

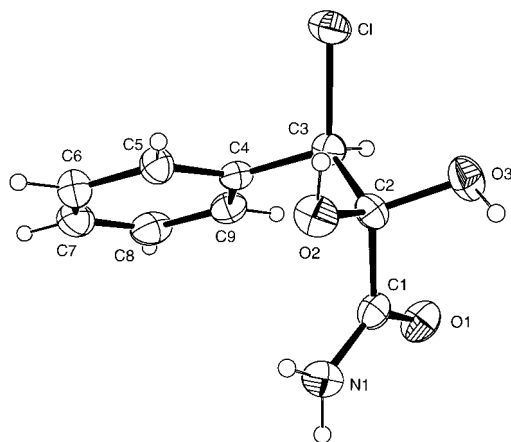
**Figure 3**  
ORTEP (Burnett & Johnson, 1996) view of (III) with atomic numbering. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms are of arbitrary size.

adjacent molecules are connected by two N—H...O bonds symmetry-related by an inversion centre. Another type of intermolecular N—H...O hydrogen bond is involved in the chain formation of stacked molecule pairs propagated down the *a* axis.

The molecular structure of compound (II) is illustrated in Fig. 2. Bond lengths and angles are in agreement with values reported for other organic compounds (Allen *et al.*, 1987). Two intermolecular hydrogen bonds are formed in the crystal. N1 acts as a donor to the N atom of the cyano group N2 at (*x* − 1, *y*, *z* − 1) while the hydroxyl O atom acts as a donor to the amide oxygen O1 at (1 + *x*, *y*, *z*).

The molecular structure of compound (III) is presented in Fig. 3. Distances and angles are typical for organic structures, except for the C3—Br distance, 1.995 (4) Å, which is longer than the upper quartile of *Csp*<sup>3</sup>—Br bond lengths for reported structures (Allen *et al.*, 1987). As expected, the crystal structure is dominated by hydrogen-bond interactions of amide–amide type. Molecules are linked *via* head-to-head amide–amide hydrogen bonds similar to those of compound (I) which form pairs of molecules [N1 acts as a donor to O1 at (−*x* + 1, −*y* + 1, −*z* + 1)] connected in infinite chains along *c* by an additional amide–amide hydrogen bond [N1 as donor to O1 at (*x*, −*y* + 1, *z* +  $\frac{1}{2}$ )].

The crystal structure of compound (IV) is depicted in Fig. 4. The geometry about the C2 atom is close to tetrahedral with the slight expansion of the O2—C2—O3 angle to 112.33 (15)°.



**Figure 4**  
ORTEP (Burnett & Johnson, 1996) view of (IV) with atomic numbering. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms are of arbitrary size.

This distortion from regular tetrahedron could be the result of the repulsion of the lone-pair electrons of the hydroxyl O atoms. A survey of the CSD (Allen & Kennard, 1993) gave only 12 structures of geminal diols for which the parent *Csp*<sup>3</sup> atom is not a part of a cyclic system. A similar deformation of the O—C—O angle was observed in most cases. Both hydroxyl groups are involved in hydrogen bonds. Molecules are linked together in infinite chains parallel to the [001] direction with two additional intermolecular hydrogen bonds; O2 acts as a donor to the hydroxyl O1 atom of a neighbouring molecule at (*x*, *y*, *z* + 1), while O3 acts as a donor to O1 at (*x*, −*y*, *z* +  $\frac{1}{2}$ ).

## Experimental

The oxirane (I) was prepared by selective hydrolysis of dicyano-oxirane as described by Majcen-Le Maréchal *et al.* (1994). The cyanohydrin (II) and the pyruvamide (III) were obtained according to a procedure of Majcen-Le Maréchal *et al.* (1994). The stable  $\alpha$ -diol was prepared by heating the corresponding pyruvamide (1.0 mmol) in water (10 ml) for 45 min at 333 K. After cooling, the solvent was partially removed *in vacuo*. The product was filtered off, washed with water and dried. Crystals of all four compounds suitable for single-crystal X-ray diffraction were selected directly from the analytical samples. Unfortunately, it was impossible to obtain suitable crystals of all products from the same starting material. Compounds (II) to (IV) have different substituents on the phenyl ring and contain different halogens, but all were prepared by the same synthesis scheme.

## Compound (I)

### Crystal data

C<sub>10</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 222.63  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 4.9992 (8) Å  
*b* = 12.694 (3) Å  
*c* = 16.442 (3) Å  
 $\beta$  = 93.540 (10)°  
*V* = 1041.4 (4) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.420 Mg m<sup>−3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 10–15°  
 $\mu$  = 0.346 mm<sup>−1</sup>  
*T* = 293 (2) K  
 Prismatic, colourless  
 0.30 × 0.30 × 0.25 mm

**Table 1**

Selected geometric parameters (Å, °) for (I).

N1—C1	1.318 (2)	C3—C4	1.487 (3)
C1—O1	1.226 (2)	C4—C5	1.386 (3)
C1—C2	1.508 (2)	C4—C9	1.391 (3)
C2—O2	1.422 (2)	C5—C6	1.389 (3)
C2—C10	1.459 (2)	C6—C7	1.381 (3)
C2—C3	1.491 (3)	C7—C8	1.373 (3)
C10—N2	1.132 (3)	C7—Cl	1.745 (2)
C3—O2	1.434 (2)	C8—C9	1.384 (3)
O1—C1—N1	125.49 (17)	C4—C3—C2	121.88 (16)
O1—C1—C2	118.63 (14)	C2—O2—C3	62.96 (11)
N1—C1—C2	115.87 (15)	C5—C4—C9	119.63 (18)
O2—C2—C10	116.49 (15)	C5—C4—C3	119.20 (17)
O2—C2—C3	58.89 (11)	C9—C4—C3	121.16 (18)
C10—C2—C3	119.11 (15)	C4—C5—C6	120.31 (19)
O2—C2—C1	117.53 (13)	C7—C6—C5	118.9 (2)
C10—C2—C1	114.35 (15)	C8—C7—C6	121.66 (19)
C3—C2—C1	119.31 (15)	C8—C7—Cl	118.78 (17)
N2—C10—C2	178.5 (2)	C6—C7—C1	119.51 (17)
O2—C3—C4	117.63 (16)	C7—C8—C9	119.3 (2)
O2—C3—C2	58.15 (11)	C8—C9—C4	120.2 (2)

**Table 2**  
Hydrogen-bonding geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H2...O1 <sup>i</sup>	0.86	2.34	2.911 (2)	124.0
N1—H1...O1 <sup>ii</sup>	0.86	2.04	2.903 (2)	178.2

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

**Data collection**

Stadi4 diffractometer	$h = -6 \rightarrow 6$
$\omega/2\theta$ scans	$k = -16 \rightarrow 15$
3492 measured reflections	$l = -22 \rightarrow 21$
2533 independent reflections	3 standard reflections
1852 reflections with $I > 2\sigma(I)$	every 300 reflections
$R_{\text{int}} = 0.025$	intensity decay: 0.8%
$\theta_{\text{max}} = 28^\circ$	

**Refinement**

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{Å}^{-3}$
$wR(F^2) = 0.152$	$\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{Å}^{-3}$
$S = 1.032$	Extinction correction: <i>SHELXL97</i>
2533 reflections	(Sheldrick, 1997)
147 parameters	Extinction coefficient: 0.061 (6)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2 + 0.2445P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

**Compound (II)**

**Crystal data**

$\text{C}_{11}\text{H}_{11}\text{BrN}_2\text{O}_2$	$D_x = 1.595 \text{ Mg m}^{-3}$
$M_r = 283.13$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 25 reflections
$a = 5.934 (3) \text{ Å}$	$\theta = 8-16^\circ$
$b = 33.653 (6) \text{ Å}$	$\mu = 3.474 \text{ mm}^{-1}$
$c = 6.1770 (10) \text{ Å}$	$T = 293 (2) \text{ K}$
$\beta = 107.12 (3)^\circ$	Prismatic, colourless
$V = 1178.9 (7) \text{ Å}^3$	$0.12 \times 0.10 \times 0.05 \text{ mm}$
$Z = 4$	

**Table 3**  
Selected geometric parameters (Å, °) for (II).

N1—C1	1.308 (4)	C3—Br	1.975 (3)
C1—O1	1.221 (4)	C4—C5	1.386 (4)
C1—C2	1.547 (4)	C4—C9	1.388 (4)
C2—O2	1.390 (3)	C5—C6	1.390 (5)
C2—C10	1.486 (4)	C6—C7	1.390 (5)
C2—C3	1.548 (4)	C7—C8	1.377 (5)
C10—N2	1.136 (4)	C7—C11	1.502 (5)
C3—C4	1.501 (4)	C8—C9	1.380 (5)
O1—C1—N1	126.3 (3)	C2—C3—Br	108.98 (18)
O1—C1—C2	118.4 (3)	C5—C4—C9	118.3 (3)
N1—C1—C2	115.2 (3)	C5—C4—C3	123.5 (3)
O2—C2—C10	111.2 (2)	C9—C4—C3	118.2 (2)
O2—C2—C1	109.3 (2)	C4—C5—C6	120.3 (3)
C10—C2—C1	106.7 (2)	C7—C6—C5	121.3 (3)
O2—C2—C3	114.8 (2)	C8—C7—C6	117.7 (3)
C10—C2—C3	108.6 (2)	C8—C7—C11	121.0 (3)
C1—C2—C3	105.9 (2)	C6—C7—C11	121.3 (3)
N2—C10—C2	177.6 (3)	C7—C8—C9	121.5 (3)
C4—C3—C2	115.1 (2)	C8—C9—C4	120.9 (3)
C4—C3—Br	110.67 (19)		

**Table 4**  
Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H2A...N2 <sup>i</sup>	0.86	2.41	3.269 (5)	172.8
O2—H1...O1 <sup>ii</sup>	0.82	1.87	2.677 (3)	165.8

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

**Data collection**

Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.077$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.91^\circ$
Absorption correction: refined from $\Delta F$ (Walker & Stuart, 1983)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.631, T_{\text{max}} = 0.855$	$k = -44 \rightarrow 44$
11 169 measured reflections	$l = -8 \rightarrow 8$
2836 independent reflections	3 standard reflections
1851 reflections with $I > 2\sigma(I)$	every 500 reflections
	intensity decay: 1.9%

**Refinement**

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.971$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2836 reflections	$\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$
146 parameters	$\Delta\rho_{\text{min}} = -0.51 \text{ e } \text{Å}^{-3}$

**Compound (III)**

**Crystal data**

$\text{C}_{10}\text{H}_{10}\text{BrNO}_2$	$D_x = 1.594 \text{ Mg m}^{-3}$
$M_r = 256.10$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3833 reflections
$a = 22.614 (5) \text{ Å}$	$\theta = 2.83-26.0^\circ$
$b = 10.257 (2) \text{ Å}$	$\mu = 3.825 \text{ mm}^{-1}$
$c = 10.099 (2) \text{ Å}$	$T = 293 (2) \text{ K}$
$\beta = 114.32 (3)^\circ$	Prismatic, colourless
$V = 2134.6 (8) \text{ Å}^3$	$0.22 \times 0.20 \times 0.20 \text{ mm}$
$Z = 8$	

**Data collection**

Nonius KappaCCD diffractometer	$\theta_{\text{max}} = 26^\circ$
$1^\circ \varphi$ and $\omega$ scans	$h = -27 \rightarrow 27$
3833 measured reflections	$k = -12 \rightarrow 12$
1966 independent reflections	$l = -10 \rightarrow 10$
1372 reflections with $I > 2\sigma(I)$	Intensity decay: 1.1%
$R_{\text{int}} = 0.021$	

**Table 5**  
Selected geometric parameters (Å, °) for (III).

Br—C3	1.995 (4)	C4—C5	1.379 (5)
O2—C2	1.212 (4)	C4—C9	1.399 (5)
O1—C1	1.225 (4)	C5—C6	1.381 (6)
N1—C1	1.322 (4)	C6—C7	1.366 (6)
C1—C2	1.526 (5)	C7—C8	1.384 (7)
C2—C3	1.500 (5)	C7—C11	1.510 (6)
C3—C4	1.485 (5)	C8—C9	1.380 (6)
O1—C1—N1	124.4 (3)	C3—C2—C1	116.5 (3)
O1—C1—C2	121.1 (3)	C4—C3—Br	118.7 (3)
N1—C1—C2	114.5 (3)	C4—C3—Br	110.0 (3)
O2—C2—C3	123.8 (3)	C2—C3—Br	101.2 (2)
O2—C2—C1	119.6 (3)	C5—C4—C3	119.8 (3)

**Table 6**  
Hydrogen-bonding geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H2...O1 <sup>i</sup>	0.86	2.11	2.885 (4)	148.9
N1—H1...O1 <sup>ii</sup>	0.86	2.13	2.988 (4)	173.4

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

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 0.973$	$\Delta\rho_{\max} = 0.64 \text{ e } \text{Å}^{-3}$
1966 reflections	$\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$
139 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0038 (6)

**Compound (IV)****Crystal data**

$C_9H_{10}ClNO_3$	$D_x = 1.515 \text{ Mg m}^{-3}$
$M_r = 215.63$	Mo $K\alpha$ radiation
Monoclinic, $Cc$	Cell parameters from 1798 reflections
$a = 5.5260 (10) \text{ Å}$	$\theta = 2.72\text{--}25.99^\circ$
$b = 29.989 (6) \text{ Å}$	$\mu = 0.383 \text{ mm}^{-1}$
$c = 5.9970 (10) \text{ Å}$	$T = 293 (2) \text{ K}$
$\beta = 107.96 (3)^\circ$	Prismatic, colourless
$V = 945.4 (3) \text{ Å}^3$	$0.40 \times 0.35 \times 0.25 \text{ mm}$
$Z = 4$	

**Data collection**

Nonius KappaCCD diffractometer	$\theta_{\max} = 25.99^\circ$
$1^\circ \varphi$ and $\omega$ scans	$h = -6 \rightarrow 6$
1798 measured reflections	$k = -36 \rightarrow 36$
1781 independent reflections	$l = -7 \rightarrow 7$
1550 reflections with $I > 2\sigma(I)$	Intensity decay: 1.7%
$R_{\text{int}} = 0.023$	

**Refinement**

Refinement on $F^2$	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
$wR(F^2) = 0.063$	$\Delta\rho_{\min} = -0.16 \text{ e } \text{Å}^{-3}$
$S = 1.006$	Extinction correction: <i>SHELXL97</i>
1781 reflections	(Sheldrick, 1997)
137 parameters	Extinction coefficient: 0.024 (2)
H-atom parameters constrained	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2]$	Flack parameter = 0.50 (5)
where $P = (F_o^2 + 2F_c^2)/3$	

**Table 7**  
Selected geometric parameters (Å, °) for (IV).

Cl—C3	1.7987 (19)	N1—C1	1.308 (3)
O2—C2	1.390 (2)	C3—C2	1.539 (3)
O1—C1	1.235 (2)	C2—C1	1.544 (3)
C4—C5	1.386 (3)	C9—C8	1.381 (3)
C4—C9	1.388 (3)	C5—C6	1.378 (3)
C4—C3	1.503 (3)	C8—C7	1.375 (3)
O3—C2	1.404 (2)	C7—C6	1.369 (4)
C4—C3—C2	115.30 (17)	C8—C9—C4	120.4 (2)
C4—C3—Cl	109.99 (13)	C6—C5—C4	120.6 (2)
C2—C3—Cl	109.04 (13)	O1—C1—N1	124.6 (2)
O2—C2—O3	112.33 (15)	O1—C1—C2	118.62 (17)
O2—C2—C3	113.66 (16)	N1—C1—C2	116.80 (19)
O3—C2—C3	107.19 (15)	C7—C8—C9	120.0 (2)
O2—C2—C1	107.17 (15)	C6—C7—C8	120.1 (2)
O3—C2—C1	109.50 (16)	C7—C6—C5	120.2 (2)
C3—C2—C1	106.81 (15)		

**Table 8**  
Hydrogen-bonding geometry (Å, °) for (IV).

D—H...A	D—H	H...A	D...A	D—H...A
O2—H21...O1 <sup>i</sup>	0.82	1.99	2.789 (2)	163.4
O3—H31...O1 <sup>ii</sup>	0.82	1.99	2.809 (2)	171.9

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

The space groups were deduced from the systematic absences and intensity statistics. H atoms were placed at calculated positions and refined as riding atoms (C—H = 0.93–0.98 Å, for each compound). For compound (IV), 941 independent reflections together with 840 Friedel equivalents were measured. The value of the Flack (1983) parameter [0.50 (5)] indicates racemic twinning of the crystal.

For compound (I), data collection and cell refinement: *DIF4* (Stoe, 1992); data reduction: *REDU4* (Stoe, 1992). For compound (II), data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *PARAM* (Stewart *et al.*, 1976); data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989). For compounds (III) and (IV), data collection: *COLLECT* (Nonius, 1998); cell refinement and data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1105). Services for accessing these data are described at the back of the journal.

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