# Carbonyl–carbonyl, carbonyl–π and carbonyl–halogen dipolar interactions as the directing motifs of the supramolecular structure of ethyl 6-chloro-2-oxo-2H-chromene-3-carboxylate and ethyl 6-bromo-2-oxo-2H-chromene-3-carboxylate

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The title compounds, $C_{12}H_9ClO_4$, (I), and $C_{12}H_9BrO_4$, (II), are isomorphous and crystallize in the monoclinic space group $P2_1/c$. Both compounds present an *anti* conformation between the 3-carboxy and the lactone carbonyl groups. Both carbonyl groups are out of the plane defined by the remaining chromene atoms, by 8.37 (6) and 17.57 (6)° for (I), and by 9.07 (8) and 18.96 (18)° for (II), owing to their involvement in intermolecular interactions. In both compounds, layers of centrosymmetric hydrogen-bonded dimers are developed in the $[\bar{5}\,\bar{2}\,22]$ plane through C—H···O interactions, involving both carbonyl groups as acceptors. Two families of dimers stack through C=O···C=O, C=O···π and C—X···C=O (X = Cl and Br) dipolar interactions, as well as a C—H···π interaction, developing the three-dimensional structure along the *c* axis.

## Comment

Coumarins have demonstrated a great variety of biological properties as anti-inflamatories (Kontogiorgis & Hadjipavlou-Litina, 2005), antibacterials (Gursoy & Karali, 2003) and antihelmintics (de Marchi *et al.*, 2004). They have been proposed in HIV (Lee & Morris, 1999) and cancer (Lacy & O'Kennedy, 2004) treatment, as well as being inhibitors of monoaminooxidase (Chimenti *et al.*, 2004; Santana *et al.*, 2006). Non-covalent interactions are involved in most of the molecular recognition processes. Particularly, hydrogen

bonding and π-stacking interactions are responsible for the self-association of coumarin derivatives in the solid state (Magaña-Vergara *et al.*, 2004; García-Báez *et al.*, 2003). Following on from these studies, we report here the molecular and supramolecular structures of the isostructural ethyl 6-chloro- and 6-bromo-2-oxo-1*H*-benzopyran-3-carboxylates, *viz.* (I) and (II), respectively.



(I)  $X$=Cl
(II)  $X$=Br
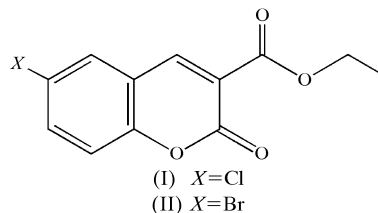
The title compounds are isomorphous; they crystallize in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular structures of (I) and (II) are shown in Figs. 1 and 2, and selected bond lengths and angles are listed in Tables 1 and 3, respectively. The geometric parameters of the coumarin ring are comparable to those reported for similar structures retrieved from the Cambridge Structural Database (Version of May 2005; Allen, 2002). Most of the bond distances and angles in (I) and (II) are very similar to the values reported for the isomorphic ethyl coumarin-3-carboxylate, (III) (García-Báez *et al.*, 2003), except for the O1—C9 bond length, which is slightly shorter; the mean value is 1.366 (2) Å for (I) and (II), compared with 1.377 (2) Å in (III). This is probably due to the inductive negative effect of the halogen atom on the lactone O atom (O1) lone pair of electrons. Compounds (I) and (II) present an *anti* conformation between the 3-carboxy and the lactone carbonyl groups, in contrast to the previously reported *syn* arrangement in (III). In both title molecules, the lactone and the carboxylate carbonyl groups are out of the plane defined by atoms O1/C3–C10 by 8.37 (6) and 17.57 (6)°, respectively, for (I), and by 9.07 (8) and 18.96 (18)°, respectively, for (II). The above-mentioned carbonyl deviations from planarity seem to be related to intermolecular interactions. It is interesting to note that the replacement of Cl by Br does not alter the molecular packing.

In the crystal structures of compounds (I) and (II), hydrogen-bonded dimers are formed by self-complementary interactions involving the carboxylate carbonyl O atom as a
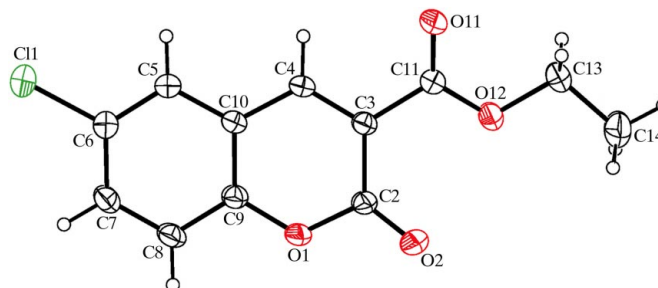


**Figure 1**
The molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level.

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hydrogen-bond acceptor, and the C4—H4 and C5—H5 groups as hydrogen-bond donors (Tables 2 and 4), so defining an $R_2^2(14)[R_2^1(6)]$ motif (Bernstein *et al.*, 1995). This dimer, which lies in the family of planes [$\bar{3}$ 3 14], is hydrogen bonded to another dimer lying in the family of planes [$\bar{3}$ $\bar{3}$ 14], through two C—H···O interactions (C7···O2$^{ii}$ and C8···O2$^{ii}$; the symmetry code is as in Tables 2 and 4), to form an $R_2^1(5)$ motif. The hydrogen-bonding motifs are shown in Fig. 3 for compound (I). Thus, layers of centrosymmetric hydrogen-bonded dimers are developed in the [$\bar{5}$ $\bar{2}$ 22] plane.

In both compounds, the two families of dimers stack through C=O···C=O, C=O···$\pi$ and C—Cl···C=O dipolar interactions to develop the third dimension (Fig. 4). In the absence of strong hydrogen-bonding donors, carbonyl dipolar interactions are strong enough to direct the crystal packing of both isomorphs. Two self-complementary sheared parallel C=O···C=O interactions (Allen *et al.*, 1998) form a stacked
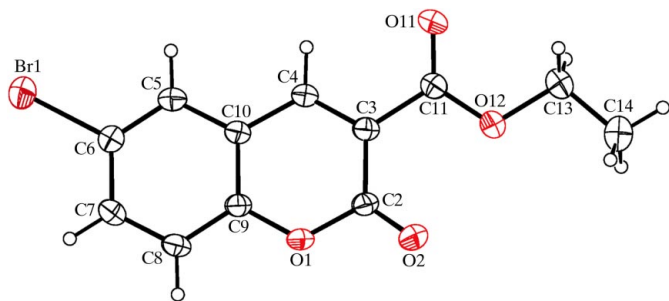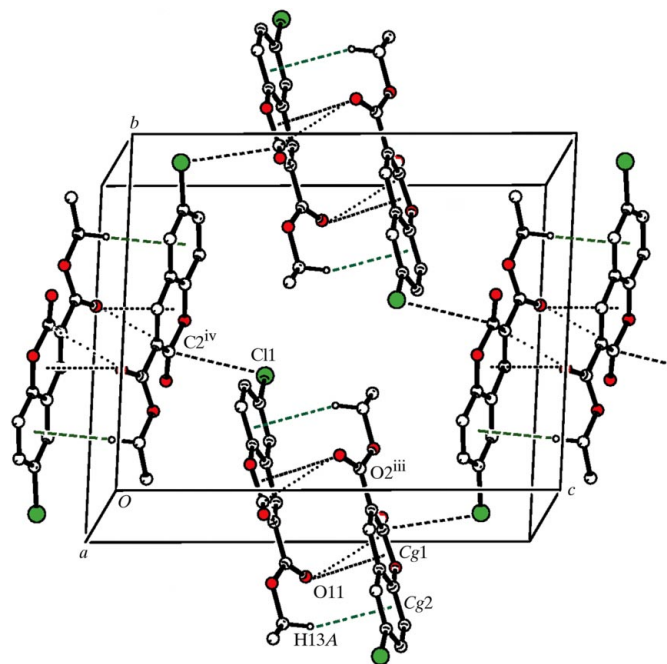


**Figure 2**
The molecular structure of (II), showing the atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level.

centrosymmetric dimer [O11···C2$^{iii}$ = 3.130 (2) Å, C11=O11···C2$^{iii}$ = 108.9 (1)° and C11···O2=C2 = 55.1 (1)° for (I); O11···C2$^{iii}$ = 3.130 (3) Å, C11=O11···C2$^{iii}$ = 109.0 (2)° and C11···O2=C2 = 55.5 (2)° for (II); symmetry code: (iii) $-x + 1$, $-y$, $-z + 1$]. In this interaction, the 3-carboxy carbonyl group acts as the donor and the lactone carbonyl group as the acceptor of electronic density. The former carbonyl group and the lactone ring (centroid $Cg1$) are almost parallel [C11=O11···$Cg1^{iii}$ = 96.5 (1) and 96.8 (2)° for (I) and (II), respectively], and are separated by 3.034 (3) Å in (I) and 3.035 (2) Å in (II). This gives rise to the interaction of the lone pair of atom O11 with the electron-deficient lactone ring (García-Báez *et al.*, 2003). This type of interaction has also been observed for 4-chloro-3-nitrocoumarin (Fujii *et al.*, 2005).

A weak Csp$^3$—H···$\pi$ interaction (Umezawa *et al.*, 1998) complements the packing [C13···$Cg2^{iii}$ = 3.787 (2) Å for (I) and 3.833 (3) Å for (II), and C13—H13A···$Cg2^{iii}$ = 150.8 (2)° for (I) and 150.3 (3)° for (II); $Cg2$ is the centroid of the benzene ring]. This set of stacked dimers lying in the family of planes [$\bar{3}$ 3 14] is linked to the set of stacked dimers lying in the family of planes [$\bar{3}$ $\bar{3}$ 14] through dipolar C—Cl($\delta-$)···C($\delta+$)=O interactions [Cl1···C2$^{iv}$ = 3.456 (2) Å and C11—Cl1···C2$^{iv}$ = 95.8 (1)° for (I); Br1···C2$^{iv}$ = 3.516 (3) Å and C11—Br1···C2$^{iv}$ = 95.5 (2)° for (II); symmetry code: (iv) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$]. This interaction shows distances below the sum of the van der Waals radii of the halogen and C atoms (C = 1.70 Å, Cl = 1.80 Å and Br = 1.90 Å; Bondi, 1964), with an almost perpendicular arrangement between the donor and the acceptor groups, in agreement with the side-on geometry
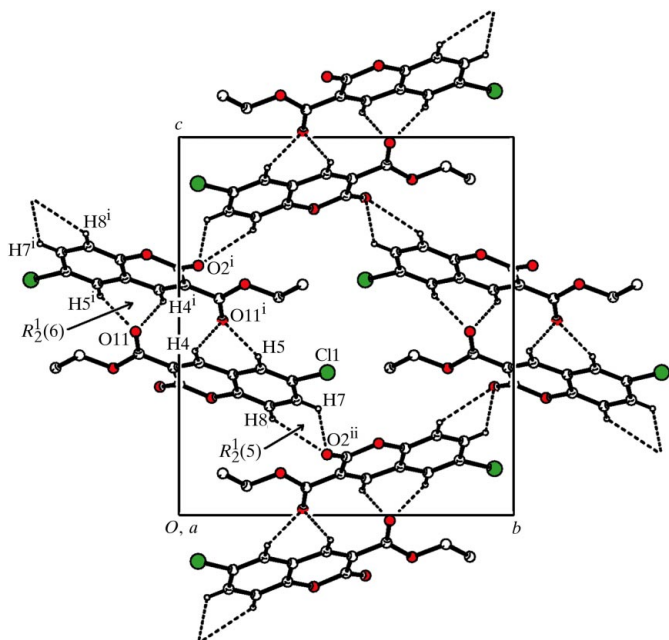


**Figure 3**
Layers of centrosymmetric hydrogen-bonded dimers of (I), viewed in the *ab* plane. $R_2^2(14)[R_2^1(6)]$ and $R_2^1(5)$ motifs are shown. Some H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 2$, $-y$, $-z + 1$; (ii) $-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$.]



**Figure 4**
The stacking arrangement of (I), in centrosymmetric pairs, viewed along the *c* axis. C11=O11···C2=O2, C11=O11···$Cg1$ and C6—*X*···C2=O2 (*X* = Cl and Br) dipolar interactions, as well as C13—H13A···$Cg2$ interactions, combine to develop the third dimension along the *c* axis. [Symmetry codes: (iii) $-x + 1$, $-y$, $-z + 1$; (iv) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$.]

proposed for C—X···E interactions (X = halogen and E = electrophile; Lommerse et al., 1996; Bosch & Barnes, 2002) and in contrast to the head-on geometry proposed for C—X···Nu (X = halogen and Nu = nucleophile) interactions (Ouvrard et al., 2003; Auffinger et al., 2004).

As a consequence of the above-mentioned group of interactions, a block of zigzag centrosymmetric pairs of dimers stacking along the c-axis direction is formed. The C3···C4$^{iii}$ distances of 3.602 (3) and 3.592 (4) Å for (I) and (II), respectively, are in the expected range for photochemical dimerization (Gnanaguru et al., 1985). Thus, further studies on the photoreactivity of compounds (I) and (II) are currently being carried out.

## Experimental

Compounds (I) and (II) were synthesized as reported by Bonsignore et al. (1995), starting from 5-chloro- or 5-bromosalicylaldehyde with diethyl malonate in equimolar amounts. All reagents were purchased from Aldrich. Crystals suitable for X-ray analysis were obtained by recrystallization from ethanol. For compound (I) (m.p. 440 K), FT–IR ($\nu$, cm$^{-1}$): 1743, 1700 (C=O); $^1$H NMR (DMSO-$d_6$): $\delta$ 8.72 (s, 1H, H-4), 8.06 (d, 1H, H-5), 7.78 (dd, 1H, H-7), 7.48 (d, 1H, H-8), 4.3 (q, 2H, OCH$_2$), 1.31 (t, 3H, CH$_3$); $^{13}$C NMR (DMSO-$d_6$): $\delta$ 155.4 (C2), 118.6 (C3), 147.3 (C4), 129.0 (C5), 128.3 (C6), 133.7 (C7), 118.2 (C8), 153.3 (C9), 119.1 (C10), 162.2 (C11), 61.3 (C13), 13.9 (C14). For compound (II) (m.p. 445 K), FT–IR ($\nu$, cm$^{-1}$): 1743, 1718 (C=O); $^1$H NMR (CDCl$_3$): $\delta$ 8.42 (s, 1H, H-4), 7.69 (d, 1H, H-5), 7.73 (dd, 1H, H-7), 7.23 (d, 1H, H-8), 4.4 (q, 2H, OCH$_2$), 1.39 (t, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$): $\delta$ 155.9 (C2), 117.3 (C3), 147.0 (C4), 131.4 (C5), 119.3 (C6), 136.8 (C7), 118.4 (C8), 153.8 (C9), 119.2 (C10), 162.5 (C11), 62.1 (C13), 14.0 (C14).

## Compound (I)

### Crystal data

| | |
|---|---|
| C$_{12}$H$_9$ClO$_4$ | V = 1119.83 (17) Å$^3$ |
| $M_r$ = 252.64 | Z = 4 |
| Monoclinic, P2$_1$/c | Mo K$\alpha$ radiation |
| a = 5.7982 (5) Å | $\mu$ = 0.34 mm$^{-1}$ |
| b = 13.0702 (12) Å | T = 293 (2) K |
| c = 15.5540 (12) Å | 0.20 × 0.18 × 0.14 mm |
| $\beta$ = 108.191 (3)° | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 8206 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 2615 independent reflections |
| | 2310 reflections with I > 2$\sigma$(I) |
| $T_{min}$ = 0.935, $T_{max}$ = 0.954 | $R_{int}$ = 0.024 |

### Table 1
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| Cl1—C6 | 1.736 (2) | O11—C11 | 1.200 (3) |
| O1—C2 | 1.382 (2) | C2—C3 | 1.470 (3) |
| O1—C9 | 1.366 (2) | C3—C4 | 1.342 (3) |
| O2—C2 | 1.188 (2) | | |
| | | | |
| C2—O1—C9 | 122.98 (15) | O11—C11—O12 | 124.10 (18) |
| O1—C2—C3 | 115.78 (15) | O11—C11—C3 | 121.72 (17) |
| C3—C4—C10 | 121.38 (17) | O12—C11—C3 | 114.18 (16) |
| Cl1—C6—C5 | 119.20 (17) | | |
| | | | |
| O2—C2—C3—C11 | 5.4 (3) | C2—C3—C11—O11 | −156.44 (19) |

## Refinement

| | |
|---|---|
| R[F$^2$ > 2$\sigma$(F$^2$)] = 0.055 | 155 parameters |
| wR(F$^2$) = 0.155 | H-atom parameters constrained |
| S = 1.08 | $\Delta\rho_{max}$ = 0.34 e Å$^{-3}$ |
| 2615 reflections | $\Delta\rho_{min}$ = −0.32 e Å$^{-3}$ |

### Table 2
Hydrogen-bond geometry (Å, °) for (I).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C4—H4···O11$^i$ | 0.93 | 2.54 | 3.346 (3) | 145 |
| C5—H5···O11$^i$ | 0.93 | 2.43 | 3.263 (3) | 149 |
| C7—H7···O2$^{ii}$ | 0.93 | 2.59 | 3.182 (3) | 122 |
| C8—H8···O2$^{ii}$ | 0.93 | 2.59 | 3.182 (3) | 122 |

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

## Compound (II)

### Crystal data

| | |
|---|---|
| C$_{12}$H$_9$BrO$_4$ | V = 1143.0 (2) Å$^3$ |
| $M_r$ = 297.10 | Z = 4 |
| Monoclinic, P2$_1$/c | Mo K$\alpha$ radiation |
| a = 5.8432 (6) Å | $\mu$ = 3.60 mm$^{-1}$ |
| b = 13.2073 (14) Å | T = 293 (2) K |
| c = 15.6959 (15) Å | 0.26 × 0.15 × 0.12 mm |
| $\beta$ = 109.327 (3)° | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 12998 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 2754 independent reflections |
| | 2091 reflections with I > 2$\sigma$(I) |
| $T_{min}$ = 0.455, $T_{max}$ = 0.672 | $R_{int}$ = 0.041 |

### Refinement

| | |
|---|---|
| R[F$^2$ > 2$\sigma$(F$^2$)] = 0.045 | 155 parameters |
| wR(F$^2$) = 0.123 | H-atom parameters constrained |
| S = 1.05 | $\Delta\rho_{max}$ = 1.00 e Å$^{-3}$ |
| 2754 reflections | $\Delta\rho_{min}$ = −0.26 e Å$^{-3}$ |

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

| | | | |
|---|---|---|---|
| Br1—C6 | 1.888 (3) | O2—C2 | 1.189 (4) |
| O1—C2 | 1.379 (3) | O11—C11 | 1.198 (4) |
| O1—C9 | 1.366 (3) | C3—C4 | 1.341 (4) |
| | | | |
| C2—O1—C9 | 123.1 (2) | Br1—C6—C5 | 119.0 (2) |
| O1—C2—C3 | 115.6 (2) | O11—C11—O12 | 124.4 (3) |
| C3—C4—C10 | 121.3 (3) | O12—C11—C3 | 114.1 (2) |
| | | | |
| O2—C2—C3—C11 | 6.1 (5) | C2—C3—C11—O11 | −155.0 (3) |

### Table 4
Hydrogen-bond geometry (Å, °) for (II).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C4—H4···O11$^i$ | 0.93 | 2.60 | 3.394 (3) | 143 |
| C5—H5···O11$^i$ | 0.93 | 2.42 | 3.264 (4) | 151 |
| C7—H7···O2$^{ii}$ | 0.93 | 2.55 | 3.171 (4) | 125 |
| C8—H8···O2$^{ii}$ | 0.93 | 2.69 | 3.239 (3) | 119 |

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

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H atoms were included in calculated positions and refined as riding atoms. The C—H distances are in the range 0.93–0.97 Å and $U_{iso}(H)$ values were set at 1.5 or 1.2 times $U_{eq}$(parent C atom).

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *WinGX2003* (Farrugia, 1999).

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# supporting information

## Carbonyl–carbonyl, carbonyl–π and carbonyl–halogen dipolar interactions as the directing motifs of the supramolecular structure of ethyl 6-chloro-2-oxo-2*H*-chromene-3-carboxylate and ethyl 6-bromo-2-oxo-2*H*-chromene-3-carboxylate

**Rocio J. Santos-Contreras, Francisco J. Martínez-Martínez, Efrén V. García-Báez, Itzia I. Padilla-Martínez, Ana L. Peraza and Herbert Höpfl**

**Computing details**

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *WinGX2003* (Farrugia, 1999).

**(I) ethyl 6-chloro-2-oxo-2*H*-chromene-3-carboxylate**

*Crystal data*

| | |
|---|---|
| $C_{12}H_9ClO_4$ | $F(000) = 520$ |
| $M_r = 252.64$ | $D_x = 1.499$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 600 reflections |
| $a = 5.7982$ (5) Å | $\theta = 20$–25° |
| $b = 13.0702$ (12) Å | $\mu = 0.34$ mm$^{-1}$ |
| $c = 15.5540$ (12) Å | $T = 293$ K |
| $\beta = 108.191$ (3)° | Block, colorless |
| $V = 1119.83$ (17) Å$^3$ | $0.20 \times 0.18 \times 0.14$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 2615 independent reflections |
| | 2310 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.024$ |
| $\varphi$ and $\omega$ scans | $\theta_{max} = 28.3°$, $\theta_{min} = 2.1°$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -5 \rightarrow 7$ |
| | $k = -17 \rightarrow 17$ |
| $T_{min} = 0.935$, $T_{max} = 0.954$ | $l = -19 \rightarrow 20$ |
| 8206 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | 155 parameters |
| Least-squares matrix: full | 0 restraints |
| $R[F^2 > 2\sigma(F^2)] = 0.055$ | Primary atom site location: structure-invariant direct methods |
| $wR(F^2) = 0.155$ | |
| $S = 1.08$ | Secondary atom site location: difference Fourier map |
| 2615 reflections | |

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0847P)^2 + 0.376P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å$^{-3}$
$\Delta\rho_{min} = -0.32$ e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

|      | *x*         | *y*          | *z*         | $U_{iso}$*/$U_{eq}$ |
|------|-------------|--------------|-------------|---------------------|
| Cl1  | 0.83937 (11) | 0.44331 (4)  | 0.37740 (5) | 0.0658 (2)          |
| O1   | 0.1703 (2)  | 0.09721 (10) | 0.31028 (10) | 0.0463 (4)          |
| O2   | 0.0698 (3)  | −0.05735 (11) | 0.33959 (12) | 0.0576 (5)          |
| O11  | 0.7769 (3)  | −0.13011 (11) | 0.48547 (11) | 0.0560 (5)          |
| O12  | 0.4434 (3)  | −0.19667 (10) | 0.38878 (11) | 0.0531 (5)          |
| C2   | 0.2323 (3)  | 0.00067 (14) | 0.34636 (13) | 0.0407 (5)          |
| C3   | 0.4928 (3)  | −0.01738 (14) | 0.39037 (12) | 0.0373 (5)          |
| C4   | 0.6526 (3)  | 0.05987 (13) | 0.40360 (13) | 0.0389 (5)          |
| C5   | 0.7355 (3)  | 0.24450 (15) | 0.38742 (14) | 0.0437 (6)          |
| C6   | 0.6460 (4)  | 0.33847 (15) | 0.35488 (14) | 0.0446 (6)          |
| C7   | 0.4034 (4)  | 0.35195 (15) | 0.30462 (14) | 0.0476 (6)          |
| C8   | 0.2464 (4)  | 0.27051 (16) | 0.28880 (14) | 0.0477 (6)          |
| C9   | 0.3332 (3)  | 0.17570 (14) | 0.32359 (12) | 0.0395 (5)          |
| C10  | 0.5774 (3)  | 0.16098 (14) | 0.37194 (12) | 0.0383 (5)          |
| C11  | 0.5865 (3)  | −0.12015 (14) | 0.42679 (13) | 0.0398 (5)          |
| C13  | 0.5294 (4)  | −0.29786 (16) | 0.42282 (18) | 0.0587 (7)          |
| C14  | 0.3247 (6)  | −0.3694 (2)  | 0.3897 (2)  | 0.0822 (10)         |
| H4   | 0.81570     | 0.04737      | 0.43398     | 0.0466*             |
| H5   | 0.89923     | 0.23631      | 0.41938     | 0.0525*             |
| H7   | 0.34762     | 0.41621      | 0.28172     | 0.0572*             |
| H8   | 0.08401     | 0.27895      | 0.25518     | 0.0573*             |
| H13A | 0.58670     | −0.29751     | 0.48846     | 0.0705*             |
| H13B | 0.66243     | −0.31838     | 0.40127     | 0.0705*             |
| H14A | 0.27332     | −0.37099     | 0.32479     | 0.1233*             |
| H14B | 0.19238     | −0.34720     | 0.40991     | 0.1233*             |
| H14C | 0.37491     | −0.43663     | 0.41291     | 0.1233*             |

*Atomic displacement parameters (Å$^2$)*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$   | $U^{23}$   |
|-----|-----------|-----------|-----------|------------|-----------|-----------|
| Cl1 | 0.0589 (4) | 0.0426 (3) | 0.0925 (5) | −0.0088 (2) | 0.0189 (3) | 0.0069 (3) |

| | | | | | | |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0318 (7) | 0.0395 (7) | 0.0544 (8) | 0.0035 (5) | −0.0054 (6) | −0.0015 (6) |
| O2 | 0.0374 (8) | 0.0467 (9) | 0.0773 (11) | −0.0043 (6) | 0.0014 (7) | −0.0066 (7) |
| O11 | 0.0412 (8) | 0.0437 (8) | 0.0684 (10) | 0.0043 (6) | −0.0041 (7) | 0.0112 (7) |
| O12 | 0.0501 (8) | 0.0338 (7) | 0.0632 (9) | 0.0023 (6) | 0.0001 (7) | 0.0012 (6) |
| C2 | 0.0326 (9) | 0.0363 (9) | 0.0455 (10) | 0.0008 (7) | 0.0009 (7) | −0.0060 (7) |
| C3 | 0.0331 (9) | 0.0355 (9) | 0.0392 (9) | 0.0042 (7) | 0.0054 (7) | 0.0005 (7) |
| C4 | 0.0286 (8) | 0.0383 (9) | 0.0449 (10) | 0.0053 (7) | 0.0045 (7) | 0.0034 (7) |
| C5 | 0.0329 (9) | 0.0408 (10) | 0.0544 (11) | 0.0012 (7) | 0.0092 (8) | 0.0033 (8) |
| C6 | 0.0435 (10) | 0.0370 (9) | 0.0527 (11) | −0.0013 (8) | 0.0141 (9) | 0.0012 (8) |
| C7 | 0.0496 (11) | 0.0380 (10) | 0.0511 (11) | 0.0101 (8) | 0.0097 (9) | 0.0085 (8) |
| C8 | 0.0400 (10) | 0.0452 (10) | 0.0487 (10) | 0.0108 (8) | 0.0006 (8) | 0.0038 (8) |
| C9 | 0.0343 (9) | 0.0389 (9) | 0.0399 (9) | 0.0033 (7) | 0.0039 (7) | −0.0021 (7) |
| C10 | 0.0319 (9) | 0.0363 (9) | 0.0432 (9) | 0.0052 (7) | 0.0066 (7) | 0.0021 (7) |
| C11 | 0.0362 (9) | 0.0372 (9) | 0.0441 (10) | 0.0019 (7) | 0.0099 (8) | 0.0016 (7) |
| C13 | 0.0564 (13) | 0.0352 (10) | 0.0757 (15) | 0.0058 (9) | 0.0078 (11) | 0.0050 (10) |
| C14 | 0.0813 (19) | 0.0428 (13) | 0.104 (2) | −0.0090 (12) | 0.0024 (16) | 0.0001 (13) |

*Geometric parameters (Å, º)*

| | | | |
|-------------|-----------|-------------|-----------|
| Cl1—C6 | 1.736 (2) | C7—C8 | 1.372 (3) |
| O1—C2 | 1.382 (2) | C8—C9 | 1.383 (3) |
| O1—C9 | 1.366 (2) | C9—C10 | 1.394 (3) |
| O2—C2 | 1.188 (2) | C13—C14 | 1.472 (4) |
| O11—C11 | 1.200 (3) | C4—H4 | 0.9300 |
| O12—C11 | 1.316 (2) | C5—H5 | 0.9300 |
| O12—C13 | 1.454 (3) | C7—H7 | 0.9300 |
| C2—C3 | 1.470 (3) | C8—H8 | 0.9300 |
| C3—C4 | 1.342 (3) | C13—H13A | 0.9700 |
| C3—C11 | 1.493 (3) | C13—H13B | 0.9700 |
| C4—C10 | 1.430 (3) | C14—H14A | 0.9600 |
| C5—C6 | 1.368 (3) | C14—H14B | 0.9600 |
| C5—C10 | 1.397 (3) | C14—H14C | 0.9600 |
| C6—C7 | 1.391 (3) | | |
| | | | |
| Cl1···C2[i] | 3.456 (2) | C3···C11[ii] | 3.514 (3) |
| O1···O11[ii] | 3.125 (2) | C4···O2[viii] | 3.270 (3) |
| O2···C4[iii] | 3.270 (3) | C4···O11[v] | 3.346 (3) |
| O2···O12 | 2.749 (2) | C4···C11[ii] | 3.433 (3) |
| O2···C8[iv] | 3.182 (3) | C5···O11[v] | 3.263 (3) |
| O2···C7[iv] | 3.182 (3) | C7···O2[vi] | 3.182 (3) |
| O11···C4[v] | 3.346 (3) | C8···O2[vi] | 3.182 (3) |
| O11···C5[v] | 3.263 (3) | C9···O11[ii] | 3.281 (2) |
| O11···C2[ii] | 3.130 (2) | C10···C11[ii] | 3.584 (3) |
| O11···C9[ii] | 3.281 (2) | C11···C3[ii] | 3.514 (3) |
| O11···O1[ii] | 3.125 (2) | C11···C4[ii] | 3.433 (3) |
| O12···O2 | 2.749 (2) | C11···C10[ii] | 3.584 (3) |
| O1···H14A[vi] | 2.8000 | H4···O2[viii] | 2.7500 |
| O2···H7[iv] | 2.5900 | H4···O11 | 2.4900 |

| | | | |
|---|---|---|---|
| O2···H4<sup>iii</sup> | 2.7500 | H4···H5 | 2.5400 |
| O2···H8<sup>iv</sup> | 2.5900 | H4···O11<sup>v</sup> | 2.5400 |
| O11···H13B | 2.7700 | H5···H4 | 2.5400 |
| O11···H13A | 2.4600 | H5···O11<sup>v</sup> | 2.4300 |
| O11···H4<sup>v</sup> | 2.5400 | H7···O2<sup>vi</sup> | 2.5900 |
| O11···H5<sup>v</sup> | 2.4300 | H8···O2<sup>vi</sup> | 2.5900 |
| O11···H4 | 2.4900 | H13A···O11 | 2.4600 |
| C2···Cl1<sup>vii</sup> | 3.456 (2) | H13B···O11 | 2.7700 |
| C2···O11<sup>ii</sup> | 3.130 (2) | H14A···O1<sup>iv</sup> | 2.8000 |
| C3···C3<sup>ii</sup> | 3.416 (3) | | |
| | | | |
| C2—O1—C9 | 122.98 (15) | O11—C11—C3 | 121.72 (17) |
| C11—O12—C13 | 115.55 (18) | O12—C11—C3 | 114.18 (16) |
| O1—C2—O2 | 116.62 (17) | O12—C13—C14 | 107.6 (2) |
| O1—C2—C3 | 115.78 (15) | C3—C4—H4 | 119.00 |
| O2—C2—C3 | 127.59 (18) | C10—C4—H4 | 119.00 |
| C2—C3—C4 | 120.70 (17) | C6—C5—H5 | 120.00 |
| C2—C3—C11 | 121.37 (16) | C10—C5—H5 | 120.00 |
| C4—C3—C11 | 117.82 (16) | C6—C7—H7 | 120.00 |
| C3—C4—C10 | 121.38 (17) | C8—C7—H7 | 120.00 |
| C6—C5—C10 | 119.03 (18) | C7—C8—H8 | 120.00 |
| Cl1—C6—C5 | 119.20 (17) | C9—C8—H8 | 120.00 |
| Cl1—C6—C7 | 119.32 (15) | O12—C13—H13A | 110.00 |
| C5—C6—C7 | 121.48 (19) | O12—C13—H13B | 110.00 |
| C6—C7—C8 | 120.04 (19) | C14—C13—H13A | 110.00 |
| C7—C8—C9 | 119.0 (2) | C14—C13—H13B | 110.00 |
| O1—C9—C8 | 117.64 (17) | H13A—C13—H13B | 108.00 |
| O1—C9—C10 | 121.07 (16) | C13—C14—H14A | 109.00 |
| C8—C9—C10 | 121.28 (18) | C13—C14—H14B | 109.00 |
| C4—C10—C5 | 123.34 (17) | C13—C14—H14C | 109.00 |
| C4—C10—C9 | 117.55 (17) | H14A—C14—H14B | 109.00 |
| C5—C10—C9 | 119.11 (17) | H14A—C14—H14C | 110.00 |
| O11—C11—O12 | 124.10 (18) | H14B—C14—H14C | 109.00 |
| | | | |
| C9—O1—C2—O2 | 170.94 (18) | C4—C3—C11—O12 | −159.90 (18) |
| C9—O1—C2—C3 | −7.9 (2) | C3—C4—C10—C5 | 177.27 (19) |
| C2—O1—C9—C8 | −176.03 (17) | C3—C4—C10—C9 | −2.5 (3) |
| C2—O1—C9—C10 | 2.9 (3) | C10—C5—C6—Cl1 | 177.71 (15) |
| C13—O12—C11—O11 | 0.3 (3) | C10—C5—C6—C7 | −1.9 (3) |
| C13—O12—C11—C3 | −179.94 (17) | C6—C5—C10—C4 | −179.58 (19) |
| C11—O12—C13—C14 | 166.4 (2) | C6—C5—C10—C9 | 0.2 (3) |
| O1—C2—C3—C4 | 7.9 (3) | Cl1—C6—C7—C8 | −177.82 (17) |
| O1—C2—C3—C11 | −175.94 (16) | C5—C6—C7—C8 | 1.8 (3) |
| O2—C2—C3—C4 | −170.8 (2) | C6—C7—C8—C9 | 0.1 (3) |
| O2—C2—C3—C11 | 5.4 (3) | C7—C8—C9—O1 | 177.03 (18) |
| C2—C3—C4—C10 | −2.9 (3) | C7—C8—C9—C10 | −1.9 (3) |
| C11—C3—C4—C10 | −179.18 (17) | O1—C9—C10—C4 | 2.6 (3) |
| C2—C3—C11—O11 | −156.44 (19) | O1—C9—C10—C5 | −177.12 (17) |

| C2—C3—C11—O12 | 23.8 (3) | C8—C9—C10—C4 | −178.52 (18) |
| C4—C3—C11—O11 | 19.9 (3) | C8—C9—C10—C5 | 1.7 (3) |

Symmetry codes: (i) −x+1, y+1/2, −z+1/2; (ii) −x+1, −y, −z+1; (iii) x−1, y, z; (iv) −x, y−1/2, −z+1/2; (v) −x+2, −y, −z+1; (vi) −x, y+1/2, −z+1/2; (vii) −x+1, y−1/2, −z+1/2; (viii) x+1, y, z.

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
| --- | --- | --- | --- | --- |
| C4—H4···O11[v] | 0.930 | 2.54 | 3.346 (3) | 145 |
| C5—H5···O11[v] | 0.93 | 2.43 | 3.263 (3) | 149 |
| C7—H7···O2[vi] | 0.93 | 2.59 | 3.182 (3) | 122 |
| C8—H8···O2[vi] | 0.93 | 2.59 | 3.182 (3) | 122 |

Symmetry codes: (v) −x+2, −y, −z+1; (vi) −x, y+1/2, −z+1/2.

**(II) ethyl 6-bromo-2-oxo-2H-chromene-3-carboxylate**

*Crystal data*

| | |
| --- | --- |
| $C_{12}H_9BrO_4$ | $F(000) = 592$ |
| $M_r = 297.10$ | $D_x = 1.726$ Mg m⁻³ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 600 reflections |
| $a = 5.8432$ (6) Å | $\theta = 20–25°$ |
| $b = 13.2073$ (14) Å | $\mu = 3.60$ mm⁻¹ |
| $c = 15.6959$ (15) Å | $T = 293$ K |
| $\beta = 109.327$ (3)° | Block, colorless |
| $V = 1143.0$ (2) Å³ | $0.26 \times 0.15 \times 0.12$ mm |
| $Z = 4$ | |

*Data collection*

| | |
| --- | --- |
| Bruker SMART CCD area-detector diffractometer | 2754 independent reflections |
| Graphite monochromator | 2091 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.041$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $\theta_{max} = 28.3°$, $\theta_{min} = 2.1°$ |
| $T_{min} = 0.455$, $T_{max} = 0.672$ | $h = -7 \rightarrow 7$ |
| 12998 measured reflections | $k = -17 \rightarrow 17$ |
| | $l = -19 \rightarrow 20$ |

*Refinement*

| | |
| --- | --- |
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.123$ | |
| $S = 1.05$ | H-atom parameters constrained |
| 2754 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.4243P]$ |
| 155 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 1.00$ e Å⁻³ |
| | $\Delta\rho_{min} = -0.26$ e Å⁻³ |

*Special details*

**Geometry**. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

|  | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.84921 (6) | 0.44363 (2) | 0.37854 (3) | 0.0644 (1) |
| O1 | 0.1635 (3) | 0.09348 (15) | 0.31200 (14) | 0.0489 (6) |
| O2 | 0.0656 (4) | −0.05880 (16) | 0.34303 (17) | 0.0592 (8) |
| O11 | 0.7741 (4) | −0.13087 (16) | 0.48632 (15) | 0.0601 (7) |
| O12 | 0.4410 (4) | −0.19686 (15) | 0.38850 (15) | 0.0583 (7) |
| C2 | 0.2270 (5) | −0.0016 (2) | 0.34845 (18) | 0.0436 (8) |
| C3 | 0.4874 (5) | −0.0194 (2) | 0.39127 (18) | 0.0421 (8) |
| C4 | 0.6471 (5) | 0.05665 (19) | 0.40357 (19) | 0.0426 (8) |
| C5 | 0.7279 (5) | 0.2389 (2) | 0.38623 (19) | 0.0464 (9) |
| C6 | 0.6385 (5) | 0.3310 (2) | 0.35353 (19) | 0.0457 (8) |
| C7 | 0.3948 (5) | 0.3448 (2) | 0.3036 (2) | 0.0502 (9) |
| C8 | 0.2387 (5) | 0.2639 (2) | 0.2888 (2) | 0.0499 (9) |
| C9 | 0.3259 (5) | 0.1710 (2) | 0.32412 (18) | 0.0420 (8) |
| C10 | 0.5710 (5) | 0.1565 (2) | 0.37181 (18) | 0.0416 (8) |
| C11 | 0.5832 (5) | −0.1214 (2) | 0.42728 (18) | 0.0430 (8) |
| C13 | 0.5305 (7) | −0.2968 (2) | 0.4225 (3) | 0.0685 (13) |
| C14 | 0.3306 (8) | −0.3683 (3) | 0.3897 (3) | 0.0901 (18) |
| H4 | 0.81076 | 0.04410 | 0.43340 | 0.0511* |
| H5 | 0.89221 | 0.23086 | 0.41794 | 0.0557* |
| H7 | 0.33805 | 0.40823 | 0.28034 | 0.0603* |
| H8 | 0.07560 | 0.27191 | 0.25516 | 0.0599* |
| H13A | 0.59040 | −0.29646 | 0.48797 | 0.0825* |
| H13B | 0.66249 | −0.31621 | 0.40127 | 0.0825* |
| H14A | 0.28028 | −0.37168 | 0.32502 | 0.1351* |
| H14B | 0.19718 | −0.34616 | 0.40785 | 0.1351* |
| H14C | 0.38270 | −0.43405 | 0.41463 | 0.1351* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0588 (2) | 0.0472 (2) | 0.0825 (3) | −0.0078 (1) | 0.0173 (2) | 0.0027 (2) |
| O1 | 0.0340 (9) | 0.0441 (10) | 0.0536 (11) | 0.0032 (8) | −0.0058 (8) | −0.0024 (9) |
| O2 | 0.0397 (11) | 0.0512 (13) | 0.0740 (15) | −0.0034 (9) | 0.0019 (10) | −0.0045 (10) |
| O11 | 0.0449 (11) | 0.0509 (12) | 0.0683 (14) | 0.0072 (9) | −0.0031 (10) | 0.0129 (10) |
| O12 | 0.0527 (12) | 0.0367 (10) | 0.0710 (14) | 0.0037 (9) | 0.0008 (10) | 0.0016 (10) |
| C2 | 0.0365 (13) | 0.0417 (15) | 0.0433 (14) | 0.0013 (12) | 0.0008 (11) | −0.0059 (12) |

| C3 | 0.0375 (13) | 0.0419 (14) | 0.0405 (14) | 0.0033 (11) | 0.0043 (11) | −0.0006 (11) |
|----|-------------|-------------|-------------|-------------|-------------|--------------|
| C4 | 0.0321 (12) | 0.0417 (14) | 0.0478 (15) | 0.0032 (10) | 0.0050 (11) | 0.0024 (11) |
| C5 | 0.0332 (12) | 0.0496 (16) | 0.0502 (16) | 0.0023 (11) | 0.0055 (11) | 0.0030 (13) |
| C6 | 0.0431 (14) | 0.0414 (14) | 0.0496 (16) | −0.0029 (12) | 0.0114 (12) | 0.0002 (12) |
| C7 | 0.0491 (15) | 0.0426 (15) | 0.0508 (16) | 0.0093 (12) | 0.0055 (12) | 0.0076 (12) |
| C8 | 0.0391 (14) | 0.0489 (16) | 0.0500 (16) | 0.0098 (12) | −0.0011 (12) | 0.0020 (13) |
| C9 | 0.0351 (12) | 0.0410 (14) | 0.0421 (14) | 0.0036 (10) | 0.0024 (10) | −0.0043 (11) |
| C10 | 0.0348 (12) | 0.0394 (14) | 0.0442 (14) | 0.0040 (10) | 0.0043 (10) | 0.0011 (11) |
| C11 | 0.0406 (13) | 0.0414 (14) | 0.0451 (14) | 0.0029 (11) | 0.0118 (12) | 0.0031 (12) |
| C13 | 0.0594 (19) | 0.0426 (17) | 0.090 (3) | 0.0066 (14) | 0.0064 (18) | 0.0068 (17) |
| C14 | 0.081 (3) | 0.049 (2) | 0.120 (4) | −0.0077 (18) | 0.006 (3) | 0.004 (2) |

*Geometric parameters (Å, °)*

| | | | |
|----|----------|-----------|----------|
| Br1—C6 | 1.888 (3) | C7—C8 | 1.374 (4) |
| O1—C2 | 1.379 (3) | C8—C9 | 1.373 (4) |
| O1—C9 | 1.366 (3) | C9—C10 | 1.392 (4) |
| O2—C2 | 1.189 (4) | C13—C14 | 1.457 (6) |
| O11—C11 | 1.198 (4) | C4—H4 | 0.9300 |
| O12—C11 | 1.311 (3) | C5—H5 | 0.9300 |
| O12—C13 | 1.455 (4) | C7—H7 | 0.9300 |
| C2—C3 | 1.465 (4) | C8—H8 | 0.9300 |
| C3—C4 | 1.341 (4) | C13—H13A | 0.9700 |
| C3—C11 | 1.496 (4) | C13—H13B | 0.9700 |
| C4—C10 | 1.428 (4) | C14—H14A | 0.9600 |
| C5—C6 | 1.356 (4) | C14—H14B | 0.9600 |
| C5—C10 | 1.392 (4) | C14—H14C | 0.9600 |
| C6—C7 | 1.392 (4) | | |
| | | | |
| Br1···C14[i] | 3.713 (5) | C3···C4[iv] | 3.592 (4) |
| Br1···O1[ii] | 3.567 (2) | C3···C11[iv] | 3.538 (4) |
| Br1···C2[ii] | 3.516 (3) | C4···O2[ix] | 3.278 (4) |
| O1···Br1[iii] | 3.567 (2) | C4···O11[vii] | 3.394 (4) |
| O1···O11[iv] | 3.104 (3) | C4···C3[iv] | 3.592 (4) |
| O2···C4[v] | 3.278 (4) | C4···C11[iv] | 3.458 (4) |
| O2···O12 | 2.759 (3) | C5···O11[vii] | 3.264 (4) |
| O2···C8[vi] | 3.239 (4) | C7···O2[viii] | 3.171 (4) |
| O2···C7[vi] | 3.171 (4) | C8···O2[viii] | 3.239 (4) |
| O11···C4[vii] | 3.394 (4) | C9···O11[iv] | 3.260 (4) |
| O11···C5[vii] | 3.264 (4) | C10···C11[iv] | 3.585 (4) |
| O11···C2[iv] | 3.130 (3) | C11···C3[iv] | 3.538 (4) |
| O11···C9[iv] | 3.260 (4) | C11···C4[iv] | 3.458 (4) |
| O11···O1[iv] | 3.104 (3) | C11···C10[iv] | 3.585 (4) |
| O12···O2 | 2.759 (3) | C14···Br1[x] | 3.713 (5) |
| O1···H14A[viii] | 2.8100 | H4···O2[ix] | 2.7300 |
| O2···H7[vi] | 2.5500 | H4···O11 | 2.4900 |
| O2···H4[v] | 2.7300 | H4···H5 | 2.5400 |
| O2···H8[vi] | 2.6900 | H4···O11[vii] | 2.6000 |

| | | | |
|---|---|---|---|
| O11···H13B | 2.7600 | H5···H4 | 2.5400 |
| O11···H13A | 2.4400 | H5···O11vii | 2.4200 |
| O11···H4vii | 2.6000 | H7···O2viii | 2.5500 |
| O11···H5vii | 2.4200 | H8···O2viii | 2.6900 |
| O11···H4 | 2.4900 | H13A···O11 | 2.4400 |
| C2···Br1iii | 3.516 (3) | H13B···O11 | 2.7600 |
| C2···O11iv | 3.130 (3) | H14A···O1vi | 2.8100 |
| C3···C3iv | 3.406 (4) | | |
| | | | |
| C2—O1—C9 | 123.1 (2) | O11—C11—C3 | 121.5 (3) |
| C11—O12—C13 | 115.1 (3) | O12—C11—C3 | 114.1 (2) |
| O1—C2—O2 | 116.8 (3) | O12—C13—C14 | 108.0 (3) |
| O1—C2—C3 | 115.6 (2) | C3—C4—H4 | 119.00 |
| O2—C2—C3 | 127.6 (3) | C10—C4—H4 | 119.00 |
| C2—C3—C4 | 120.9 (2) | C6—C5—H5 | 120.00 |
| C2—C3—C11 | 121.3 (2) | C10—C5—H5 | 120.00 |
| C4—C3—C11 | 117.7 (3) | C6—C7—H7 | 120.00 |
| C3—C4—C10 | 121.3 (3) | C8—C7—H7 | 120.00 |
| C6—C5—C10 | 119.3 (3) | C7—C8—H8 | 120.00 |
| Br1—C6—C5 | 119.0 (2) | C9—C8—H8 | 120.00 |
| Br1—C6—C7 | 119.3 (2) | O12—C13—H13A | 110.00 |
| C5—C6—C7 | 121.7 (3) | O12—C13—H13B | 110.00 |
| C6—C7—C8 | 119.5 (3) | C14—C13—H13A | 110.00 |
| C7—C8—C9 | 119.3 (3) | C14—C13—H13B | 110.00 |
| O1—C9—C8 | 117.8 (3) | H13A—C13—H13B | 108.00 |
| O1—C9—C10 | 121.0 (2) | C13—C14—H14A | 109.00 |
| C8—C9—C10 | 121.2 (3) | C13—C14—H14B | 109.00 |
| C4—C10—C5 | 123.6 (3) | C13—C14—H14C | 109.00 |
| C4—C10—C9 | 117.4 (3) | H14A—C14—H14B | 109.00 |
| C5—C10—C9 | 119.0 (2) | H14A—C14—H14C | 110.00 |
| O11—C11—O12 | 124.4 (3) | H14B—C14—H14C | 110.00 |
| | | | |
| C9—O1—C2—O2 | 170.7 (3) | C4—C3—C11—O12 | −158.2 (3) |
| C9—O1—C2—C3 | −8.1 (4) | C3—C4—C10—C5 | 177.2 (3) |
| C2—O1—C9—C8 | −176.4 (3) | C3—C4—C10—C9 | −2.7 (4) |
| C2—O1—C9—C10 | 2.7 (4) | C10—C5—C6—Br1 | 176.9 (2) |
| C13—O12—C11—O11 | 0.2 (4) | C10—C5—C6—C7 | −1.9 (4) |
| C13—O12—C11—C3 | −180.0 (3) | C6—C5—C10—C4 | −179.9 (3) |
| C11—O12—C13—C14 | 166.1 (3) | C6—C5—C10—C9 | 0.0 (4) |
| O1—C2—C3—C4 | 8.1 (4) | Br1—C6—C7—C8 | −177.0 (2) |
| O1—C2—C3—C11 | −175.3 (2) | C5—C6—C7—C8 | 1.7 (5) |
| O2—C2—C3—C4 | −170.5 (3) | C6—C7—C8—C9 | 0.4 (4) |
| O2—C2—C3—C11 | 6.1 (5) | C7—C8—C9—O1 | 176.8 (3) |
| C2—C3—C4—C10 | −2.9 (4) | C7—C8—C9—C10 | −2.4 (4) |
| C11—C3—C4—C10 | −179.7 (3) | O1—C9—C10—C4 | 3.0 (4) |
| C2—C3—C11—O11 | −155.0 (3) | O1—C9—C10—C5 | −176.9 (3) |

| C2—C3—C11—O12 | 25.1 (4) | C8—C9—C10—C4 | −178.0 (3) |
| C4—C3—C11—O11 | 21.7 (4) | C8—C9—C10—C5 | 2.2 (4) |

Symmetry codes: (i) $x+1$, $y+1$, $z$; (ii) $-x+1$, $y+1/2$, $-z+1/2$; (iii) $-x+1$, $y-1/2$, $-z+1/2$; (iv) $-x+1$, $-y$, $-z+1$; (v) $x-1$, $y$, $z$; (vi) $-x$, $y-1/2$, $-z+1/2$; (vii) $-x+2$, $-y$, $-z+1$; (viii) $-x$, $y+1/2$, $-z+1/2$; (ix) $x+1$, $y$, $z$; (x) $x-1$, $y-1$, $z$.

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
| --- | --- | --- | --- | --- |
| C4—H4···O11[vii] | 0.93 | 2.60 | 3.394 (3) | 143 |
| C5—H5···O11[vii] | 0.93 | 2.42 | 3.264 (4) | 151 |
| C7—H7···O2[viii] | 0.93 | 2.55 | 3.171 (4) | 125 |
| C8—H8···O2[viii] | 0.93 | 2.69 | 3.239 (3) | 119 |

Symmetry codes: (vii) $-x+2$, $-y$, $-z+1$; (viii) $-x$, $y+1/2$, $-z+1/2$.