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3-Dibromoacetyl-2*H*-chromen-2-one

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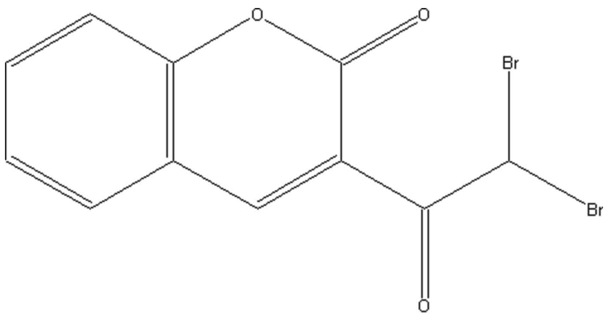
Key indicators: single-crystal X-ray study; *T* = 2930 K; mean σ(C–C) = 0.005 Å; *R* factor = 0.029; *wR* factor = 0.076; data-to-parameter ratio = 12.8.

The molecular structure of the title compound, $C_{11}H_6Br_2O_3$, contains a planar coumarin ring system which makes a dihedral angle of 18.5 (1)° with the bromoacetyl group. The structure is stabilized by intermolecular C—H···O hydrogen bonds and π–π aromatic stacking interactions, with centroid–centroid distances of 3.567 (2) (symmetry code: $-x$, $-y$, $-z$) and 3.642 (2) Å ($-x + 1$, $-y$, $-z$). A short Br···Br [3.4605 (8) Å] contact also stabilizes the crystal structure.

Related literature

For applications and photochemical reactivity of coumarins, see: Vishnumurthy *et al.* (1996, 1997, 1999, 2001).



Experimental

Crystal data

$C_{11}H_6Br_2O_3$
M_r = 345.98
Triclinic, $P\bar{1}$
a = 7.1998 (17) Å
b = 8.969 (2) Å
c = 9.722 (2) Å
α = 69.094 (5)°
β = 85.974 (6)°
γ = 71.177 (4)°
V = 554.4 (2) Å^3
Z = 2
Mo *K*α radiation
μ = 7.30 mm^{-1}
T = 2930 (2) K
0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.189, T_{max} = 0.232
5722 measured reflections
2184 independent reflections
1885 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.076
S = 1.05
2184 reflections
170 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O2^{i}	0.92 (4)	2.46 (4)	3.278 (4)	148 (3)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2003).

The authors thank the Department of Science and Technology for data collection on the CCD facility under the IRHPA–DST scheme. DC thanks CSIR, India, and the IISc for a Senior Research Fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2309).

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supplementary materials

Acta Cryst. (2007). E**63**, o2826 [**doi:10.1107/S1600536807021472**]

3-Dibromoacetyl-2*H*-chromen-2-one

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Comment

Coumarins are an important class of organic compounds with vast structural diversity and find useful applications in synthetic chemistry, medicinal chemistry and photochemistry (Vishnumurthy *et al.*, 1996, 1997, 1999). The formation of [2+2] cycloaddition products upon irradiation (Vishnumurthy *et al.*, 2001) of coumarin and its derivatives has demonstrated the importance of preorganisation of molecules in the crystalline solid state.

In the title compound, (I) (Fig. 1, Table 1), the coumarin system is planar, with maximum deviations of 0.012 (4)Å and 0.018 (3)Å for atoms C1 and C9 respectively.

The molecules are held by C—H···O intermolecular hydrogen bonds forming dimeric units. A pair of such dimers are stabilised by Br2···Br2 short contacts [d = 3.4605 Å, symmetry code: -x-1, -y+1, -z+1], [Fig. 2]. Furthermore, π···π stacking interactions link Cg1..Cg2, (the centroids of the pyanone O, C4···C9 and benzene C1···C6 rings) with separations of 3.567 (2), [Symmetry code: -x, -y, -z] and 3.642 (2)Å -x+1, -y, -z] respectively between the centroids, Fig. 2.

Experimental

To a solution of compound (I) (4.7 g, 0.025 mol) in 20 ml of alcohol free chloroform, bromine (7.9 g, 0.05 mol) was added in 25 ml of chloroform, with intermittent shaking. The mixture was warmed to decompose an addition product. heated for 15 min on a water bath to expel most of the hydrogen bromide, cooled and filtered. The solid on washing with ether gave 6.98 g (81%) of almost pure product, which on crystallization from acetic acid gave colorless crystals of (I).

Refinement

All the hydrogens were located in a difference Fourier map and refined isotropically with C—H bond lengths in the range 0.89 (4)-0.94 (3) Å.

Figures

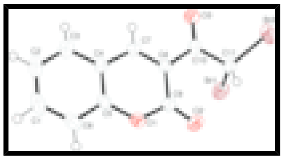

Fig. 1. The structure of (I) drawn with 50% ellipsoidal probability.

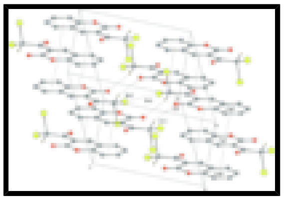

Fig. 2. Packing diagram of compound (I) highlighting the C—H···O and π···π contacts. Cg1 and Cg2 are the centroids of the pyranone O1/C7 and benzene C1/C6 rings. Hydrogen bonds are drawn and ring centroids are joined by dotted lines.

3-Dibromoacetyl-2*H*-chromen-2-one

Crystal data

$C_{11}H_6Br_2O_3$

$M_r = 345.98$

Triclinic, $P\overline{1}$

Hall symbol: -P 1

$a = 7.1998$ (17) Å

$b = 8.969$ (2) Å

$c = 9.722$ (2) Å

$\alpha = 69.094$ (5)°

$\beta = 85.974$ (6)°

$\gamma = 71.177$ (4)°

$V = 554.4$ (2) Å^3

$Z = 2$

$F_{000} = 332$

$D_x = 2.073$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 565 reflections

$\theta = 1.6$–26.4°

$\mu = 7.30$ mm^{-1}

$T = 2930$ (2) K

Block, yellow

0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 290(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{min} = 0.189$, $T_{max} = 0.232$

5722 measured reflections

2184 independent reflections

1885 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$

$\theta_{max} = 26.4$°

$\theta_{min} = 2.3$°

$h = -8 \rightarrow 8$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.076$

$S = 1.05$

2184 reflections

170 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.543P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.57$ e Å^{-3}

$\Delta\rho_{min} = -0.88$ e Å^{-3}

Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.027 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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	0.13625 (5)	0.36757 (5)	0.37268 (4)	0.04873 (15)
Br2	−0.32868 (6)	0.45590 (5)	0.37414 (4)	0.05603 (16)
O1	0.2817 (3)	−0.0994 (2)	0.1884 (2)	0.0345 (5)
O2	0.1724 (4)	−0.0165 (3)	0.3736 (2)	0.0468 (6)
O3	−0.1836 (3)	0.4487 (3)	0.0802 (2)	0.0395 (5)
C4	0.1934 (4)	0.0809 (4)	−0.0648 (3)	0.0282 (6)
C1	0.4394 (5)	−0.1793 (5)	−0.1471 (4)	0.0453 (8)
C2	0.3357 (5)	−0.0283 (5)	−0.2541 (4)	0.0461 (9)
C3	0.2151 (5)	0.1004 (4)	−0.2145 (4)	0.0381 (7)
C5	0.2981 (4)	−0.0728 (4)	0.0405 (3)	0.0289 (6)
C6	0.4211 (5)	−0.2033 (4)	0.0004 (4)	0.0386 (7)
C7	0.0709 (4)	0.2073 (4)	−0.0126 (3)	0.0262 (6)
C8	0.0564 (4)	0.1833 (3)	0.1321 (3)	0.0245 (5)
C9	0.1687 (4)	0.0216 (3)	0.2422 (3)	0.0296 (6)
C10	−0.0809 (4)	0.3233 (3)	0.1739 (3)	0.0283 (6)
C11	−0.0879 (5)	0.3081 (4)	0.3347 (3)	0.0345 (7)
H1	0.517 (5)	−0.277 (4)	−0.164 (3)	0.035 (8)*
H2	0.350 (6)	−0.018 (5)	−0.348 (5)	0.053 (11)*
H3	0.157 (5)	0.203 (5)	−0.283 (4)	0.043 (10)*
H6	0.484 (6)	−0.300 (5)	0.072 (4)	0.054 (11)*
H7	0.002 (5)	0.307 (5)	−0.078 (4)	0.039 (9)*
H11	−0.078 (5)	0.200 (5)	0.397 (4)	0.043 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0557 (2)	0.0580 (3)	0.0382 (2)	−0.01529 (18)	−0.00347 (15)	−0.02506 (17)
Br2	0.0527 (3)	0.0579 (3)	0.0504 (2)	−0.00193 (18)	0.01973 (17)	−0.02811 (19)
O1	0.0362 (11)	0.0262 (10)	0.0330 (11)	0.0015 (9)	−0.0035 (9)	−0.0104 (9)
O3	0.0463 (13)	0.0281 (11)	0.0339 (11)	0.0012 (10)	−0.0012 (10)	−0.0102 (9)
C10	0.0317 (15)	0.0268 (14)	0.0282 (14)	−0.0116 (12)	0.0053 (11)	−0.0108 (12)
C8	0.0267 (14)	0.0221 (13)	0.0244 (13)	−0.0080 (11)	0.0018 (10)	−0.0080 (11)

C4	0.0292 (14)	0.0297 (14)	0.0297 (15)	−0.0133 (12)	0.0058 (11)	−0.0125 (12)
C11	0.0388 (17)	0.0306 (16)	0.0299 (15)	−0.0056 (13)	0.0095 (12)	−0.0121 (13)
C7	0.0284 (14)	0.0221 (13)	0.0270 (14)	−0.0095 (11)	0.0013 (11)	−0.0061 (11)
C9	0.0311 (15)	0.0263 (14)	0.0295 (15)	−0.0076 (12)	0.0015 (11)	−0.0092 (12)
C5	0.0232 (13)	0.0326 (15)	0.0347 (15)	−0.0088 (11)	0.0025 (11)	−0.0165 (12)
O2	0.0617 (16)	0.0375 (12)	0.0249 (12)	−0.0004 (11)	0.0004 (10)	−0.0055 (9)
C3	0.0438 (18)	0.0430 (19)	0.0318 (17)	−0.0180 (15)	0.0075 (14)	−0.0156 (15)
C1	0.0332 (17)	0.056 (2)	0.064 (2)	−0.0149 (16)	0.0159 (16)	−0.0424 (19)
C2	0.050 (2)	0.062 (2)	0.041 (2)	−0.0258 (18)	0.0204 (16)	−0.0328 (18)
C6	0.0262 (15)	0.0370 (17)	0.055 (2)	−0.0039 (13)	0.0006 (14)	−0.0248 (16)

Geometric parameters (Å, °)

Br1—C11	1.951 (3)	C11—H11	0.92 (4)
Br2—C11	1.922 (3)	C7—H7	0.90 (4)
O1—C5	1.374 (4)	C9—O2	1.199 (4)
O1—C9	1.375 (3)	C5—C6	1.384 (4)
O3—C10	1.212 (3)	C3—C2	1.363 (5)
C10—C8	1.492 (4)	C3—H3	0.90 (4)
C10—C11	1.519 (4)	C1—C6	1.375 (5)
C8—C7	1.347 (4)	C1—C2	1.387 (6)
C8—C9	1.470 (4)	C1—H1	0.94 (3)
C4—C5	1.395 (4)	C2—H2	0.89 (4)
C4—C3	1.407 (4)	C6—H6	0.90 (4)
C4—C7	1.422 (4)		
C5—O1—C9	123.3 (2)	O2—C9—O1	116.4 (3)
O3—C10—C8	120.2 (3)	O2—C9—C8	127.2 (3)
O3—C10—C11	120.5 (3)	O1—C9—C8	116.3 (2)
C8—C10—C11	119.3 (2)	O1—C5—C6	117.7 (3)
C7—C8—C9	119.9 (2)	O1—C5—C4	120.7 (2)
C7—C8—C10	117.6 (2)	C6—C5—C4	121.6 (3)
C9—C8—C10	122.5 (2)	C2—C3—C4	120.3 (3)
C5—C4—C3	118.2 (3)	C2—C3—H3	121 (2)
C5—C4—C7	117.4 (3)	C4—C3—H3	118 (2)
C3—C4—C7	124.5 (3)	C6—C1—C2	121.0 (3)
C10—C11—Br2	111.9 (2)	C6—C1—H1	113 (2)
C10—C11—Br1	105.6 (2)	C2—C1—H1	126 (2)
Br2—C11—Br1	110.47 (15)	C3—C2—C1	120.3 (3)
C10—C11—H11	112 (2)	C3—C2—H2	121 (3)
Br2—C11—H11	107 (2)	C1—C2—H2	119 (3)
Br1—C11—H11	110 (2)	C1—C6—C5	118.6 (3)
C8—C7—C4	122.3 (3)	C1—C6—H6	123 (3)
C8—C7—H7	118 (2)	C5—C6—H6	118 (3)
C4—C7—H7	119 (2)		
O3—C10—C8—C7	4.5 (4)	C7—C8—C9—O1	−1.3 (4)
C11—C10—C8—C7	−174.4 (3)	C10—C8—C9—O1	176.6 (2)
O3—C10—C8—C9	−173.4 (3)	C9—O1—C5—C6	178.2 (3)
C11—C10—C8—C9	7.6 (4)	C9—O1—C5—C4	−2.0 (4)
O3—C10—C11—Br2	21.6 (4)	C3—C4—C5—O1	−179.6 (3)

C8—C10—C11—Br2	−159.5 (2)	C7—C4—C5—O1	0.1 (4)
O3—C10—C11—Br1	−98.7 (3)	C3—C4—C5—C6	0.3 (4)
C8—C10—C11—Br1	80.3 (3)	C7—C4—C5—C6	180.0 (3)
C9—C8—C7—C4	−0.4 (4)	C5—C4—C3—C2	−0.1 (5)
C10—C8—C7—C4	−178.4 (2)	C7—C4—C3—C2	−179.7 (3)
C5—C4—C7—C8	1.0 (4)	C4—C3—C2—C1	−0.5 (5)
C3—C4—C7—C8	−179.3 (3)	C6—C1—C2—C3	0.9 (5)
C5—O1—C9—O2	−177.7 (3)	C2—C1—C6—C5	−0.7 (5)
C5—O1—C9—C8	2.5 (4)	O1—C5—C6—C1	179.9 (3)
C7—C8—C9—O2	178.9 (3)	C4—C5—C6—C1	0.1 (5)
C10—C8—C9—O2	−3.2 (5)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O2^{i}	0.92 (4)	2.46 (4)	3.278 (4)	148 (3)

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

Fig. 1

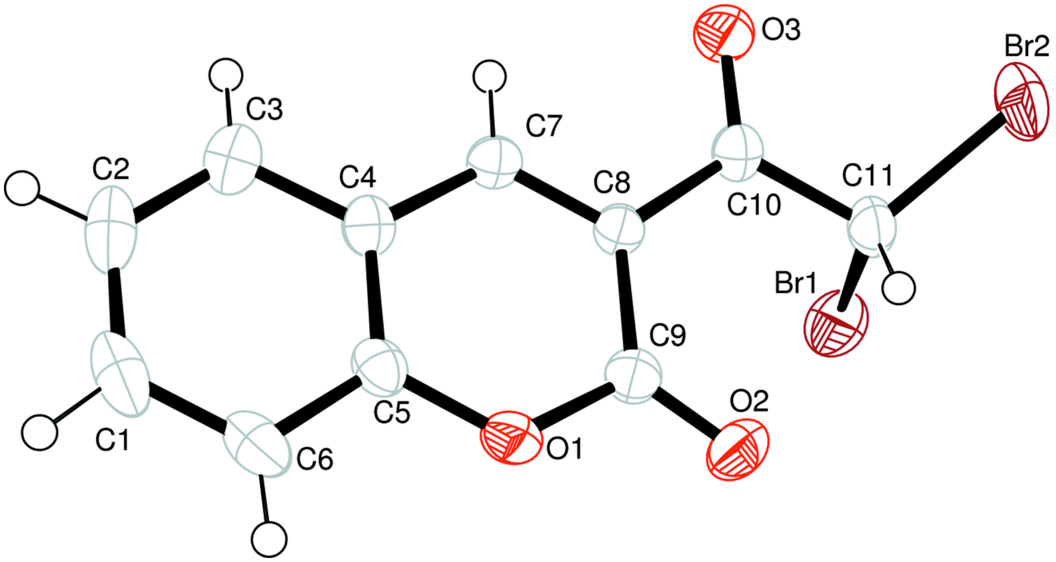

Fig. 2