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Similarities and differences in the structures of 5-bromo-6-hydroxy-7,8-dimethylchroman-2-one and 6-hydroxy-7,8-dimethyl-5-nitrochroman-2-one

Shailesh K. Goswami, Lyall R. Hanton, C. John McAdam, Stephen C. Moratti and Jim Simpson*

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand
Correspondence e-mail: jsimpson@alkali.otago.ac.nz

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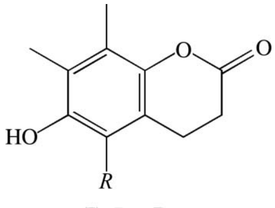
The title compounds, $C_{11}H_{11}BrO_3$, (I), and $C_{11}H_{11}NO_5$, (II), respectively, are derivatives of 6-hydroxy-5,7,8-trimethylchroman-2-one substituted at the 5-position by a Br atom in (I) and by a nitro group in (II). The pyranone rings in both molecules adopt half-chair conformations, and intramolecular O—H$\cdots$Br [in (I)] and O—H$\cdots$O$_{\rm nitro}$ [in (II)] hydrogen bonds affect the dispositions of the hydroxy groups. Classical intermolecular O—H$\cdots$O hydrogen bonds are found in both molecules but play quite dissimilar roles in the crystal structures. In (I), O—H$\cdots$O hydrogen bonds form zigzag *C*(9) chains of molecules along the *a* axis. Because of the tetragonal symmetry, similar chains also form along *b*. In (II), however, similar contacts involving an O atom of the nitro group form inversion dimers and generate $R_2^2(12)$ rings. These also result in a close intermolecular O$\cdots$O contact of 2.686 (4) Å. For (I), four additional C—H$\cdots$O hydrogen bonds combine with π–π stacking interactions between the benzene rings to build an extensive three-dimensional network with molecules stacked along the *c* axis. The packing in (II) is much simpler and centres on the inversion dimers formed through O—H$\cdots$O contacts. These dimers are stacked through additional C—H$\cdots$O hydrogen bonds, and further weak C—H$\cdots$O interactions generate a three-dimensional network of dimer stacks.

Comment

We are currently interested in polymer gel actuators and, in particular, the utilization of an electric potential as the actuation stimulus (Goswami, McAdam *et al.*, 2013). The search for suitable components for such gels leads readily to quinone-based systems, due to the accessibility and versatility of their synthetic chemistry, and their reversible redox behaviour which is tunable by variation of the quinone substituents. The synthesis of dimethylpropylquinones proceeds through a coumarin intermediate and we have previously reported the crystallographic details and intermolecular interactions of several of these (Goswami *et al.*, 2011, 2012; Cameron *et al.*, 2011).



(I) *R* = Br
(II) *R* = NO$_2$

In the course of this work, attempts to attach electron-withdrawing substituents to the dimethylpropylquinone fragment generated crystalline coumarins with bromo, (I), nitro, (II), and trifluoromethyl, (III), substituent groups at the 5-position. The structures of (I) and (II) are reported here. However, the data obtained from crystals of the trifluoromethyl derivative, 6-hydroxy-7,8-dimethyl-5-(trifluoromethyl)-chroman-2-one, (III), were not of sufficient quality to provide a definitive refinement of the structure and gave poor residuals, although the data did provide us with a connectivity map that showed all non-H atoms in the structure in reasonable locations, allowing confirmation of the proposed molecular identity. The data for (III) have been deposited with the Cambridge Structural Database [CSD (Allen, 2002); Goswami, Hanton *et al.*, 2013], but synthetic details are included here.

Compound (I) was isolated as an intermediate during the preparation of quinone monomers in a three-step process

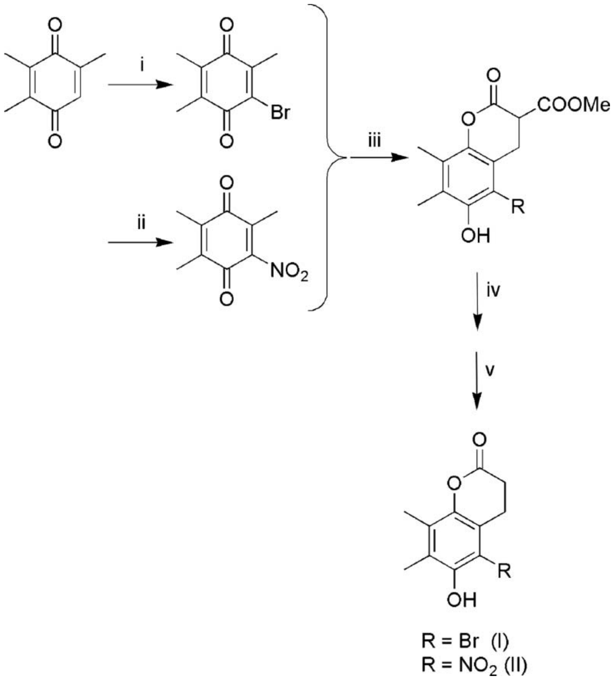


Figure 1
Reaction scheme showing the preparation of (I) and (II). Details: (i) Br_2/HOAc; (ii) HNO_3/H_2SO_4; (iii) dimethyl malonate/magnesium methoxide; (iv) dilute HCl reflux; (v) 4-methylbenzenesulfonic acid/toluene reflux.

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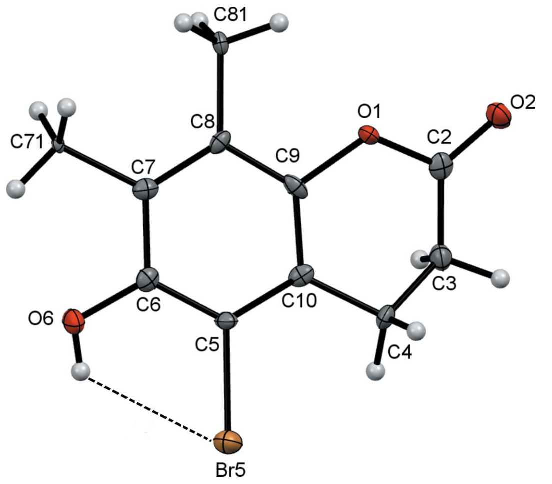

Figure 2
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is shown as a dashed line.

from trimethyl-*p*-benzoquinone (Fieser & Ardao, 1956), as described in the *Experimental* section. A reasonable yield of 5-nitro-6-hydroxy-7,8-dimethylchroman-2-one, (II), was obtained from nitrotrimethylquinone (Smith & Cutler, 1949) in a similar series of steps (Fig. 1).

Compound (I) (Fig. 2) is isomorphous with 5-chloro-6-hydroxy-7,8-dimethylchroman-2-one, (IV) (Cameron *et al.*, 2011). The unit-cell volumes of the two structures [V = 2016.1 (4) Å^3 in (I) and 1976.24 (19) Å^3 in (IV)] reveal a small but not unexpected increase for the bromo derivative. The molecular structures of (I) and (IV) are similar, with the major difference being the C5—Br5 distance which, at 1.891 (4) Å, is predictably extended from the equivalent vector observed for (IV) [1.735 (3) Å; Cameron *et al.*, 2011]. Other bond distances (Allen *et al.*, 1987) and angles in (I) are normal and similar to those found in (IV) (Cameron *et al.*, 2011) and four other related structures (Budzianowski & Katrusiak, 2002; Goswami *et al.*, 2011, 2012; Patel *et al.*, 2007) found in the CSD.

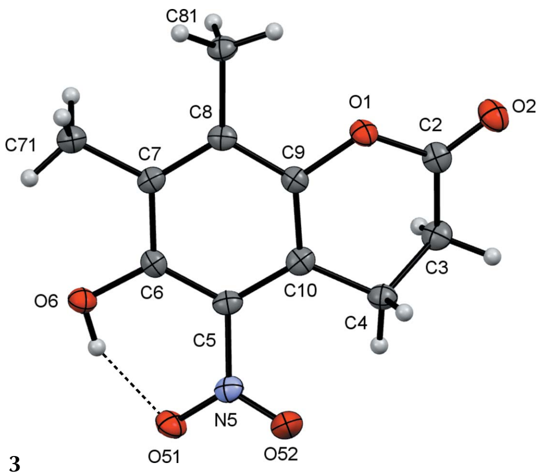

Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is shown as a dashed line.

Both structures reported here contain the archetypal 6-hydroxy-5,7,8-trimethylchroman-2-one unit (Goswami *et al.*, 2011), substituted at the 5-position by a Br atom in (I) and a nitro group in (II) (Fig. 3). Both molecules display intramolecular hydrogen bonds involving the O6 hydroxy substituents and atom Br5 in (I) or atom O51 of the nitro group in (II). These contacts generate *S*5 and *S*6 ring motifs, respectively (Bernstein *et al.*, 1995). The fused pyranone rings in both molecules adopt half-chair conformations, with the C3 methylene groups lying out of the mean planes through the remaining atoms (O1/C2/C4/C9/C10; r.m.s. deviations = 0.0759 and 0.0896 Å) by 0.485 (7) and 0.628 (3) Å in (I) and (II), respectively. The planes of the C5–C10 aromatic rings form dihedral angles of 5.8 (2) and 9.15 (14)°, respectively, with these planes. The methyl and bromo substituents lie very close to the aromatic ring plane in (I) [maximum deviation = 0.127 (6) Å for atom Br5], while the nitro substituent in (II) is inclined to the aromatic ring plane at an angle of 24.8 (3)°.

Although classical intermolecular O—H$\cdots$O hydrogen bonds are found in both molecules, they play quite dissimilar roles in the crystal structures. In (I) (Table 1), O6—H6O$\cdots$O2$^{\rm i}$ [symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$] hydrogen bonds form zigzag *C*(9) chains of molecules (Bernstein *et al.*, 1995) along the *a* axis, with similar chains generated along *b* under tetragonal symmetry. In contrast, for (II), an intramolecular O6—H6O$\cdots$O51 contact occurs generating an *S*(6) ring, while intermolecular O6—H6O$\cdots$O51$^{\rm v}$ contacts also involve this O atom of the nitro group and form inversion dimers with $R_2^2(12)$ rings (Table 2). This also imposes a close intermolecular O51$\cdots$O51$^{\rm v}$ contact of 2.686 (4) Å [symmetry code: (v) $-x-1, -y+1, -z+1$].

In the crystal structure of (I), the C3—H3$A\cdots$O2$^{\rm ii}$ [symmetry code: (ii) $-x, -y, z$] hydrogen bond links the

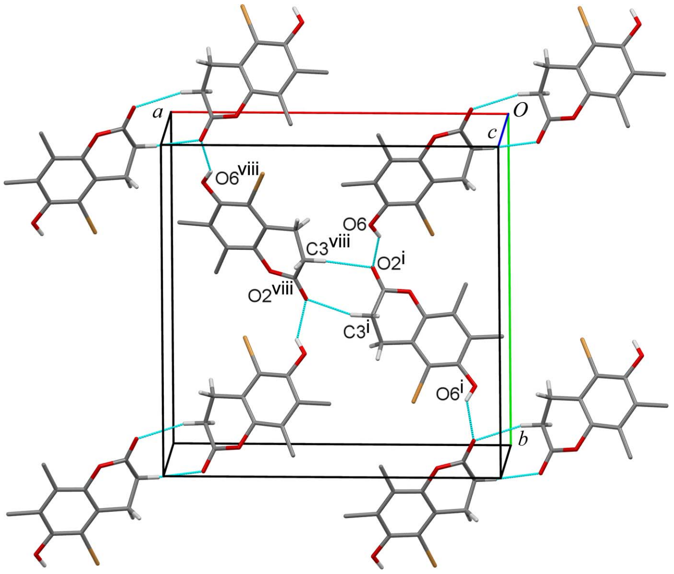

Figure 4
The corrugated sheets of (I), viewed along *c*, with hydrogen bonds drawn as dashed lines. For clarity, H atoms on atoms not involved in hydrogen-bond formation have been omitted from this and all subsequent packing diagrams. [Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$.]

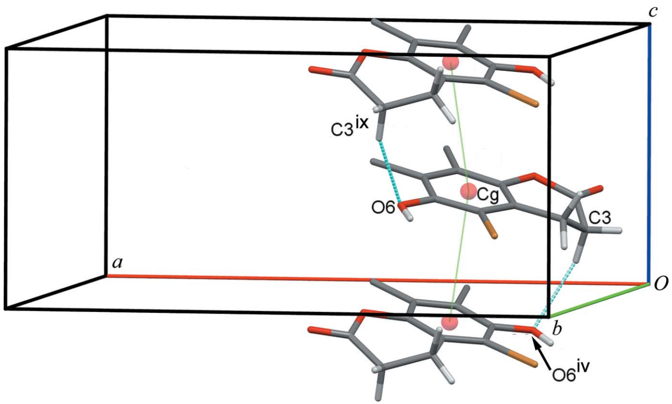

Figure 5
π–π contacts (thin dashed lines) and C—H$\cdots$O hydrogen bonds (thick dashed lines), stacking molecules of (I) in a head-to-tail fashion along *c*. [Symmetry codes: (iv) $-y+\frac{1}{2}, -x+\frac{1}{2}, z-\frac{1}{2}$; (ix) $-y+\frac{1}{2}, -x+\frac{1}{2}, z+\frac{1}{2}$.]

molecules into inversion dimers and generates $R_2^2(8)$ ring motifs. A classical O6—H6O$\cdots$O2^{i} hydrogen bonds and its symmetry-related counterparts link each dimer to four others, forming a corrugated sheet in the (001) plane (Fig. 4). The zigzag *C*(9) chains mentioned above are also seen clearly in this view. Bifurcated C4—H4*B*$\cdots$O1^{iii} and C4—H4*B*$\cdots$O2^{iii} [symmetry code: (iii) $-y, x, -z+1$] hydrogen bonds extend the packing to three dimensions. Molecules are also stacked in a head-to-tail fashion along *c* through π–π stacking interactions between adjacent C5–C10 benzene rings [$Cg\cdots Cg^{iv}$ = 3.885 (3) Å, where *Cg* denotes the ring centroid; symmetry code: (iv) $-y+\frac{1}{2}, -x+\frac{1}{2}, z-\frac{1}{2}$], supported by C3—H3*B*$\cdots$O6^{iv} contacts (Fig. 5). The overall packing thus comprises an intricate three-dimensional network of molecules stacked along *c* (Fig. 6).

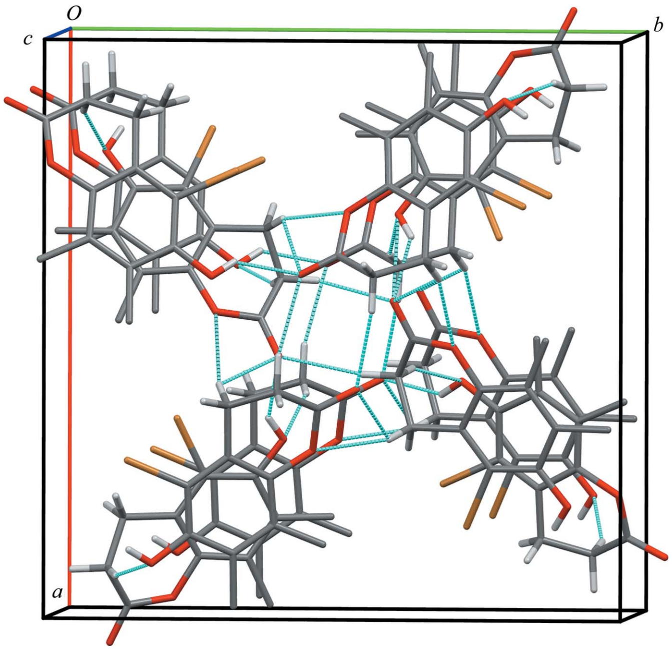

Figure 6
The overall packing of (I), viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

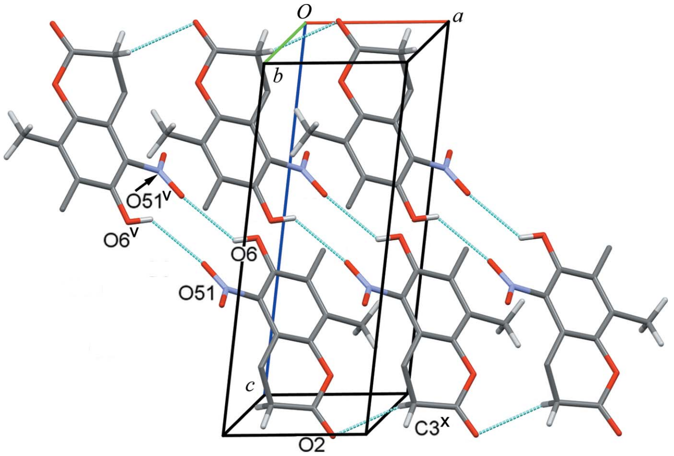

Figure 7
Stacks of inversion dimers of (II) approximately parallel to ($\overline{1}\overline{1}3$). Dashed lines indicate hydrogen bonds. [Symmetry codes: (v) $-x-1, -y+1, -z+1$; (x) $x+1, y, z$.]

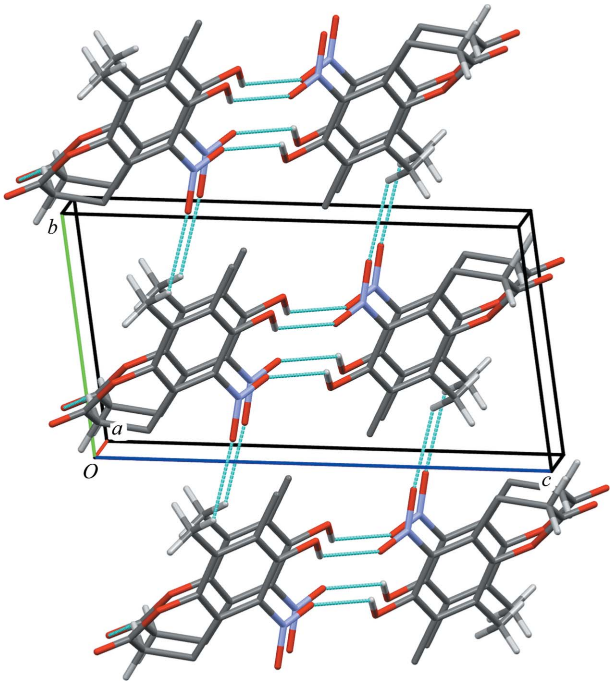

Figure 8
The overall packing of (II), viewed along the *a* axis.

In contrast, the crystal structure of (II) is dominated by the inversion dimers formed through intermolecular O6—H6O$\cdots$O51^{v} contacts. Additional C3—H3*B*$\cdots$O2^{vi} [symmetry code: (vi) $x-1, y, z$] contacts stack adjacent dimers approximately parallel to ($\overline{1}\overline{1}3$) (Fig. 7). Additional weak C81—H81*A*$\cdots$O52^{vii} [symmetry code: (vii) $x+1, y-1, z$] contacts link these dimer stacks to generate a much simpler three-dimensional network (Fig. 8).

Experimental

Compound (I) was synthesized from trimethyl-*p*-benzoquinone (Fieser & Ardao, 1956) in three steps. The first two steps, bromination of the quinone and coumarin ring formation, follow a literature preparation utilizing bromine/acetic acid and then dimethyl malonate/magnesium methoxide (Smith & Wiley, 1946). Characterization was by NMR (previously unreported). The third step is hydrolysis of the methyl ester followed by decarboxylation, a methodology used in the preparation of the chloro analogue (Cameron *et al.*, 2011), which in turn was based on the work of Stoffman & Clive (2009). The product was obtained in 72% yield and X-ray quality crystals of (I) were obtained from $CDCl_3$ layered with EtOH (m.p. 444–445 K). FT–IR (ATR, ν, cm^{-1}): 1735 (O—C═O); ^1H NMR (400 MHz, $CDCl_3$): δ 2.20 (*s*, 3H), 2.24 (*s*, 3H), 2.74 (*t*, *J* = 8 Hz, 2H), 3.04 (*t*, *J* = 8 Hz, 2H), 5.48 (*s*, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 12.8, 24.7, 28.8, 107.3, 119.3, 123.6, 125.7, 144.0, 146.8, 168.4.

Nitrotrimethylquinone (Smith & Cutler, 1949) was similarly used to prepare the nitro derivative, (II). The product was obtained in 66% yield and X-ray quality crystals were obtained from Et_2O. ^1H NMR (400 MHz, $CDCl_3$): δ 2.23 (*s*, 3H, CH_3), 2.27 (*s*, 3H, CH_3), 2.65 (*t*, *J* = 8 Hz, 2H, CH_2), 3.27 (*t*, *J* = 8 Hz, 2H, CH_2). HR–MS (ESI), calculated for $C_{11}H_{10}NO_5$: $[M - H]^-$ *m*/*z* 236.0553; found: *m*/*z* 236.0564. Details of the preparative routes to (I) and (II) are shown in Fig. 1.

Compound (III), the trifluoromethyl analogue of (I) and (II), was prepared from 6-hydroxy-7,8-dimethylchroman-2-one (Goswami *et al.*, 2012) *via* photoredox catalysis utilizing the methodology of Nagib & MacMillan (2011). The product was obtained in 35% yield and poor quality crystals were obtained from Et_2O. ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (*s*, 3H, CH_3), 2.20 (*s*, 3H, CH_3), 2.70 (*t*, *J* = 8 Hz, 2H, CH_2), 2.87 (*t*, *J* = 8 Hz, 2H, CH_2).

Compound (I)

Crystal data

$C_{11}H_{11}BrO_3$
M_r = 271.11
Tetragonal, $P\overline{4}2_1c$
a = 16.2247 (19) Å
c = 7.6586 (8) Å
V = 2016.1 (4) Å^3
Z = 8
Mo *Kα* radiation
μ = 4.06 mm^{-1}
T = 91 K
0.25 × 0.13 × 0.13 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)
T_{min} = 0.579, T_{max} = 0.745
9841 measured reflections
1715 independent reflections
1615 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.078
S = 1.10
1715 reflections
141 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Absolute structure: Flack (1983), with 717 Friedel pairs
Flack parameter: 0.023 (15)

Compound (II)

Crystal data

$C_{11}H_{11}NO_5$
M_r = 237.21
Triclinic, $P\overline{1}$
a = 5.0922 (12) Å
b = 7.3347 (15) Å
c = 13.942 (3) Å
α = 97.657 (12)°
β = 100.072 (11)°
γ = 90.862 (12)°
V = 507.75 (19) Å^3
Z = 2
Mo *Kα* radiation
μ = 0.12 mm^{-1}
T = 93 K
0.43 × 0.17 × 0.05 mm

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6O···Br5	0.79 (2)	2.57 (4)	3.089 (3)	124 (4)
O6—H6O···O2^{i}	0.79 (2)	2.12 (4)	2.778 (4)	140 (5)
C3—H3*A*···O2^{ii}	0.99	2.57	3.469 (6)	152
C4—H4*B*···O1^{iii}	0.99	2.62	3.575 (6)	162
C4—H4*B*···O2^{iii}	0.99	2.68	3.349 (6)	125
C3—H3*B*···O6^{iv}	0.99	2.41	3.343 (6)	156

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6O···O51	0.86 (3)	1.80 (3)	2.588 (3)	151 (3)
O6—H6O···O51^{v}	0.86 (3)	2.45 (3)	3.078 (3)	130 (3)
C3—H3*B*···O2^{vi}	0.99	2.59	3.245 (3)	124
C81—H81*A*···O52^{vii}	0.98	2.63	3.362 (3)	131

Symmetry codes: (v) $-x-1, -y+1, -z+1$; (vi) $x-1, y, z$; (vii) $x+1, y-1, z$.

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)
T_{min} = 0.649, T_{max} = 0.746
7686 measured reflections
2317 independent reflections
1367 reflections with $I > 2\sigma(I)$
R_{int} = 0.300

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.204
S = 0.96
2317 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

In both molecules, the O-bound H atoms, labelled H6O, were clearly located in difference Fourier maps and their coordinates were refined, with $U_{iso}(H) = 1.5U_{eq}(O)$ and with the O—H bond length restrained to 0.80 (2) Å. Methyl and methylene H atoms were refined using a riding model, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl, and with C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene H atoms.

For (I), the absolute structure was determined unequivocally, with the Flack parameter (Flack, 1983) refining to 0.022 (16). For (II), the data were clearly not of the best quality, despite several attempts with different crystals. The best of these gave data for which R_{int} = 0.2995. Despite this, a solution was readily obtained and clearly revealed full details of the molecular structure and crystal packing, and the refinement converged with acceptable residuals and s.u. values for the geometric data. Despite the high R_{int} value there were no unusual characteristics in the multi-scan absorption correction applied with *SADABS* (Bruker, 2011).

For both compounds, data collection: *APEX2* (Bruker, 2011); cell refinement: *APEX2* and *SAINT* (Bruker, 2011); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *TITAN2000* (Hunter & Simpson, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *TITAN2000*; molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*, *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3310). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2013). C**69**, 407-411 [doi:10.1107/S0108270113005325]

Similarities and differences in the structures of 5-bromo-6-hydroxy-7,8-dimethylchroman-2-one and 6-hydroxy-7,8-dimethyl-5-nitrochroman-2-one

Shailesh K. Goswami, Lyall R. Hanton, C. John McAdam, Stephen C. Moratti and Jim Simpson

(I) 5-Bromo-6-hydroxy-7,8-dimethylchroman-2-one

Crystal data

$C_{11}H_{11}BrO_3$
$M_r = 271.11$
Tetragonal, $P\bar{4}2_1c$
Hall symbol: P -4 2n
$a = 16.2247$ (19) Å
$c = 7.6586$ (8) Å
$V = 2016.1$ (4) Å^3
$Z = 8$
$F(000) = 1088$
$D_x = 1.786$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3775 reflections
$\theta = 2.5$–24.6°
$\mu = 4.06$ mm^{-1}
$T = 91$ K
Rectangular block, colourless
0.25 × 0.13 × 0.13 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)
$T_{\min} = 0.579$, $T_{\max} = 0.745$
9841 measured reflections
1715 independent reflections
1615 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 24.8°$, $\theta_{\min} = 2.8°$
$h = -19 \rightarrow 15$
$k = -14 \rightarrow 19$
$l = -9 \rightarrow 6$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.078$
$S = 1.10$
1715 reflections
141 parameters
7 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 1.9393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Absolute structure: Flack (1983), with 717 Friedel pairs
Flack parameter: 0.023 (15)

Special details

Experimental. ADDITIONAL EXPERIMENTAL & CHARACTERISATION DETAILS
Bromotrimethylquinone: 70% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ, p.p.m.): 2.04 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 2.21 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 12.6, 13.2, 17.1, 135.4, 140.7, 140.9, 145.6, 179.4, 184.4.
Methyl 5-bromo-6-hydroxy-7,8-dimethyl-2-oxochroman-3-carboxylate: 76% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ, p.p.m.): 2.20 (s, 3H, CH$_3$), 2.24 (s, 3H, CH$_3$), 3.23 (dd, J = 4 and 16 Hz, 1H, CH), 3.45 (dd, J = 8 and 16 Hz, 1H, CH), 3.76 (m, 1H, CH), 3.37 (s, 3H, OCH$_3$),5.51 (bs, 1H, OH); ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 12.1, 13.0, 20.1, 45.8, 53.1, 107.4, 117.8, 124.3, 125.8, 143.3, 147.2, 164.3, 167.7. HR MS (ESI): calculated for $C_{13}H_{13}BrO_5$: [M]+ m/z 327.9940, found: m/z 327.9682.
5-Bromo-6-hydroxy-7,8-dimethylchroman-2-one, (I), 72% yield. ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 11.8, 12.8, 24.7, 28.8, 107.3, 119.3, 123.6, 125.7, 144.0, 146.8, 168.4.
Nitrotrimethylquinone: 60% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ, p.p.m.): 2.06 (s, 3H, CH$_3$), 2.09 (m, 6H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 11.3, 12.2, 12.8, 134.3, 139.7, 142.2, 150.2, 177.2, 185.5.
Methyl 7,8-dimethyl-5-nitro-2,6-dioxo-3,4,6,8a-tetrahydro-2H-chromene- 3-carboxylate: 50% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ, p.p.m.): 2.28 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 3.52 (dd, J = 4 and 16 Hz, 1H, CH), 3.67–3.75 (m, 2H, CH$_2$), 3.77 (s, 3H, OCH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 12.2, 13.4, 25.5, 45.0, 53.3, 114.9, 117.8, 127.8, 135.8, 143.2, 150.5, 163.5, 167.3. HR MS (ESI): calculated for $C_{13}H_{13}NO_7$: [M]+ m/z 295.0686, found: m/z 295.0687.
5-Nitro-6-hydroxy-7,8-dimethylchroman-2-one (II) 66% yield. ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 12.1, 12.6, 23.7, 29.1, 116.8, 127.1, 131.1, 135.7, 143.8, 149.9, 167.5.
6-Hydroxy-7,8-dimethyl-5-(trifluoromethyl)chroman-2-one,(III). ^{13}C NMR (100 MHz, CDCl$_3$, δ, p.p.m.): 12.1, 13.3, 22.2, 28.1, 118.0, 126.2, 132.2, 140.5, 145.2, 148.7, 168.1; ^{19}F NMR (376 MHz, CDCl$_3$, δ, p.p.m.): -79.1.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.20618 (19)	0.02966 (18)	0.4131 (4)	0.0138 (7)
O2	0.0990 (2)	−0.04812 (19)	0.3584 (4)	0.0196 (8)
C2	0.1321 (3)	0.0176 (3)	0.3337 (6)	0.0139 (10)
C3	0.1009 (3)	0.0836 (3)	0.2165 (7)	0.0168 (10)
H3A	0.0400	0.0810	0.2146	0.020*
H3B	0.1206	0.0724	0.0965	0.020*
C4	0.1266 (2)	0.1706 (3)	0.2666 (6)	0.0147 (10)
H4A	0.1175	0.2082	0.1666	0.018*
H4B	0.0924	0.1900	0.3654	0.018*
C5	0.2662 (3)	0.2413 (2)	0.3011 (6)	0.0120 (9)
Br5	0.22113 (3)	0.34214 (3)	0.22181 (7)	0.02019 (16)
C6	0.3503 (3)	0.2402 (3)	0.3475 (6)	0.0129 (10)
O6	0.4009 (2)	0.30533 (19)	0.3291 (4)	0.0175 (8)
H6O	0.377 (3)	0.342 (2)	0.284 (6)	0.026*
C7	0.3844 (3)	0.1678 (3)	0.4196 (6)	0.0125 (10)
C71	0.4768 (2)	0.1693 (3)	0.4774 (5)	0.0054 (9)
H71A	0.4810	0.1523	0.5998	0.008*
H71B	0.4986	0.2253	0.4644	0.008*
H71C	0.5086	0.1314	0.4042	0.008*

C8	0.3351 (3)	0.0981 (3)	0.4391 (6)	0.0118 (10)
C81	0.3700 (3)	0.0164 (3)	0.5104 (6)	0.0098 (10)
H81A	0.3989	−0.0128	0.4168	0.015*
H81B	0.3247	−0.0178	0.5540	0.015*
H81C	0.4085	0.0280	0.6059	0.015*
C9	0.2528 (3)	0.1024 (3)	0.3874 (6)	0.0134 (10)
C10	0.2159 (3)	0.1724 (3)	0.3178 (5)	0.0111 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0118 (17)	0.0080 (16)	0.0218 (17)	−0.0011 (14)	−0.0016 (15)	0.0034 (13)
O2	0.0179 (18)	0.0118 (18)	0.0291 (19)	−0.0020 (14)	0.0033 (16)	−0.0020 (15)
C2	0.014 (3)	0.016 (3)	0.011 (2)	0.001 (2)	0.0053 (19)	−0.0043 (19)
C3	0.014 (2)	0.017 (2)	0.020 (2)	−0.0031 (19)	0.001 (2)	0.000 (2)
C4	0.007 (2)	0.018 (2)	0.019 (2)	0.0015 (17)	0.001 (2)	0.002 (2)
C5	0.013 (2)	0.009 (2)	0.013 (2)	0.0015 (18)	−0.002 (2)	0.002 (2)
Br5	0.0211 (3)	0.0144 (3)	0.0250 (3)	0.00195 (19)	0.0010 (2)	0.0031 (2)
C6	0.013 (2)	0.015 (2)	0.011 (2)	0.0016 (19)	0.003 (2)	−0.0018 (18)
O6	0.0148 (18)	0.0153 (18)	0.0223 (19)	−0.0047 (14)	−0.0046 (15)	0.0031 (15)
C7	0.015 (2)	0.013 (2)	0.010 (2)	0.003 (2)	0.001 (2)	0.000 (2)
C71	0.0053 (12)	0.0054 (12)	0.0054 (12)	−0.0004 (9)	0.0018 (9)	0.0002 (9)
C8	0.009 (2)	0.016 (2)	0.011 (2)	0.003 (2)	0.001 (2)	−0.002 (2)
C81	0.008 (2)	0.011 (2)	0.010 (2)	−0.0035 (19)	0.0010 (19)	−0.0003 (19)
C9	0.020 (3)	0.008 (2)	0.012 (2)	−0.0031 (19)	0.005 (2)	−0.0022 (19)
C10	0.013 (2)	0.013 (2)	0.008 (2)	0.0033 (19)	−0.0010 (19)	−0.0038 (18)

Geometric parameters (Å, º)

O1—C2	1.361 (6)	C6—C7	1.411 (6)
O1—C9	1.416 (5)	O6—H6O	0.794 (19)
O2—C2	1.209 (5)	C7—C8	1.392 (6)
C2—C3	1.486 (6)	C7—C71	1.563 (6)
C3—C4	1.520 (6)	C71—H71A	0.9800
C3—H3A	0.9900	C71—H71B	0.9800
C3—H3B	0.9900	C71—H71C	0.9800
C4—C10	1.500 (6)	C8—C9	1.395 (6)
C4—H4A	0.9900	C8—C81	1.541 (6)
C4—H4B	0.9900	C81—H81A	0.9800
C5—C10	1.390 (6)	C81—H81B	0.9800
C5—C6	1.409 (6)	C81—H81C	0.9800
C5—Br5	1.892 (4)	C9—C10	1.390 (6)
C6—O6	1.347 (5)		

C2—O1—C9	121.9 (3)	C8—C7—C71	122.3 (4)
O2—C2—O1	116.7 (4)	C6—C7—C71	118.3 (4)
O2—C2—C3	125.4 (4)	C7—C71—H71A	109.5
O1—C2—C3	117.8 (4)	C7—C71—H71B	109.5
C2—C3—C4	115.0 (4)	H71A—C71—H71B	109.5
C2—C3—H3A	108.5	C7—C71—H71C	109.5

C4—C3—H3A	108.5	H71A—C71—H71C	109.5
C2—C3—H3B	108.5	H71B—C71—H71C	109.5
C4—C3—H3B	108.5	C7—C8—C9	118.6 (4)
H3A—C3—H3B	107.5	C7—C8—C81	121.7 (4)
C10—C4—C3	110.4 (3)	C9—C8—C81	119.6 (4)
C10—C4—H4A	109.6	C8—C81—H81A	109.5
C3—C4—H4A	109.6	C8—C81—H81B	109.5
C10—C4—H4B	109.6	H81A—C81—H81B	109.5
C3—C4—H4B	109.6	C8—C81—H81C	109.5
H4A—C4—H4B	108.1	H81A—C81—H81C	109.5
C10—C5—C6	122.3 (4)	H81B—C81—H81C	109.5
C10—C5—Br5	119.8 (3)	C10—C9—C8	124.2 (4)
C6—C5—Br5	117.8 (3)	C10—C9—O1	120.3 (4)
O6—C6—C5	123.6 (4)	C8—C9—O1	115.5 (4)
O6—C6—C7	117.1 (4)	C5—C10—C9	116.0 (4)
C5—C6—C7	119.3 (4)	C5—C10—C4	124.0 (4)
C6—O6—H6O	110 (4)	C9—C10—C4	120.0 (4)
C8—C7—C6	119.5 (4)		

C9—O1—C2—O2	176.9 (4)	C7—C8—C9—C10	−0.4 (7)
C9—O1—C2—C3	0.3 (6)	C81—C8—C9—C10	−178.5 (4)
O2—C2—C3—C4	152.6 (4)	C7—C8—C9—O1	−179.2 (4)
O1—C2—C3—C4	−31.2 (6)	C81—C8—C9—O1	2.7 (6)
C2—C3—C4—C10	43.1 (5)	C2—O1—C9—C10	16.8 (6)
C10—C5—C6—O6	178.5 (4)	C2—O1—C9—C8	−164.3 (4)
Br5—C5—C6—O6	−3.9 (6)	C6—C5—C10—C9	1.5 (6)
C10—C5—C6—C7	−2.4 (6)	Br5—C5—C10—C9	−176.0 (3)
Br5—C5—C6—C7	175.2 (3)	C6—C5—C10—C4	−178.7 (4)
O6—C6—C7—C8	−179.0 (4)	Br5—C5—C10—C4	3.7 (6)
C5—C6—C7—C8	1.8 (7)	C8—C9—C10—C5	−0.1 (6)
O6—C6—C7—C71	1.8 (6)	O1—C9—C10—C5	178.6 (4)
C5—C6—C7—C71	−177.4 (4)	C8—C9—C10—C4	−179.9 (4)
C6—C7—C8—C9	−0.4 (7)	O1—C9—C10—C4	−1.1 (6)
C71—C7—C8—C9	178.7 (4)	C3—C4—C10—C5	152.4 (4)
C6—C7—C8—C81	177.6 (4)	C3—C4—C10—C9	−27.9 (6)
C71—C7—C8—C81	−3.2 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*O*···Br5	0.79 (2)	2.57 (4)	3.089 (3)	124 (4)
O6—H6*O*···O2^{i}	0.79 (2)	2.12 (4)	2.778 (4)	140 (5)
C3—H3*A*···O2^{ii}	0.99	2.57	3.469 (6)	152
C4—H4*B*···O1^{iii}	0.99	2.62	3.575 (6)	162
C4—H4*B*···O2^{iii}	0.99	2.68	3.349 (6)	125
C3—H3*B*···O6^{iv}	0.99	2.41	3.343 (6)	156

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

(II) 6-Hydroxy-7,8-dimethyl-5-nitrochroman-2-one

Crystal data

$C_{11}H_{11}NO_5$	$Z = 2$
$M_r = 237.21$	$F(000) = 248$
Triclinic, $P\overline{1}$	$D_x = 1.552$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.0922$ (12) Å	Cell parameters from 1620 reflections
$b = 7.3347$ (15) Å	$\theta = 3.0$–27.4°
$c = 13.942$ (3) Å	$\mu = 0.12$ mm^{-1}
$\alpha = 97.657$ (12)°	$T = 93$ K
$\beta = 100.072$ (11)°	Plate, yellow
$\gamma = 90.862$ (12)°	0.43 × 0.17 × 0.05 mm
$V = 507.75$ (19) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	7686 measured reflections
Radiation source: fine-focus sealed tube	2317 independent reflections
Graphite monochromator	1367 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.300$
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.8°$
$T_{min} = 0.649$, $T_{max} = 0.746$	$h = -6 \rightarrow 6$
	$k = -9 \rightarrow 8$
	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.076$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.204$	$w = 1/[\sigma^2(F_o^2) + (0.0872P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} < 0.001$
2317 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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}
O1	0.5980 (3)	0.5812 (2)	0.88673 (12)	0.0211 (5)
O2	0.7046 (3)	0.7507 (3)	1.03108 (14)	0.0278 (5)
C2	0.5337 (5)	0.7046 (4)	0.96087 (19)	0.0211 (6)

C3	0.2542 (5)	0.7678 (4)	0.9441 (2)	0.0241 (6)
H3A	0.2431	0.8830	0.9890	0.029*
H3B	0.1338	0.6736	0.9602	0.029*
C4	0.1604 (5)	0.8018 (4)	0.83830 (19)	0.0218 (6)
H4A	−0.0314	0.8295	0.8281	0.026*
H4B	0.2619	0.9085	0.8245	0.026*
C5	0.0373 (5)	0.5664 (3)	0.68000 (19)	0.0192 (6)
N5	−0.1732 (4)	0.6805 (3)	0.63995 (16)	0.0209 (5)
O51	−0.3682 (3)	0.6060 (3)	0.58054 (14)	0.0251 (5)
O52	−0.1494 (4)	0.8473 (3)	0.66469 (14)	0.0307 (5)
C6	0.0720 (5)	0.3954 (3)	0.62688 (18)	0.0180 (6)
O6	−0.0884 (3)	0.3227 (3)	0.54185 (13)	0.0222 (5)
H6O	−0.223 (6)	0.393 (4)	0.541 (2)	0.033*
C7	0.2890 (5)	0.2897 (3)	0.66103 (19)	0.0178 (6)
C71	0.3268 (5)	0.1090 (4)	0.6017 (2)	0.0240 (6)
H71A	0.3359	0.0113	0.6436	0.036*
H71B	0.4930	0.1157	0.5757	0.036*
H71C	0.1762	0.0820	0.5469	0.036*
C8	0.4606 (5)	0.3538 (3)	0.74836 (18)	0.0178 (6)
C81	0.6915 (5)	0.2437 (4)	0.7883 (2)	0.0219 (6)
H81A	0.7798	0.1912	0.7344	0.033*
H81B	0.6259	0.1441	0.8193	0.033*
H81C	0.8193	0.3240	0.8371	0.033*
C9	0.4106 (5)	0.5231 (3)	0.80064 (19)	0.0176 (6)
C10	0.2038 (5)	0.6325 (3)	0.77009 (19)	0.0190 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0141 (9)	0.0273 (10)	0.0217 (11)	0.0010 (7)	0.0036 (7)	0.0019 (8)
O2	0.0191 (9)	0.0378 (12)	0.0254 (11)	−0.0019 (8)	0.0033 (8)	0.0016 (9)
C2	0.0203 (12)	0.0248 (14)	0.0205 (15)	−0.0032 (10)	0.0085 (11)	0.0053 (12)
C3	0.0206 (13)	0.0299 (15)	0.0240 (15)	0.0025 (11)	0.0097 (11)	0.0044 (12)
C4	0.0187 (12)	0.0240 (14)	0.0236 (15)	0.0025 (10)	0.0043 (11)	0.0051 (12)
C5	0.0146 (12)	0.0216 (14)	0.0236 (15)	0.0020 (10)	0.0073 (10)	0.0063 (12)
N5	0.0203 (11)	0.0237 (12)	0.0211 (12)	0.0041 (9)	0.0085 (9)	0.0048 (10)
O51	0.0149 (9)	0.0313 (11)	0.0278 (11)	0.0003 (7)	0.0004 (7)	0.0037 (9)
O52	0.0343 (11)	0.0246 (11)	0.0316 (12)	0.0079 (8)	0.0012 (9)	0.0036 (9)
C6	0.0171 (12)	0.0215 (14)	0.0163 (13)	−0.0025 (10)	0.0050 (10)	0.0041 (11)
O6	0.0167 (9)	0.0254 (11)	0.0236 (11)	0.0026 (7)	0.0018 (8)	0.0027 (8)
C7	0.0174 (12)	0.0187 (13)	0.0200 (14)	0.0010 (10)	0.0086 (10)	0.0052 (11)
C71	0.0237 (13)	0.0234 (15)	0.0248 (15)	0.0031 (11)	0.0035 (11)	0.0038 (12)
C8	0.0141 (11)	0.0221 (14)	0.0199 (14)	0.0007 (9)	0.0076 (10)	0.0067 (11)
C81	0.0179 (12)	0.0240 (14)	0.0251 (15)	0.0044 (10)	0.0065 (11)	0.0042 (12)
C9	0.0157 (11)	0.0211 (14)	0.0175 (13)	−0.0009 (10)	0.0057 (10)	0.0047 (11)
C10	0.0161 (12)	0.0203 (14)	0.0231 (15)	−0.0019 (10)	0.0091 (10)	0.0051 (11)

Geometric parameters (Å, º)

O1—C2	1.369 (3)	O51—O51$^{\rm i}$	2.686 (4)
O1—C9	1.409 (3)	C6—O6	1.355 (3)
O2—C2	1.198 (3)	C6—C7	1.410 (3)
C2—C3	1.492 (4)	O6—H6O	0.86 (3)
C3—C4	1.524 (4)	C7—C8	1.389 (3)
C3—H3A	0.9900	C7—C71	1.500 (4)
C3—H3B	0.9900	C71—H71A	0.9800
C4—C10	1.504 (4)	C71—H71B	0.9800
C4—H4A	0.9900	C71—H71C	0.9800
C4—H4B	0.9900	C8—C9	1.404 (4)
C5—C6	1.399 (4)	C8—C81	1.505 (3)
C5—C10	1.409 (4)	C81—H81A	0.9800
C5—N5	1.450 (3)	C81—H81B	0.9800
N5—O52	1.225 (3)	C81—H81C	0.9800
N5—O51	1.243 (3)	C9—C10	1.376 (3)

C2—O1—C9	121.11 (19)	C6—O6—H6O	101 (2)
O2—C2—O1	117.5 (2)	C8—C7—C6	119.7 (2)
O2—C2—C3	127.2 (2)	C8—C7—C71	121.7 (2)
O1—C2—C3	115.3 (2)	C6—C7—C71	118.6 (2)
C2—C3—C4	112.2 (2)	C7—C71—H71A	109.5
C2—C3—H3A	109.2	C7—C71—H71B	109.5
C4—C3—H3A	109.2	H71A—C71—H71B	109.5
C2—C3—H3B	109.2	C7—C71—H71C	109.5
C4—C3—H3B	109.2	H71A—C71—H71C	109.5
H3A—C3—H3B	107.9	H71B—C71—H71C	109.5
C10—C4—C3	108.9 (2)	C7—C8—C9	118.5 (2)
C10—C4—H4A	109.9	C7—C8—C81	121.4 (2)
C3—C4—H4A	109.9	C9—C8—C81	120.1 (2)
C10—C4—H4B	109.9	C8—C81—H81A	109.5
C3—C4—H4B	109.9	C8—C81—H81B	109.5
H4A—C4—H4B	108.3	H81A—C81—H81B	109.5
C6—C5—C10	122.0 (2)	C8—C81—H81C	109.5
C6—C5—N5	118.9 (2)	H81A—C81—H81C	109.5
C10—C5—N5	119.1 (2)	H81B—C81—H81C	109.5
O52—N5—O51	122.5 (2)	C10—C9—C8	124.2 (2)
O52—N5—C5	118.6 (2)	C10—C9—O1	120.7 (2)
O51—N5—C5	118.9 (2)	C8—C9—O1	115.0 (2)
N5—O51—O51$^{\rm i}$	157.66 (18)	C9—C10—C5	116.1 (2)
O6—C6—C5	124.3 (2)	C9—C10—C4	118.1 (2)
O6—C6—C7	116.3 (2)	C5—C10—C4	125.6 (2)
C5—C6—C7	119.4 (2)		

Symmetry code: (i) $-x-1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*O*···O51	0.86 (3)	1.80 (3)	2.588 (3)	151 (3)

O6—H6*O*···O51^{i}	0.86 (3)	2.45 (3)	3.078 (3)	130 (3)
C3—H3*B*···O2^{ii}	0.99	2.59	3.245 (3)	124
C81—H81*A*···O52^{iii}	0.98	2.63	3.362 (3)	131

Symmetry codes: (i) −*x*−1, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*−1, *z*.