Crystal structure of 3-(2,2-dibromoacetyl)-4-hydroxy-2H-chromen-2-one

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The title compound, $C_{11}H_6Br_2O_4$, is a new coumarin derivative obtained from the reaction of 3-acetyl-4-hydroxy-2H-chromen-2-one with bromine in acetic acid. The hydroxyl group in involved in an intramolecular O—H···O hydrogen bond. In the crystal, π–π interactions between the rings of the bicycle [intercentroid distances = 3.498 (2) and 3.539 (2) Å] pack molecules into stacks along the b axis, and weak intermolecular C—H···O hydrogen bonds further link these stacks into layers parallel to the ab plane.

1. Chemical context

3-Acetyl-4-hydroxy-2H-chromen-2-one is one of the well-known 3-substituted-4-hydroxycoumarins, which form a class of fused-ring heterocycles and occur widely among natural products. Several natural products with the coumarinic moiety exhibit interesting biological properties such as anti-oxidant and antibacterial (Kayser & Kolodziej, 1997). They also possess pharmacological activities including anti-inflammatory (Mahidol et al., 2004), anticancer (Wang et al., 2002) and inhibition of platelet aggregation (Cravotto et al., 2001). These derivatives are very susceptible to electrophilic substitutions (Dou et al., 1969); their reaction with bromine can give rise to several compounds used as intermediate products which are susceptible to interesting substitutions (Takase et al., 1971) in a wide range of organic syntheses. The bromination of these compounds increases their anticonvulsant activity (Dimmock et al., 2000), which gives them pharmacological importance. Thus, as part of a study of the effects of substituents on the crystal structures of 3-acetyl-4-hydroxycoumarins (Traven et al., 2000), the structure of 3-(2,2-dibromoacetyl)-4-hydroxy-2H-chromen-2-one, (I), has been determined.
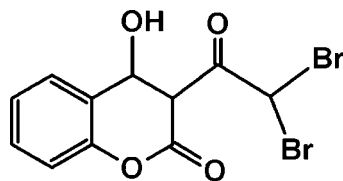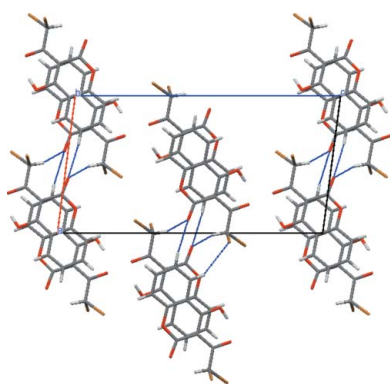
2. Structural commentary

In the title compound (Fig. 1), the hydroxy group is involved in formation of an intramolecular O—H···O hydrogen bond (Table 1). In fact, the O3—H5 distance of 0.94 (7) Å has decreased from 1.02 (3) Å, observed in the starting reagent 3-acetyl-4-hydroxy-2H-chromen-2-one (Lyssenko & Antipin, 2001). The H5···O4 distance of 1.65 (7) Å is elongated
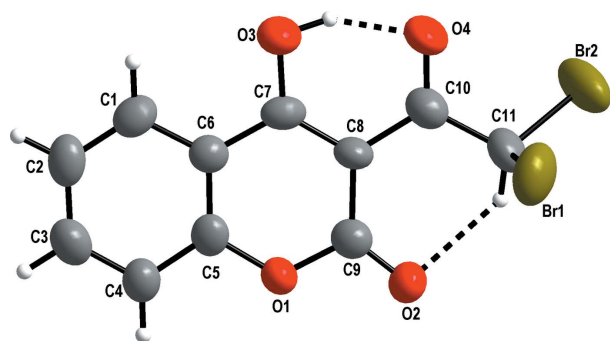
Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H5···O4	0.94 (7)	1.65 (7)	2.489 (6)	147 (6)
C11—H11···O2	0.98	2.12	2.793 (7)	125
C11—H11···O2^i	0.98	2.51	3.362 (8)	146
C2—H2···O2^{ii}	0.93	2.62	3.458 (8)	151

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

Table 2
Details of π–π interactions: intercentroid distances (Å).

$Cg1$ and $Cg2$ are centroids of the C1–C6 and O1/C5–C9 rings, respectively.

$Cg1$···$Cg2^i$	3.498 (7)
$Cg1$···$Cg2^{ii}$	3.539 (7)

compared with its value in the parent compound [1.45 (3) Å], and the O3—H5···O4 angle of 147 (6)° is significantly smaller than that found for the starting reagent [161 (2)°]. This trend has already been observed in the fluorinated compound 2-difluoroacetyl-1,3-cyclohexadione (Grieco *et al.*, 2011), in which the O3—H5 and H5···O4 distances are even more affected (0.908 and 1.658 Å respectively). These observations can be easily understood from the point of view of the strong attractive effect of the halogen atoms due to their high electronegativities. All these geometrical parameters are in good agreement with the significant attractor effect of the halogen atoms, which affects the lone pairs of the oxygen atom O4, leading to a decrease of the attractor effect of O4 in the H5···O4 hydrogen bond and, consequently, an increase in the H5···O4 distance.

The C—C and C—O bond lengths in (I) correspond well to those observed in the parent compound, so they are not affected by the α-ketodibromation except for C10—C11 [1.523 (9) Å] which is elongated compared to the distance in the starting reagent [1.485 (2) Å; Lyssenko & Antipin, 2001].
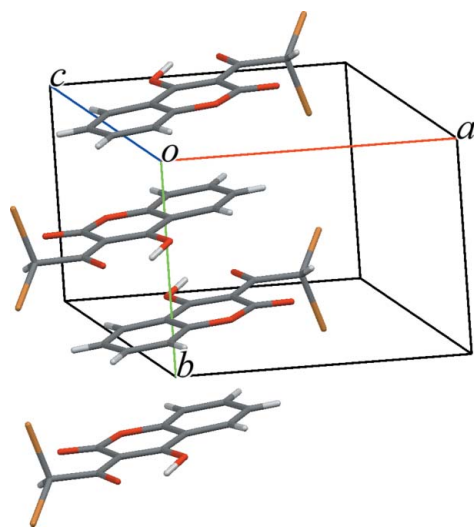
This trend had previously been observed in the similar structure of 2-difluoroacetyl-1,3-cyclohexadione (Grieco *et al.*, 2011), in which the difluoration reaction affects the C10—C11 distance [1.529 (2) Å].

3. Supramolecular features

In the crystal structure of (I), the molecules are assembled in a head-to-tail overlapping manner as a result of the π–π interactions between the benzene and lactone rings of neighbouring molecules (Table 2) into stacks along the *b*-axis direction (Fig. 2). The observed stacking arrangement can be considered as a balance between van der Waals dispersion and repulsion interactions, and electrostatic interactions between two rings of opposed polarity – the benzene ring (high electron density) and the lactone ring (low electron density)
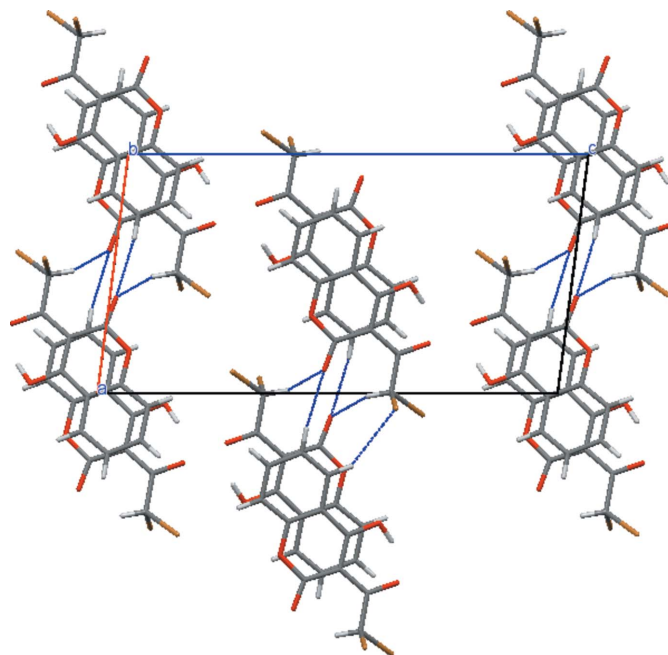

Figure 2
A portion of the crystal packing showing one stack of molecules parallel to the *b* axis.

Figure 3
The crystal packing, viewed down the *b* axis, showing the intermolecular C—H···O hydrogen bonds as thin blue lines.
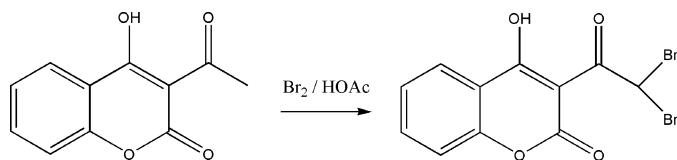
Figure 4
The synthetic route for (I).

(Hunter & Sanders, 1990). Weak intermolecular C—H···O hydrogen bonds (Table 2) further link these stacks into layers parallel to the *ab* plane (Fig. 3).

4. Synthesis and crystallization

An excess amount of bromine dissolved in acetic acid was added dropwise to a solution of 3-acetyl-4-hydroxy-2*H*-chromen-2-one in acetic acid (Fig. 4). During the reaction, the dropwise addition was made after every disappearance of the brown colour of the bromine. The reaction mixture was maintained under stirring at 373 K until the bromine colour persisted. The resulting solution was left to crystallize at room temperature to obtain transparent crystals of a light-yellow colour. Yield: 70%; m.p. = 375 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydroxy atom H5 was located from an electron density difference map and freely refined. C-bound H atoms were fixed geometrically (C—H = 0.93 or 0.98 Å) and refined as riding, with $U_{iso}(H)$ set to $1.2U_{eq}$ of the parent atom.

References

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Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_6Br_2O_4$
M_r	361.98
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	9.399 (4), 6.916 (3), 17.967 (7)
β (°)	97.37 (3)
V (Å^3)	1158.4 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.00
Crystal size (mm)	$0.15 \times 0.12 \times 0.10$
Data collection	
Diffractometer	Bruker *SMART* CCD area detector
Absorption correction	For a sphere (*WinGX*; Farrugia, 2012)
T_{min}, T_{max}	0.58, 0.75
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11685, 3234, 1094
R_{int}	0.089
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.712
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.133, 0.96
No. of reflections	3234
No. of parameters	158
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.43, −0.48

Computer programs: *SMART* and *SAINT* (Bruker, 2001), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

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supporting information

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Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

3-(2,2-Dibromoacetyl)-4-hydroxy-2*H*-chromen-2-one

Crystal data

$C_{11}H_6Br_2O_4$	$Z = 4$
$M_r = 361.98$	$F(000) = 696$
Monoclinic, $P2_1/n$	$D_x = 2.076$ Mg m^{-3}
Hall symbol: -P 2yn	Melting point: 375 K
$a = 9.399$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 6.916$ (3) Å	$\mu = 7.00$ mm^{-1}
$c = 17.967$ (7) Å	$T = 296$ K
$\beta = 97.37$ (3)°	Needle, yellow
$V = 1158.4$ (8) Å^3	$0.15 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	11685 measured reflections
Radiation source: fine-focus sealed tube	3234 independent reflections
Graphite monochromator	1094 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.089$
Absorption correction: for a sphere (*WinGX*; Farrugia, 2012)	$\theta_{max} = 30.4°$, $\theta_{min} = 2.3°$
	$h = -10 \rightarrow 13$
	$k = -6 \rightarrow 8$
$T_{min} = 0.58$, $T_{max} = 0.75$	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.133$	
$S = 0.96$	H atoms treated by a mixture of independent and constrained refinement
3234 reflections	
158 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.259P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.43$ e Å^{-3}
	$\Delta\rho_{min} = -0.48$ e Å^{-3}

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}
Br1	0.56249 (8)	0.89000 (12)	0.15244 (5)	0.0906 (3)
Br2	0.58984 (10)	0.45607 (13)	0.21230 (4)	0.1029 (4)
O1	0.1772 (4)	0.7341 (5)	−0.05777 (19)	0.0525 (10)
O2	0.4010 (5)	0.6891 (6)	−0.0136 (2)	0.0637 (12)
O3	0.0411 (5)	0.6852 (6)	0.1484 (2)	0.0639 (12)
O4	0.2923 (5)	0.6171 (7)	0.2042 (2)	0.0782 (14)
C1	−0.1597 (7)	0.7718 (8)	0.0249 (3)	0.0552 (16)
H1	−0.1941	0.7656	0.0711	0.066*
C2	−0.2515 (7)	0.8099 (8)	−0.0390 (4)	0.0609 (17)
H2	−0.3490	0.8267	−0.0365	0.073*
C3	−0.1981 (8)	0.8233 (8)	−0.1075 (3)	0.0590 (17)
H3	−0.2612	0.8507	−0.1504	0.071*
C4	−0.0559 (7)	0.7973 (8)	−0.1138 (3)	0.0533 (16)
H4	−0.0219	0.8061	−0.1601	0.064*
C5	0.0358 (7)	0.7576 (7)	−0.0489 (3)	0.0453 (15)
C6	−0.0123 (6)	0.7421 (7)	0.0202 (3)	0.0426 (14)
C7	0.0922 (7)	0.7009 (8)	0.0839 (3)	0.0476 (15)
C8	0.2351 (7)	0.6807 (8)	0.0762 (3)	0.0448 (14)
C9	0.2804 (8)	0.7008 (8)	0.0022 (3)	0.0489 (15)
C10	0.3352 (7)	0.6382 (8)	0.1427 (3)	0.0576 (17)
C11	0.4958 (7)	0.6271 (9)	0.1383 (3)	0.0637 (18)
H11	0.5117	0.5825	0.0883	0.076*
H5	0.117 (8)	0.628 (9)	0.180 (3)	0.08 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0551 (5)	0.1001 (6)	0.1139 (7)	−0.0050 (4)	0.0000 (4)	−0.0223 (5)
Br2	0.1112 (8)	0.1317 (8)	0.0614 (5)	0.0584 (6)	−0.0057 (4)	0.0091 (4)
O1	0.044 (3)	0.071 (3)	0.042 (2)	0.005 (2)	0.004 (2)	0.0054 (18)
O2	0.044 (3)	0.093 (3)	0.055 (3)	0.010 (2)	0.008 (2)	0.006 (2)
O3	0.061 (3)	0.088 (3)	0.044 (3)	0.006 (3)	0.012 (2)	−0.003 (2)
O4	0.066 (3)	0.130 (4)	0.037 (2)	0.005 (3)	0.003 (2)	0.001 (2)
C1	0.052 (5)	0.054 (4)	0.062 (4)	−0.001 (3)	0.017 (4)	−0.007 (3)
C2	0.048 (4)	0.054 (4)	0.078 (5)	0.003 (3)	−0.005 (4)	−0.002 (3)
C3	0.062 (5)	0.053 (4)	0.058 (4)	0.002 (3)	−0.006 (4)	0.006 (3)

C4	0.046 (5)	0.054 (4)	0.058 (4)	0.000 (3)	0.001 (3)	0.004 (3)
C5	0.045 (4)	0.035 (4)	0.055 (4)	0.001 (3)	0.003 (3)	0.004 (3)
C6	0.048 (4)	0.036 (4)	0.043 (4)	−0.003 (3)	0.006 (3)	−0.003 (2)
C7	0.059 (5)	0.046 (4)	0.040 (4)	−0.008 (3)	0.016 (3)	−0.004 (3)
C8	0.050 (4)	0.054 (4)	0.031 (3)	0.001 (3)	0.007 (3)	0.000 (3)
C9	0.054 (5)	0.045 (4)	0.048 (4)	0.005 (3)	0.007 (4)	0.000 (3)
C10	0.062 (5)	0.064 (4)	0.045 (4)	0.005 (3)	0.002 (4)	−0.001 (3)
C11	0.058 (5)	0.086 (5)	0.044 (4)	0.011 (4)	−0.006 (3)	−0.004 (3)

Geometric parameters (Å, º)

Br1—C11	1.930 (6)	C2—H2	0.9300
Br2—C11	1.910 (6)	C3—C4	1.368 (8)
O1—C5	1.368 (6)	C3—H3	0.9300
O1—C9	1.374 (6)	C4—C5	1.386 (7)
O2—C9	1.206 (7)	C4—H4	0.9300
O3—C7	1.315 (6)	C5—C6	1.379 (7)
O3—H5	0.94 (7)	C6—C7	1.438 (7)
O4—C10	1.233 (7)	C7—C8	1.375 (8)
C1—C2	1.370 (7)	C8—C10	1.453 (7)
C1—C6	1.413 (8)	C8—C9	1.454 (8)
C1—H1	0.9300	C10—C11	1.523 (9)
C2—C3	1.391 (8)	C11—H11	0.9800
C5—O1—C9	121.8 (5)	C1—C6—C7	123.8 (5)
C7—O3—H5	103 (4)	O3—C7—C8	123.5 (5)
C2—C1—C6	119.7 (6)	O3—C7—C6	115.4 (6)
C2—C1—H1	120.2	C8—C7—C6	121.1 (5)
C6—C1—H1	120.2	C7—C8—C10	118.4 (5)
C1—C2—C3	119.6 (6)	C7—C8—C9	119.1 (5)
C1—C2—H2	120.2	C10—C8—C9	122.5 (6)
C3—C2—H2	120.2	O2—C9—O1	114.7 (5)
C4—C3—C2	122.2 (6)	O2—C9—C8	127.1 (6)
C4—C3—H3	118.9	O1—C9—C8	118.2 (6)
C2—C3—H3	118.9	O4—C10—C8	120.7 (6)
C3—C4—C5	117.7 (6)	O4—C10—C11	118.7 (5)
C3—C4—H4	121.1	C8—C10—C11	120.6 (6)
C5—C4—H4	121.1	C10—C11—Br2	111.6 (4)
O1—C5—C6	122.1 (5)	C10—C11—Br1	104.7 (4)
O1—C5—C4	115.7 (5)	Br2—C11—Br1	112.2 (3)
C6—C5—C4	122.2 (6)	C10—C11—H11	109.4
C5—C6—C1	118.7 (5)	Br2—C11—H11	109.4
C5—C6—C7	117.5 (6)	Br1—C11—H11	109.4

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
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