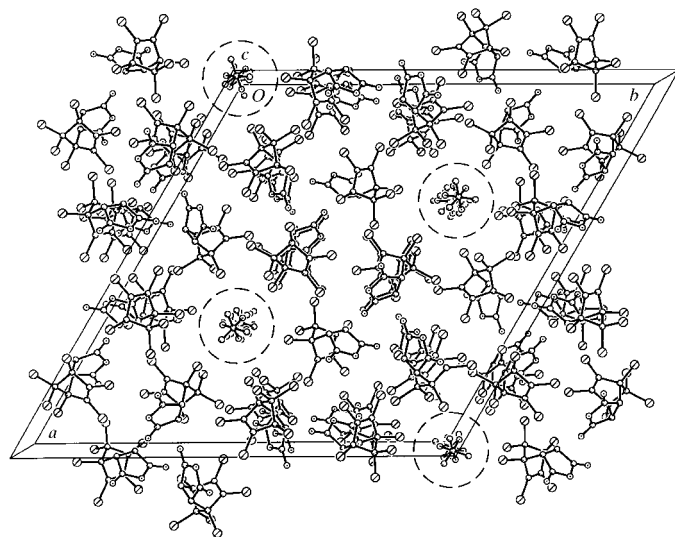
with the crystal structure of (I) determined at room temperature using Weissenberg photographs (Destro *et al.*, 1969).

Our second starting material, (II) (Fig. 2), crystallized with one-sixth of a diethyl ether molecule in the asymmetric unit disordered about a site of crystallographic  $\bar{3}$  symmetry. The packing diagram (Fig. 3) reveals that the diethyl ether molecules are located in channels parallel to the crystallographic *c* axis. A least-squares fit of the C and O atoms of (I) and (II) (r.m.s. deviation = 0.053 Å) shows that the substitution by six Cl atoms does not change the conformation of the molecule markedly. The main difference between (I) and (II) is the enhanced reactivity of (II) caused by the electron-withdrawing effect of the six Cl substituents. As a result, the anhydride ring can be easily opened.

Crystals of (III) were obtained by simple isothermal evaporation of a solution of (I) in commercial tetrahydrofuran, which had not been dried prior to use. The result is



**Figure 2**  
A perspective view of (II) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

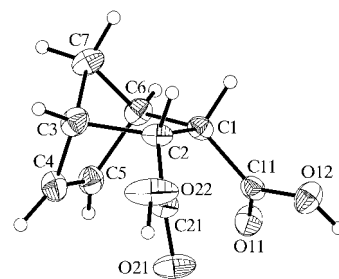


**Figure 3**  
The packing diagram for (II), viewed along the *c* axis. H atoms have been omitted for clarity. The channels filled with disordered diethyl ether molecules are indicated by dashed circles.

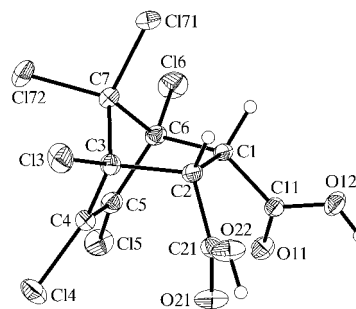
shown in Fig. 4. The anhydride ring has been opened and hydrolyzed to two carboxyl groups, which form intermolecular hydrogen bonds (Table 1). A least-squares fit of all atoms of the norbornene skeleton of (I) and (III) does not show any significant differences (r.m.s. deviation = 0.019 Å). The structure of (III) has already been determined at room temperature (Avitabile *et al.*, 1973; Pfluger *et al.*, 1973) and as a potassium salt sesquihydrate (Cser & Sasvari, 1976). The formation of a salt has no significant effect on the conformation of the molecule [r.m.s. deviation between all C atoms of (III) and the potassium salt = 0.074 Å]. Even the conformation of the carboxyl groups is similar: the torsion angles C1–C2–C21–O21 and C2–C1–C11–O11 are  $-29.4$  (4) and  $124.7$  (3)° in (III), and 6.8 and 105.2° in the potassium salt, respectively.

During our attempts to recrystallize (II) from various solvents we obtained astonishing results. Whereas recrystallization of (II) from dichloromethane or toluene afforded the same compound but as different polymorphs, (IVa) and (IVb), dissolving (II) in a chloroform/ethanol solution led to crystals of (V).

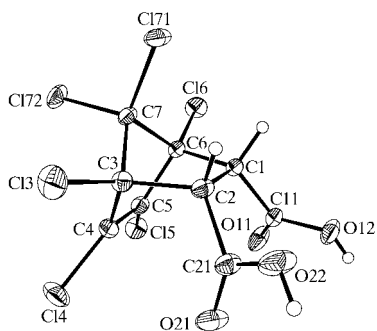
Compound (IVa) (Fig. 5) crystallizes in the chiral space group  $P2_1$  and compound (IVb) (Figs. 6 and 7) in the centrosymmetric space group  $P2_1/c$ . The conformation of the norbornene skeleton including the Cl substituents is nearly the same for (IVa) and the two symmetry-independent molecules of (IVb). These structures differ only in the exact orientation of the carboxyl groups (Table 5). In spite of the different torsion angles, the crystal packing in both structures is very similar and is stabilized by hydrogen-bonded zigzag chains



**Figure 4**  
A perspective view of (III) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.



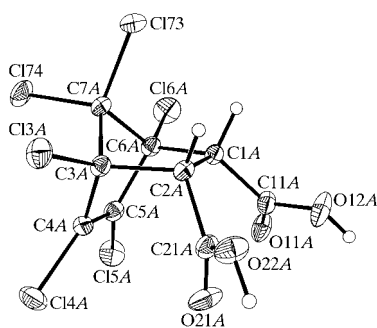
**Figure 5**  
A perspective view of (IVa) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.



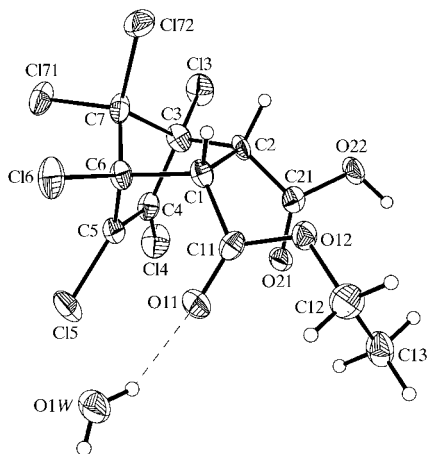
**Figure 6**  
A perspective view of molecule 1 of (IVb) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

with the two independent molecules of (IVb) alternating. A comparison of (IVa) with (III) shows that the Cl atoms do not change the conformation of the norbornene skeleton (r.m.s. deviation = 0.064 Å for all C atoms).

Compound (V), the last in this series, was obtained by dissolving compound (II) in a mixture of chloroform and ethanol and evaporating the solvent under isothermal condi-



**Figure 7**  
A perspective view of molecule 2 of (IVb) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.



**Figure 8**  
A perspective view of (V) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

tions. In this case, the dicarboxylic acid monoester was formed and crystallized as a monohydrate (Fig. 8). The water molecule acts as a hydrogen-bonding bridge between the two carbonyl groups of symmetry-equivalent molecules. Moreover, the water O atom is an acceptor of a hydrogen bond from the hydroxyl group (Table 4). The geometry of the hexachloronorbornene skeleton does not show any significant differences compared with the unsubstituted acid (III); a least-squares fit of all the Cl and C atoms (except C12 and C13) gives an r.m.s. deviation of 0.037 Å. The orientation of the carboxyl and ester groups relative to the norbornene skeleton is the same as that of the carboxyl groups in (IVb). The corresponding torsion angles (Table 5) show differences of less than 10°.

The results described here underline that it is extremely important to choose a suitable solvent and appropriate conditions when crystallizing a reaction product. If the solvent reacts with the compound to be crystallized, the result of the experiment might be an awkward surprise.

## Experimental

Compounds (I) and (II) were synthesized according to Hünig *et al.* (1979). For (I), after cooling a solution of maleic anhydride (2.94 g, 30 mmol) in benzene (25 ml) to 278 K, freshly distilled cyclopentadiene (2.18 g, 33 mmol) was added dropwise. The mixture was stirred for 10 min at room temperature and then for 10 min at 353 K. After cooling to room temperature, the product was crystallized by adding petroleum ether. Crystals of (I) suitable for X-ray structure analysis were grown by rapid evaporation from diethyl ether. For (II), a mixture of maleic anhydride (1.96 g, 20 mmol) and hexachlorocyclopentadiene (5.56 g, 20 mmol) was heated to 413 K and stirred at this temperature for 3 h. After cooling to room temperature, the reaction product was dissolved in boiling benzene (5 ml) and recrystallized at 273 K. Suitable crystals of (II) were grown by rapid evaporation from petroleum ether. Compound (III) was obtained by recrystallizing (I) from tetrahydrofuran. Recrystallization of (II) from dichloromethane led to (IVa), from toluene to (IVb) and from chloroform/ethanol to (V).

## Compound (I)

### Crystal data

C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 164.15  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 5.926 (2) Å  
*b* = 9.489 (3) Å  
*c* = 13.452 (5) Å  
*V* = 756.4 (4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.441 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 7065 reflections  
 $\theta$  = 1–25°  
 $\mu$  = 0.109 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, colourless  
 0.50 × 0.40 × 0.18 mm

### Data collection

Siemens CCD three-circle diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.948, *T<sub>max</sub>* = 0.981  
 20 569 measured reflections  
 1155 independent reflections  
 1082 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.037  
 $\theta_{\max}$  = 28.69°  
*h* = −8 → 8  
*k* = −12 → 12  
*l* = −18 → 18  
 260 standard reflections  
 frequency: 1440 min  
 intensity decay: none

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.110$   
 $S = 1.138$   
 1155 reflections  
 109 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 0.0338P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

Compound (II)

Crystal data

$\text{C}_9\text{H}_2\text{Cl}_6\text{O}_3 \cdot 0.16\text{C}_4\text{H}_{10}\text{O}$   
 $M_r = 383.16$   
 Trigonal,  $R\bar{3}$   
 $a = 29.639 \text{ (4) } \text{Å}$   
 $c = 8.119 \text{ (2) } \text{Å}$   
 $V = 6176.8 \text{ (19) } \text{Å}^3$   
 $Z = 18$   
 $D_x = 1.854 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 512 reflections  
 $\theta = 1\text{--}20^\circ$   
 $\mu = 1.249 \text{ mm}^{-1}$   
 $T = 173 \text{ (2) K}$   
 Block, colourless  
 $0.30 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Siemens CCD three-circle diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.706$ ,  $T_{\max} = 0.835$   
 31 306 measured reflections  
 2811 independent reflections  
 2314 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$   
 $\theta_{\max} = 26.37^\circ$   
 $h = -36 \rightarrow 37$   
 $k = -37 \rightarrow 37$   
 $l = -10 \rightarrow 10$   
 317 standard reflections  
 frequency: 1800 min  
 intensity decay: none

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.078$   
 $S = 1.060$   
 2811 reflections  
 173 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 19.3097P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.73 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{Å}^{-3}$

Compound (III)

Crystal data

$\text{C}_9\text{H}_{10}\text{O}_4$   
 $M_r = 182.17$   
 Monoclinic,  $P2_1/c$   
 $a = 10.999 \text{ (2) } \text{Å}$   
 $b = 7.389 \text{ (1) } \text{Å}$   
 $c = 10.410 \text{ (2) } \text{Å}$   
 $\beta = 98.75 \text{ (3) }^\circ$   
 $V = 836.2 \text{ (2) } \text{Å}^3$   
 $Z = 4$

$D_x = 1.447 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 4135 reflections  
 $\theta = 0\text{--}25^\circ$   
 $\mu = 0.115 \text{ mm}^{-1}$   
 $T = 173 \text{ (2) K}$   
 Block, colourless  
 $0.5 \times 0.1 \times 0.1 \text{ mm}$

Data collection

Siemens CCD three-circle diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.945$ ,  $T_{\max} = 0.989$   
 12 009 measured reflections  
 1707 independent reflections  
 1304 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$   
 $\theta_{\max} = 26.37^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -9 \rightarrow 9$   
 $l = -13 \rightarrow 13$   
 116 standard reflections  
 frequency: 960 min  
 intensity decay: none

Table 1

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

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{O12--H12}\cdots\text{O11}^i$	0.84	1.86	2.685 (3)	168
$\text{O22--H22}\cdots\text{O21}^{ii}$	0.84	1.88	2.704 (3)	168

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

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.152$   
 $S = 1.095$   
 1707 reflections  
 121 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 1.4698P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.021 (4)

Compound (IVa)

Crystal data

$\text{C}_9\text{H}_4\text{Cl}_6\text{O}_4$   
 $M_r = 388.82$   
 Monoclinic,  $P2_1$   
 $a = 7.499 \text{ (1) } \text{Å}$   
 $b = 7.924 \text{ (2) } \text{Å}$   
 $c = 11.873 \text{ (2) } \text{Å}$   
 $\beta = 101.65 \text{ (1) }^\circ$   
 $V = 691.0 \text{ (2) } \text{Å}^3$   
 $Z = 2$

$D_x = 1.869 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 511 reflections  
 $\theta = 1\text{--}25^\circ$   
 $\mu = 1.246 \text{ mm}^{-1}$   
 $T = 173 \text{ (2) K}$   
 Block, colourless  
 $0.40 \times 0.30 \times 0.15 \text{ mm}$

Data collection

Siemens CCD three-circle diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.636$ ,  $T_{\max} = 0.835$   
 19 175 measured reflections  
 3424 independent reflections  
 3293 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$   
 $\theta_{\max} = 28.28^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -10 \rightarrow 10$   
 $l = -15 \rightarrow 15$   
 325 standard reflections  
 frequency: 1200 min  
 intensity decay: none

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.048$   
 $S = 1.044$   
 3424 reflections  
 180 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.0924P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter = 0.02 (4)

Table 2

Hydrogen-bonding geometry ( $\text{Å}$ ,  $^\circ$ ) for (IVa).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{O12--H12}\cdots\text{O21}^i$	0.79 (2)	1.83 (3)	2.6214 (17)	179 (3)
$\text{O22--H22}\cdots\text{O11}^{ii}$	0.83 (3)	1.95 (3)	2.7716 (17)	171 (3)

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

Compound (IVb)

Crystal data

$\text{C}_9\text{H}_4\text{Cl}_6\text{O}_4$   
 $M_r = 388.82$   
 Monoclinic,  $P2_1/c$   
 $a = 8.443 \text{ (1) } \text{Å}$   
 $b = 24.809 \text{ (1) } \text{Å}$   
 $c = 13.594 \text{ (1) } \text{Å}$   
 $\beta = 90.38 \text{ (1) }^\circ$   
 $V = 2847.4 \text{ (4) } \text{Å}^3$   
 $Z = 8$

$D_x = 1.814 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 8192 reflections  
 $\theta = 1\text{--}25^\circ$   
 $\mu = 1.209 \text{ mm}^{-1}$   
 $T = 173 \text{ (2) K}$   
 Block, colourless  
 $0.5 \times 0.4 \times 0.4 \text{ mm}$

Data collection

Siemens CCD three-circle diffractometer	$R_{\text{int}} = 0.022$
$\omega$ scans	$\theta_{\text{max}} = 28.28^\circ$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.583$ , $T_{\text{max}} = 0.643$	$k = -33 \rightarrow 33$
61 228 measured reflections	$l = -18 \rightarrow 18$
7069 independent reflections	943 standard reflections
6477 reflections with $I > 2\sigma(I)$	frequency: 1000 min intensity decay: none

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 2.1579P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.142$	$\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$
7069 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
359 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 3

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O12—H12 $\cdots$ O11A <sup>i</sup>	0.79 (3)	1.88 (3)	2.6627 (17)	174 (3)
O22—H22 $\cdots$ O21A <sup>ii</sup>	0.76 (3)	1.86 (3)	2.6186 (17)	175 (3)
O12A—H12A $\cdots$ O11 <sup>i</sup>	0.83 (3)	1.80 (3)	2.6320 (17)	178 (3)
O22A—H22A $\cdots$ O21 <sup>ii</sup>	0.90 (4)	1.84 (4)	2.7347 (17)	171 (3)

Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $2-x, 1-y, 1-z$ .

Compound (V)

Crystal data

$C_{11}H_8Cl_6O_4 \cdot H_2O$	$Z = 2$
$M_r = 434.89$	$D_x = 1.770 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.616 (3) \text{ \AA}$	Cell parameters from 2320 reflections
$b = 9.281 (2) \text{ \AA}$	$\theta = 1-20^\circ$
$c = 10.460 (4) \text{ \AA}$	$\mu = 1.069 \text{ mm}^{-1}$
$\alpha = 100.53 (2)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 94.00 (2)^\circ$	Plate, colourless
$\gamma = 95.06 (2)^\circ$	$0.25 \times 0.20 \times 0.10 \text{ mm}$
$V = 816.0 (5) \text{ \AA}^3$	

Data collection

Siemens CCD three-circle diffractometer	$R_{\text{int}} = 0.086$
$\omega$ scans	$\theta_{\text{max}} = 25.03^\circ$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.776$ , $T_{\text{max}} = 0.901$	$k = -11 \rightarrow 11$
11 168 measured reflections	$l = -12 \rightarrow 12$
2886 independent reflections	69 standard reflections
1709 reflections with $I > 2\sigma(I)$	frequency: 900 min intensity decay: none

Table 4

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O22—H22 $\cdots$ O1W <sup>i</sup>	0.96 (7)	1.60 (7)	2.564 (6)	176 (6)
O1W—H1W $\cdots$ O11	0.94 (7)	2.01 (7)	2.852 (6)	148 (6)
O1W—H2W $\cdots$ O21 <sup>ii</sup>	0.74 (6)	2.12 (6)	2.835 (6)	165 (7)

Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $2-x, 2-y, 1-z$ .

Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.003$	$(\Delta/\sigma)_{\text{max}} = 0.003$
2886 reflections	$\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$
211 parameters	$\Delta\rho_{\text{min}} = -0.45 \text{ e } \text{\AA}^{-3}$

Table 5

Torsion angles ( $^\circ$ ).

	(III)	(IVa)	(IVb)	(IVb)	(V)
			Molecule 1	Molecule 2	
C2—C1—C11—O11	124.7 (3)	105.94 (17)	114.75 (17)	128.70 (17)	119.7 (6)
C2—C1—C11—O12	-61.3 (3)	-73.11 (16)	-65.44 (17)	-54.89 (18)	-61.3 (5)
C1—C2—C21—O21	-29.4 (4)	-41.7 (2)	-69.4 (2)	-44.7 (2)	-50.9 (7)
C1—C2—C21—O22	154.0 (3)	138.93 (14)	109.20 (16)	134.35 (14)	127.9 (5)

The C and O atoms of the disordered solvent in (II) were refined isotropically. All H atoms on C atoms, except those of the disordered solvent in (II), were located by difference Fourier synthesis and were refined with fixed individual displacement parameters [ $U(H) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$  or  $U(H) = 1.2U_{\text{eq}}(\text{C})$ ] using a riding model with aromatic C—H = 0.95  $\text{\AA}$ , methyl C—H = 0.98  $\text{\AA}$ , secondary C—H = 0.99  $\text{\AA}$  and tertiary C—H = 1.00  $\text{\AA}$ . The hydroxyl H atoms of (IVa), (IVb) and (V) were refined isotropically, whereas the hydroxyl H atoms in (III) were refined with fixed individual displacement parameters [ $U(H) = 1.2U_{\text{eq}}(\text{O})$ ] using a riding model with O—H = 0.84  $\text{\AA}$  and allowing the OH groups to rotate about the C—O axis. The absolute structure of (I) could not be determined reliably [Flack (1983) parameter 0.3 (13)].

For all compounds, data collection: SMART (Siemens, 1995); cell refinement: SMART; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1412). Services for accessing these data are described at the back of the journal.

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