# organic compounds

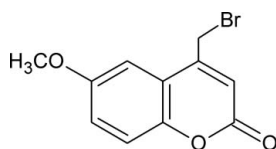# 4-Bromomethyl-6-methoxy-2*H*-chromen-2-one

## Ramakrishna Gowda,[a]*‡ Mahantesha Basanagouda,[b] Manohar V. Kulkarni[b] and K.V. Arjuna Gowda[c]

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The structure of the title coumarin derivative, $C_{11}H_9BrO_3$, is stabilized by weak intermolecular C—H···O hydrogen bonds.

## Related literature

For the properties of coumarins, see: Kulkarni *et al.* (2006); Fylaktakidou *et al.* (2004); Neyts *et al.* (2009); Kempen *et al.* (2003). For structural analysis of coumarins, see: Gnanaguru *et al.* (1985); Munshi & Guru Row (2005); Gavuzzo *et al.* (1974); Moorthy *et al.* (2003); Katerinopoulos (2004). For Br-containing coumarins, see: Gaultier & Hauw (1965); Kokila *et al.* (1996); Vasudevan *et al.* (1991).



## Experimental

### Crystal data

$C_{11}H_9BrO_3$
$M_r = 269.09$
Monoclinic, $P2_1/n$
$a = 4.3573\ (3)$ Å
$b = 9.2859\ (6)$ Å
$c = 25.2677\ (17)$ Å
$\beta = 91.927\ (3)°$

$V = 1021.79\ (12)$ Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.01$ mm$^{-1}$
$T = 293$ K
$0.25 \times 0.15 \times 0.1$ mm

### Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.434$, $T_{max} = 0.501$

9950 measured reflections
2128 independent reflections
1501 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.101$
$S = 0.96$
2128 reflections

137 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.93$ e Å$^{-3}$
$\Delta\rho_{min} = -0.26$ e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2···O1[i] | 0.93 | 2.60 | 3.451 (4) | 152 |
| C2—H2···O2[i] | 0.93 | 2.58 | 3.446 (5) | 155 |
| C10—H10A···O2[i] | 0.97 | 2.57 | 3.437 (5) | 148 |
| C8—H8···O2[ii] | 0.93 | 2.56 | 3.433 (5) | 156 |
| C10—H10A···O1[iii] | 0.97 | 2.98 | 3.601 (4) | 122 |

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

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# supporting information

## 4-Bromomethyl-6-methoxy-2*H*-chromen-2-one

### Ramakrishna Gowda, Mahantesha Basanagouda, Manohar V. Kulkarni and K.V. Arjuna Gowda

### S1. Comment

Coumarins are a class of naturally occurring oxygen heterocycles which have been found to exhibit wide ranging biological activities (Kulkarni *et al.*, 2006; Fylaktakidou *et al.*, 2004; Neyts *et al.*, 2009) through its innumerable derivatives. Structural studies on coumarins have been focused on their solid state photochemical dimerization (Gnanaguru *et al.*, 1985), hydrogen bonding (Munshi *et al.*, 2005), mode of packing (Gavuzzo *et al.*, 1974), molecular self assembling (Moorthy *et al.*, 2003) and photophysical properties (Katerinopoulos *et al.*, 2004). Introduction of bromine has resulted in formation of hydrates, intermolecular hydrogen bonds, and eclipsed conformation, as observed in 3-bromocoumarin (Gaultier *et al.*, 1965), 6-bromo-3-acetylcoumarin (Kokila *et al.*, 1996), and 3-bromoacetylcoumarin (Vasudevan *et al.*, 1991), respectively. 3-Bromophenyl-6-acetoxymethyl-coumarin-3-carboxylates have been found to exhibit potential anticancer and antitumour activity (Kempen *et al.*, 2003).

The title compound is cyclic, planar and aromatic in nature due to the continuous delocalization of electrons over the coumarin rings system. There is a significant deviation from trigonality in bond angle at O1—C1—C2 [117.0 (3)°], due to the electronic repulsion of atom O2 which is bonded to C1. This is also reflected at C9—C4—C5 [117.9 (3)°] and C9—C4—C3 [117.6 (3)°] but these are due to fused benzene and *α* pyrone rings. Another significant deviation in bond angle is observed at C6—O3—C11 [118.0 (3)°] due to the repulsion between lone pair electrons of atom O3 with valence electrons of C6—O3 and O3—C11 bonds.

### S2. Experimental

To a mixture of equimolar quantity of 4-methoxy phenol (0.1 mol) and 4-bromoethylacetoacetate (0.1 mol) was added drop wise sulfuric acid (30 ml) with stirring and maintaining the temperature between 0-5 °C. The reaction mixture was allowed to stand in ice chest overnight and deep red coloured solution was poured into the stream of crushed ice. Solid separated was filtered and washed with water and then with cold ethanol so as to get a colourless compound. Finally, it is recrystallized from acetic acid.

### S3. Refinement

All the H atoms were positioned geometrically and refined using a riding model with bond lengths 0.97 (methylene), 0.96 (methyl) or 0.93 Å (aromatic). Isotropic displacement parameters were calculated as $U\text{iso}\sim(H) = 1.5U\sim\text{eq}\sim(C)$ for methyl group C11 and $U\text{iso}\sim(H) = 1.2U\sim\text{eq}\sim(C)$ for all other H atoms.
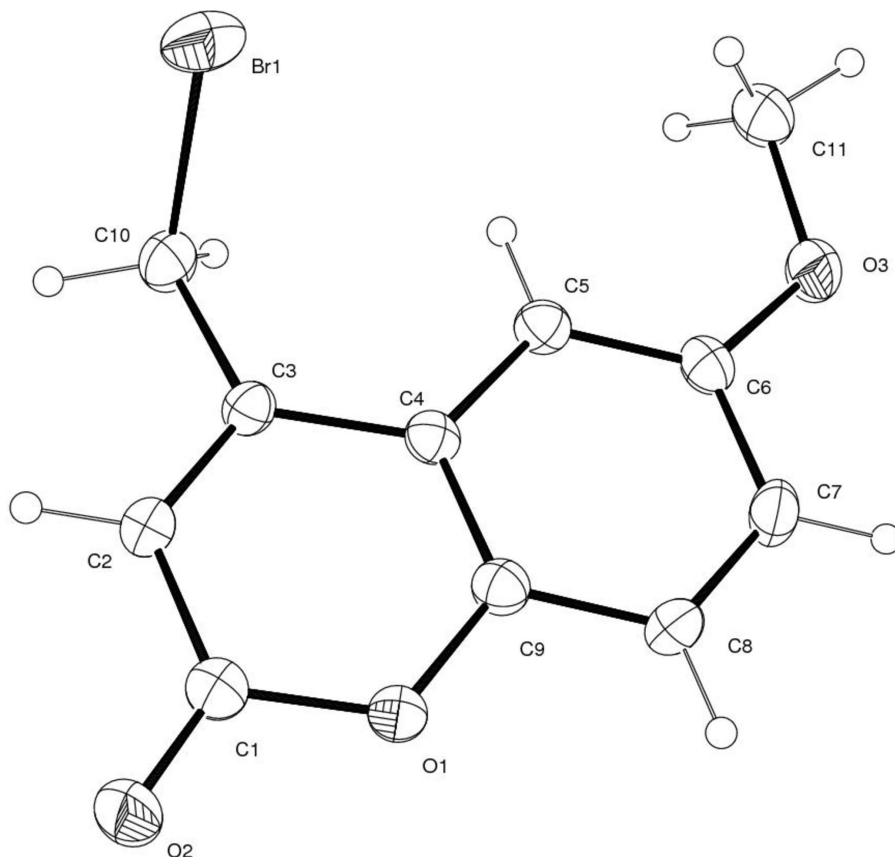
**Figure 1**
*ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

**4-Bromomethyl-6-methoxy-2*H*-chromen-2-one**

*Crystal data*

| | |
|---|---|
| $C_{11}H_9BrO_3$ | $F(000) = 536$ |
| $M_r = 269.09$ | $D_x = 1.749$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 3217 reflections |
| $a = 4.3573$ (3) Å | $\theta = 2.3$–25.4° |
| $b = 9.2859$ (6) Å | $\mu = 4.01$ mm$^{-1}$ |
| $c = 25.2677$ (17) Å | $T = 293$ K |
| $\beta = 91.927$ (3)° | Needle, colourless |
| $V = 1021.79$ (12) Å$^3$ | $0.25 \times 0.15 \times 0.1$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker Kappa APEXII CCD diffractometer | 9950 measured reflections |
| Radiation source: fine-focus sealed tube | 2128 independent reflections |
| Graphite monochromator | 1501 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scans | $R_{int} = 0.037$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2004) | $\theta_{max} = 26.6°$, $\theta_{min} = 2.3°$ |
| $T_{min} = 0.434$, $T_{max} = 0.501$ | $h = -5 \rightarrow 3$ |
| | $k = -11 \rightarrow 11$ |
| | $l = -31 \rightarrow 31$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.101$ | |
| $S = 0.96$ | H-atom parameters constrained |
| 2128 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 1.203P]$ |
| 137 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} = 0.008$ |
| 0 constraints | $\Delta\rho_{max} = 0.93$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{min} = -0.26$ e Å$^{-3}$ |

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.3658 (8) | 0.2636 (4) | 0.73840 (14) | 0.0406 (9) |
| C2 | 0.4641 (8) | 0.1339 (4) | 0.71330 (13) | 0.0375 (8) |
| H2 | 0.3944 | 0.0462 | 0.7260 | 0.045* |
| C3 | 0.6518 (7) | 0.1332 (4) | 0.67239 (13) | 0.0321 (7) |
| C4 | 0.7577 (7) | 0.2706 (4) | 0.65171 (12) | 0.0318 (7) |
| C5 | 0.9489 (7) | 0.2851 (4) | 0.60828 (13) | 0.0348 (8) |
| H5 | 1.0139 | 0.2035 | 0.5905 | 0.042* |
| C6 | 1.0401 (7) | 0.4188 (4) | 0.59198 (13) | 0.0378 (9) |
| C7 | 0.9456 (8) | 0.5407 (4) | 0.61872 (14) | 0.0429 (9) |
| H7 | 1.0121 | 0.6311 | 0.6081 | 0.051* |
| C8 | 0.7556 (8) | 0.5293 (4) | 0.66048 (14) | 0.0401 (9) |
| H8 | 0.6889 | 0.6113 | 0.6778 | 0.048* |
| C9 | 0.6642 (7) | 0.3941 (4) | 0.67652 (13) | 0.0345 (8) |
| C10 | 0.7530 (9) | −0.0074 (4) | 0.65024 (14) | 0.0421 (9) |
| H10A | 0.7086 | −0.0837 | 0.6751 | 0.050* |
| H10B | 0.9733 | −0.0052 | 0.6460 | 0.050* |
| C11 | 1.2815 (9) | 0.3270 (5) | 0.51587 (15) | 0.0535 (11) |
| H11A | 1.4005 | 0.2554 | 0.5347 | 0.080* |
| H11B | 1.3939 | 0.3612 | 0.4863 | 0.080* |
| H11C | 1.0908 | 0.2856 | 0.5033 | 0.080* |
| O1 | 0.4744 (5) | 0.3905 (3) | 0.71899 (9) | 0.0397 (6) |
| O2 | 0.1939 (7) | 0.2719 (3) | 0.77495 (11) | 0.0569 (7) |
| O3 | 1.2213 (6) | 0.4438 (3) | 0.55030 (10) | 0.0500 (7) |
| Br1 | 0.54925 (10) | −0.04981 (5) | 0.582134 (17) | 0.0612 (2) |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0437 (19) | 0.039 (2) | 0.039 (2) | −0.0003 (18) | 0.0059 (16) | −0.0004 (17) |
| C2 | 0.0442 (19) | 0.029 (2) | 0.0390 (19) | −0.0025 (16) | 0.0024 (16) | 0.0004 (16) |
| C3 | 0.0345 (17) | 0.027 (2) | 0.0344 (18) | 0.0024 (15) | 0.0010 (14) | −0.0003 (14) |
| C4 | 0.0310 (16) | 0.034 (2) | 0.0301 (17) | 0.0032 (15) | −0.0022 (13) | 0.0012 (15) |
| C5 | 0.0338 (17) | 0.036 (2) | 0.0350 (18) | 0.0037 (16) | 0.0031 (14) | −0.0014 (16) |
| C6 | 0.0371 (18) | 0.042 (2) | 0.0343 (19) | −0.0030 (16) | 0.0050 (15) | 0.0044 (15) |

| C7 | 0.051 (2) | 0.030 (2) | 0.048 (2) | −0.0055 (18) | 0.0027 (17) | 0.0076 (17) |
| C8 | 0.050 (2) | 0.029 (2) | 0.042 (2) | 0.0018 (17) | 0.0008 (16) | −0.0045 (16) |
| C9 | 0.0335 (17) | 0.037 (2) | 0.0333 (18) | −0.0008 (15) | 0.0020 (14) | −0.0007 (15) |
| C10 | 0.048 (2) | 0.032 (2) | 0.046 (2) | 0.0050 (17) | 0.0039 (17) | 0.0013 (17) |
| C11 | 0.063 (3) | 0.053 (3) | 0.045 (2) | 0.000 (2) | 0.0162 (19) | 0.002 (2) |
| O1 | 0.0483 (14) | 0.0339 (15) | 0.0376 (13) | 0.0013 (12) | 0.0117 (11) | −0.0024 (11) |
| O2 | 0.0759 (19) | 0.0461 (18) | 0.0508 (16) | 0.0039 (15) | 0.0305 (15) | −0.0005 (13) |
| O3 | 0.0618 (16) | 0.0435 (17) | 0.0460 (15) | −0.0072 (13) | 0.0208 (13) | 0.0030 (13) |
| Br1 | 0.0732 (3) | 0.0518 (3) | 0.0587 (3) | 0.0043 (2) | 0.0017 (2) | −0.0214 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O2 | 1.211 (4) | C7—C8 | 1.367 (5) |
| C1—O1 | 1.367 (4) | C7—H7 | 0.9300 |
| C1—C2 | 1.434 (5) | C8—C9 | 1.382 (5) |
| C2—C3 | 1.340 (5) | C8—H8 | 0.9300 |
| C2—H2 | 0.9300 | C9—O1 | 1.377 (4) |
| C3—C4 | 1.459 (5) | C10—Br1 | 1.950 (4) |
| C3—C10 | 1.493 (5) | C10—H10A | 0.9700 |
| C4—C9 | 1.375 (5) | C10—H10B | 0.9700 |
| C4—C5 | 1.406 (5) | C11—O3 | 1.420 (5) |
| C5—C6 | 1.371 (5) | C11—H11A | 0.9600 |
| C5—H5 | 0.9300 | C11—H11B | 0.9600 |
| C6—O3 | 1.357 (4) | C11—H11C | 0.9600 |
| C6—C7 | 1.388 (5) | | |
| | | | |
| O2—C1—O1 | 116.7 (3) | C7—C8—C9 | 119.0 (3) |
| O2—C1—C2 | 126.3 (4) | C7—C8—H8 | 120.5 |
| O1—C1—C2 | 117.0 (3) | C9—C8—H8 | 120.5 |
| C3—C2—C1 | 123.0 (3) | C4—C9—C8 | 122.1 (3) |
| C3—C2—H2 | 118.5 | C4—C9—O1 | 122.0 (3) |
| C1—C2—H2 | 118.5 | C8—C9—O1 | 115.9 (3) |
| C2—C3—C4 | 118.7 (3) | C3—C10—Br1 | 112.1 (2) |
| C2—C3—C10 | 119.3 (3) | C3—C10—H10A | 109.2 |
| C4—C3—C10 | 122.0 (3) | Br1—C10—H10A | 109.2 |
| C9—C4—C5 | 117.9 (3) | C3—C10—H10B | 109.2 |
| C9—C4—C3 | 117.6 (3) | Br1—C10—H10B | 109.2 |
| C5—C4—C3 | 124.5 (3) | H10A—C10—H10B | 107.9 |
| C6—C5—C4 | 120.4 (3) | O3—C11—H11A | 109.5 |
| C6—C5—H5 | 119.8 | O3—C11—H11B | 109.5 |
| C4—C5—H5 | 119.8 | H11A—C11—H11B | 109.5 |
| O3—C6—C5 | 124.7 (3) | O3—C11—H11C | 109.5 |
| O3—C6—C7 | 115.4 (3) | H11A—C11—H11C | 109.5 |
| C5—C6—C7 | 119.9 (3) | H11B—C11—H11C | 109.5 |
| C8—C7—C6 | 120.7 (3) | C1—O1—C9 | 121.6 (3) |
| C8—C7—H7 | 119.7 | C6—O3—C11 | 118.0 (3) |
| C6—C7—H7 | 119.7 | | |

| | | | |
|---|---|---|---|
| O2—C1—C2—C3 | 179.0 (3) | C5—C4—C9—C8 | −0.9 (5) |
| O1—C1—C2—C3 | −0.5 (5) | C3—C4—C9—C8 | 179.0 (3) |
| C1—C2—C3—C4 | −1.0 (5) | C5—C4—C9—O1 | 179.3 (3) |
| C1—C2—C3—C10 | 177.4 (3) | C3—C4—C9—O1 | −0.8 (4) |
| C2—C3—C4—C9 | 1.6 (4) | C7—C8—C9—C4 | −0.2 (5) |
| C10—C3—C4—C9 | −176.7 (3) | C7—C8—C9—O1 | 179.6 (3) |
| C2—C3—C4—C5 | −178.5 (3) | C2—C3—C10—Br1 | 106.3 (3) |
| C10—C3—C4—C5 | 3.2 (5) | C4—C3—C10—Br1 | −75.4 (3) |
| C9—C4—C5—C6 | 0.7 (5) | O2—C1—O1—C9 | −178.1 (3) |
| C3—C4—C5—C6 | −179.2 (3) | C2—C1—O1—C9 | 1.4 (5) |
| C4—C5—C6—O3 | −179.3 (3) | C4—C9—O1—C1 | −0.8 (5) |
| C4—C5—C6—C7 | 0.5 (5) | C8—C9—O1—C1 | 179.4 (3) |
| O3—C6—C7—C8 | 178.2 (3) | C5—C6—O3—C11 | 10.6 (5) |
| C5—C6—C7—C8 | −1.6 (5) | C7—C6—O3—C11 | −169.2 (3) |
| C6—C7—C8—C9 | 1.4 (5) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2···O1[i] | 0.93 | 2.60 | 3.451 (4) | 152 |
| C2—H2···O2[i] | 0.93 | 2.58 | 3.446 (5) | 155 |
| C10—H10*A*···O2[i] | 0.97 | 2.57 | 3.437 (5) | 148 |
| C8—H8···O2[ii] | 0.93 | 2.56 | 3.433 (5) | 156 |
| C10—H10*A*···O1[iii] | 0.97 | 2.98 | 3.601 (4) | 122 |

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+3/2; (ii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iii) −*x*+3/2, *y*−1/2, −*z*+3/2.