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6,8-Dibromo-4-oxo-4*H*-chromene-3-carbaldehyde

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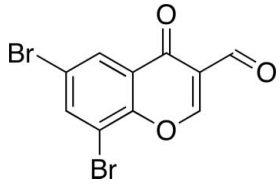
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.019; wR factor = 0.045; data-to-parameter ratio = 15.9.

In the title compound, $C_{10}H_4Br_2O_3$, the atoms of the 6,8-dibromochromone unit are essentially coplanar [largest deviation from the mean planes = 0.1109 (3) Å] and the formyl group is twisted slightly with respect to the attached ring [C—C—C—O torsion angles = 11.5 (4) and −168.9 (3)°]. In the crystal, molecules are linked to each other through halogen bonds [Br···O = 3.118 (2) Å, C—Br···O = 162.37 (8) and C=O···Br = 140.20 (15)°]. The molecules are further assembled *via* π–π stacking interactions [centroid–centroid distance = 3.850 (2) Å].

Related literature

For the biological activity of the title compound, see: Kawase *et al.* (2007). For its use as a starting material for the synthesis of alkaline phosphatase inhibitorsrelated literature, see: al-Rashida *et al.* (2013). For a related structure, see: Ishikawa & Motohashi (2013). For halogen bonding, see: Auffinger *et al.* (2004); Metrangolo *et al.* (2005); Wilcken *et al.* (2013); Sirimulla *et al.* (2013).



Experimental

Crystal data

$C_{10}H_4Br_2O_3$ M_r = 331.95
Monoclinic, $P2_1/c$
a = 11.910 (4) Å
b = 3.8500 (12) Å
c = 20.817 (6) Å
β = 95.69 (3)°
V = 949.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 8.54 mm^{-1}
T = 100 K
0.42 × 0.25 × 0.23 mm

Data collection

Rigaku AFC-7R diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.086, T_{max} = 0.140
2871 measured reflections
2163 independent reflections
1937 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.010
3 standard reflections every 150 reflections
intensity decay: −0.1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.045
S = 1.06
2163 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Data collection: *WinAFC* (Rigaku, 1999); cell refinement: *WinAFC*; data reduction: *WinAFC*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RN2123).

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supporting information

Acta Cryst. (2014). E**70**, o439 [doi:10.1107/S1600536814005327]

6,8-Dibromo-4-oxo-4*H*-chromene-3-carbaldehyde

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S1. Comment

The title compound shows tumor cell-cytotoxic, anti-HIV, anti-*Helicobacter pylori*, and urease inhibitory activities (Kawase *et al.* 2007). In addition, it is used as a starting material for the synthesis of alkaline phosphatase inhibitors (al-Rashida *et al.* 2013).

The atoms of 6,8-dibromo-chromone ring in the title compound is essentially coplanar, and the largest deviations is 0.1109 (3) Å for Br2. The formyl group is slightly twisted with respect to the attached ring [C1–C2–C10–O3 = 11.5 (4)° and C3–C2–C10–O3 = -168.9 (3)°].

In the crystal, the molecules are linked to each other through intermolecular interactions of the Br2 atom with the O3 atom of the formyl group [Br2···O3; 3.118 (2) Å, C7–Br2···O3^{i} = 162.37 (8)°, Br2···O^{i}–C10^{i} = 140.20 (15)° (i): -*x* + 2, -*y* + 1, -*z* + 1], as shown in Fig. 1. The short contact and the geometry of the Br···O interactions come within the range of halogen bonding (Auffinger *et al.* 2004). The similar geometry is found in the crystal structure of 6,8-dichloro-4-oxochromene-3-carbaldehyde (Ishikawa *et al.* 2013).

Halogen bonds have been found to occur in organic, inorganic, and biological systems, and have recently attracted much attention in medicinal chemistry, chemical biology, and supramolecular chemistry (Auffinger *et al.* 2004, Metrangolo *et al.* 2005, Wilcken *et al.* 2013, Sirimulla *et al.* 2013). Our analysis suggests that the strong inhibitory activity of the title compound against urease might be attributable to the halogen bond observed in the crystal, because 3-formylchromones without any halogen atom at the 8-position in the literature do not show the urease inhibitory activity (Kawase *et al.* 2007).

S2. Experimental

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a 2-butanone solution of commercially available title compound at room temperature.

S3. Refinement

The C(sp^2)-bound hydrogen atoms were placed in geometrical positions [C—H 0.95 Å, U_{iso}(H) = 1.2U_{eq}(C)], and refined using a riding model.

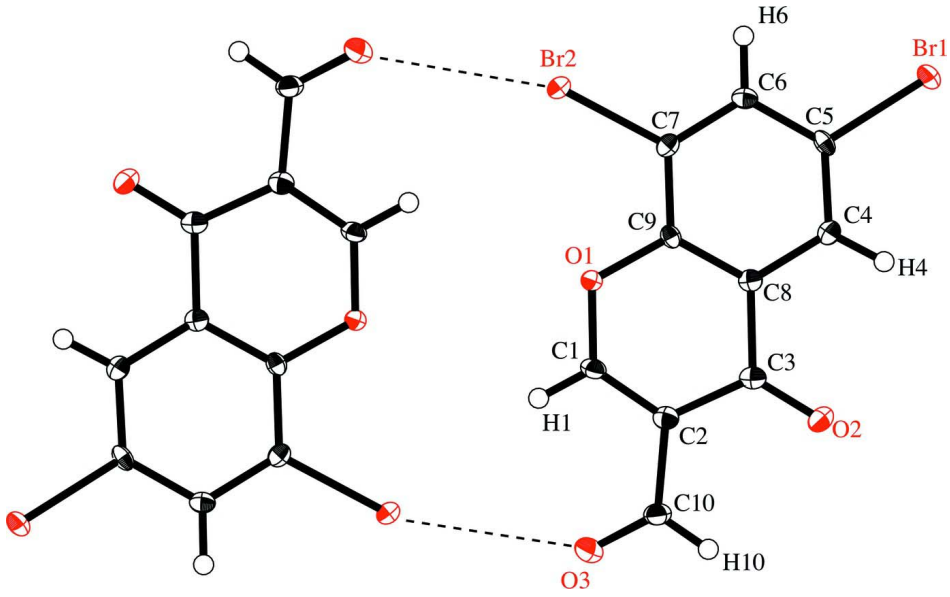

Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius. The intermolecular interaction of the title compound is represented as dashed lines for Br···O.

6,8-Dibromo-4-oxo-4*H*-chromene-3-carbaldehyde

Crystal data

$C_{10}H_4Br_2O_3$
$M_r = 331.95$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.910$ (4) Å
$b = 3.8500$ (12) Å
$c = 20.817$ (6) Å
$\beta = 95.69$ (3)°
$V = 949.8$ (5) Å^3
$Z = 4$
$F(000) = 632.00$
$D_x = 2.321$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.0$–$17.3°$
$\mu = 8.54$ mm^{-1}
$T = 100$ K
Block, colorless
0.42 × 0.25 × 0.23 mm

Data collection

Rigaku AFC-7R diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.086$, $T_{max} = 0.140$
2871 measured reflections
2163 independent reflections
1937 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.010$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -2 \rightarrow 4$
$l = -14 \rightarrow 26$
3 standard reflections every 150 reflections
intensity decay: −0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.045$
$S = 1.06$
2163 reflections
136 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2 + 0.9331P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.573035 (18)	0.93086 (6)	0.699129 (10)	0.01429 (7)
Br2	0.985432 (18)	0.27016 (6)	0.660364 (10)	0.01402 (6)
O1	0.88801 (13)	0.2982 (5)	0.52224 (7)	0.0135 (4)
O2	0.59071 (14)	0.7059 (5)	0.43970 (8)	0.0183 (4)
O3	0.78264 (15)	0.1122 (6)	0.32871 (8)	0.0230 (4)
C1	0.85463 (19)	0.2641 (7)	0.45870 (10)	0.0137 (5)
C2	0.75650 (19)	0.3792 (7)	0.42904 (10)	0.0138 (5)
C3	0.67683 (19)	0.5722 (7)	0.46469 (10)	0.0132 (5)
C4	0.63812 (18)	0.7387 (6)	0.57688 (10)	0.0125 (5)
C5	0.67063 (18)	0.7382 (7)	0.64209 (10)	0.0122 (5)
C6	0.77314 (18)	0.5989 (7)	0.66820 (10)	0.0129 (5)
C7	0.84520 (18)	0.4570 (7)	0.62724 (10)	0.0123 (5)
C8	0.71085 (18)	0.5882 (7)	0.53541 (10)	0.0119 (5)
C9	0.81363 (18)	0.4500 (6)	0.56088 (10)	0.0111 (5)
C10	0.7291 (2)	0.3114 (7)	0.35894 (11)	0.0173 (5)
H1	0.9046	0.1492	0.4329	0.0165*
H4	0.5682	0.8381	0.5602	0.0149*
H6	0.7932	0.6016	0.7135	0.0155*
H10	0.6668	0.4296	0.3368	0.0208*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01503 (11)	0.01571 (12)	0.01299 (11)	0.00054 (9)	0.00562 (8)	−0.00072 (9)
Br2	0.01206 (11)	0.01685 (12)	0.01260 (11)	0.00133 (9)	−0.00153 (8)	0.00018 (9)
O1	0.0109 (8)	0.0193 (9)	0.0102 (7)	0.0017 (7)	0.0008 (6)	−0.0015 (7)
O2	0.0151 (8)	0.0233 (10)	0.0159 (8)	0.0032 (8)	−0.0015 (7)	0.0023 (8)
O3	0.0206 (9)	0.0327 (11)	0.0157 (8)	0.0031 (9)	0.0015 (7)	−0.0066 (8)
C1	0.0151 (11)	0.0162 (12)	0.0099 (10)	−0.0017 (10)	0.0013 (8)	−0.0029 (9)
C2	0.0142 (11)	0.0145 (12)	0.0128 (11)	−0.0025 (10)	0.0013 (9)	−0.0005 (9)
C3	0.0142 (11)	0.0137 (12)	0.0117 (10)	−0.0038 (10)	0.0013 (8)	0.0008 (9)
C4	0.0107 (10)	0.0117 (12)	0.0148 (11)	−0.0015 (9)	0.0003 (8)	0.0009 (9)
C5	0.0121 (11)	0.0114 (12)	0.0141 (10)	−0.0025 (10)	0.0072 (8)	−0.0014 (9)
C6	0.0150 (11)	0.0135 (12)	0.0103 (10)	−0.0022 (10)	0.0013 (8)	0.0006 (9)

C7	0.0109 (10)	0.0123 (12)	0.0136 (11)	−0.0007 (9)	−0.0004 (8)	0.0012 (9)
C8	0.0114 (10)	0.0125 (12)	0.0119 (10)	−0.0029 (10)	0.0017 (8)	0.0012 (9)
C9	0.0108 (10)	0.0110 (11)	0.0122 (10)	−0.0008 (9)	0.0041 (8)	0.0002 (9)
C10	0.0157 (11)	0.0241 (14)	0.0117 (11)	−0.0008 (11)	−0.0006 (9)	−0.0006 (10)

Geometric parameters (Å, º)

Br1—C5	1.893 (3)	C4—C5	1.374 (3)
Br2—C7	1.885 (3)	C4—C8	1.407 (4)
O1—C1	1.349 (3)	C5—C6	1.394 (3)
O1—C9	1.384 (3)	C6—C7	1.381 (4)
O2—C3	1.217 (3)	C7—C9	1.395 (3)
O3—C10	1.213 (4)	C8—C9	1.391 (3)
C1—C2	1.342 (3)	C1—H1	0.950
C2—C3	1.464 (4)	C4—H4	0.950
C2—C10	1.486 (3)	C6—H6	0.950
C3—C8	1.489 (3)	C10—H10	0.950
Br2···O1	2.9940 (17)	C10···O2^{v}	3.395 (4)
O1···C3	2.877 (3)	C10···O3^{iii}	3.223 (4)
O2···C1	3.561 (3)	Br1···H4	2.9089
O2···C4	2.858 (3)	Br1···H6	2.9009
O2···C10	2.898 (4)	Br2···H6	2.9323
O3···C1	2.818 (3)	O2···H4	2.5993
C1···C7	3.599 (4)	O2···H10	2.6314
C1···C8	2.753 (4)	O3···H1	2.4918
C2···C9	2.775 (3)	C1···H10	3.2748
C4···C7	2.801 (3)	C3···H1	3.2875
C5···C9	2.750 (4)	C3···H4	2.6802
C6···C8	2.790 (3)	C3···H10	2.7091
Br1···Br1^{i}	3.4567 (8)	C4···H6	3.2769
Br1···Br1^{ii}	3.4567 (8)	C6···H4	3.2818
Br1···C5^{iii}	3.563 (3)	C9···H1	3.1918
Br2···O3^{iv}	3.118 (2)	C9···H4	3.2814
Br2···C7^{v}	3.583 (3)	C9···H6	3.2634
O1···O1^{vi}	3.298 (3)	C10···H1	2.5478
O1···C1^{vi}	3.486 (3)	H1···H10	3.4736
O1···C8^{v}	3.481 (3)	Br1···H10^{vii}	3.1969
O1···C9^{v}	3.498 (3)	Br1···H10^{xi}	3.0191
O2···C2^{iii}	3.280 (3)	Br2···H1^{iv}	2.9314
O2···C3^{iii}	3.513 (4)	Br2···H1^{vi}	3.3140
O2···C4^{vii}	3.208 (3)	Br2···H6^{xii}	3.5908
O2···C4^{viii}	3.455 (3)	O1···H1^{iv}	3.0794
O2···C10^{iii}	3.395 (4)	O1···H1^{vi}	3.3226
O3···Br2^{iv}	3.118 (2)	O2···H4^{vii}	2.8234
O3···C2^{v}	3.543 (4)	O2···H4^{viii}	2.5820
O3···C6^{ix}	3.430 (3)	O3···H6^{ix}	2.5500
O3···C10^{v}	3.223 (4)	O3···H10^{v}	2.9808

C1···O1^{vi}	3.486 (3)	C1···H1^{iii}	3.5101
C1···C3^{v}	3.413 (4)	C2···H1^{iii}	3.4467
C1···C8^{v}	3.577 (4)	C3···H4^{vii}	3.3142
C2···O2^{v}	3.280 (3)	C4···H4^{v}	3.5744
C2···O3^{iii}	3.543 (4)	C8···H4^{v}	3.4152
C2···C3^{v}	3.353 (4)	C10···H6^{ix}	3.5682
C3···O2^{v}	3.513 (4)	C10···H10^{v}	3.4959
C3···C1^{iii}	3.413 (4)	H1···Br2^{iv}	2.9314
C3···C2^{iii}	3.353 (4)	H1···Br2^{vi}	3.3140
C4···O2^{vii}	3.208 (3)	H1···O1^{iv}	3.0794
C4···O2^{viii}	3.455 (3)	H1···O1^{vi}	3.3226
C4···C8^{iii}	3.513 (4)	H1···C1^{v}	3.5101
C4···C9^{iii}	3.481 (4)	H1···C2^{v}	3.4467
C5···Br1^{v}	3.563 (3)	H4···O2^{vii}	2.8234
C5···C6^{iii}	3.555 (4)	H4···O2^{viii}	2.5820
C5···C7^{iii}	3.493 (4)	H4···C3^{vii}	3.3142
C6···O3^{x}	3.430 (3)	H4···C4^{iii}	3.5744
C6···C5^{v}	3.555 (4)	H4···C8^{iii}	3.4152
C6···C7^{iii}	3.539 (4)	H4···H4^{viii}	3.1095
C7···Br2^{iii}	3.583 (3)	H6···Br2^{xiii}	3.5908
C7···C5^{v}	3.493 (4)	H6···O3^{x}	2.5500
C7···C6^{v}	3.539 (4)	H6···C10^{x}	3.5682
C8···O1^{iii}	3.481 (3)	H6···H10^{xi}	3.5884
C8···C1^{iii}	3.577 (4)	H10···Br1^{vii}	3.1969
C8···C4^{v}	3.513 (4)	H10···Br1^{xiv}	3.0191
C8···C9^{iii}	3.558 (4)	H10···O3^{iii}	2.9808
C9···O1^{iii}	3.498 (3)	H10···C10^{iii}	3.4959
C9···C4^{v}	3.481 (4)	H10···H6^{xiv}	3.5884
C9···C8^{v}	3.558 (4)		

C1—O1—C9	117.88 (17)	C3—C8—C4	119.99 (19)
O1—C1—C2	125.3 (3)	C3—C8—C9	120.3 (2)
C1—C2—C3	120.9 (2)	C4—C8—C9	119.73 (19)
C1—C2—C10	119.3 (3)	O1—C9—C7	117.29 (19)
C3—C2—C10	119.8 (2)	O1—C9—C8	122.01 (19)
O2—C3—C2	124.0 (2)	C7—C9—C8	120.7 (2)
O2—C3—C8	122.7 (3)	O3—C10—C2	123.0 (3)
C2—C3—C8	113.31 (19)	O1—C1—H1	117.367
C5—C4—C8	118.4 (2)	C2—C1—H1	117.366
Br1—C5—C4	119.25 (17)	C5—C4—H4	120.820
Br1—C5—C6	118.34 (16)	C8—C4—H4	120.803
C4—C5—C6	122.4 (2)	C5—C6—H6	120.481
C5—C6—C7	119.05 (19)	C7—C6—H6	120.472
Br2—C7—C6	120.49 (16)	O3—C10—H10	118.496
Br2—C7—C9	119.78 (17)	C2—C10—H10	118.482
C6—C7—C9	119.7 (2)		

C1—O1—C9—C7	174.68 (18)	C8—C4—C5—Br1	−178.77 (18)

C1—O1—C9—C8	−4.8 (3)	C8—C4—C5—C6	0.9 (4)
C9—O1—C1—C2	3.1 (4)	H4—C4—C5—Br1	1.2
C9—O1—C1—H1	−176.9	H4—C4—C5—C6	−179.1
O1—C1—C2—C3	2.7 (4)	H4—C4—C8—C3	−2.2
O1—C1—C2—C10	−177.74 (19)	H4—C4—C8—C9	178.8
H1—C1—C2—C3	−177.3	Br1—C5—C6—C7	179.91 (14)
H1—C1—C2—C10	2.3	Br1—C5—C6—H6	−0.1
C1—C2—C3—O2	174.2 (3)	C4—C5—C6—C7	0.3 (4)
C1—C2—C3—C8	−6.2 (4)	C4—C5—C6—H6	−179.8
C1—C2—C10—O3	11.5 (4)	C5—C6—C7—Br2	179.31 (18)
C1—C2—C10—H10	−168.5	C5—C6—C7—C9	−1.1 (4)
C3—C2—C10—O3	−168.9 (3)	H6—C6—C7—Br2	−0.7
C3—C2—C10—H10	11.1	H6—C6—C7—C9	178.9
C10—C2—C3—O2	−5.4 (4)	Br2—C7—C9—O1	0.9 (3)
C10—C2—C3—C8	174.23 (19)	Br2—C7—C9—C8	−179.62 (14)
O2—C3—C8—C4	5.1 (4)	C6—C7—C9—O1	−178.7 (2)
O2—C3—C8—C9	−175.9 (2)	C6—C7—C9—C8	0.8 (4)
C2—C3—C8—C4	−174.51 (19)	C3—C8—C9—O1	0.8 (4)
C2—C3—C8—C9	4.5 (3)	C3—C8—C9—C7	−178.61 (19)
C5—C4—C8—C3	177.82 (19)	C4—C8—C9—O1	179.8 (2)
C5—C4—C8—C9	−1.2 (4)	C4—C8—C9—C7	0.4 (4)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*+1, *y*+1/2, −*z*+3/2; (iii) *x*, *y*+1, *z*; (iv) −*x*+2, −*y*, −*z*+1; (v) *x*, *y*−1, *z*; (vi) −*x*+2, −*y*+1, −*z*+1; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*+2, −*z*+1; (ix) *x*, −*y*+1/2, *z*−1/2; (x) *x*, −*y*+1/2, *z*+1/2; (xi) *x*, −*y*+3/2, *z*+1/2; (xii) −*x*+2, *y*−1/2, −*z*+3/2; (xiii) −*x*+2, *y*+1/2, −*z*+3/2; (xiv) *x*, −*y*+3/2, *z*−1/2.