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4-Bromomethyl-7-methyl-6,8-dinitrocoumarin

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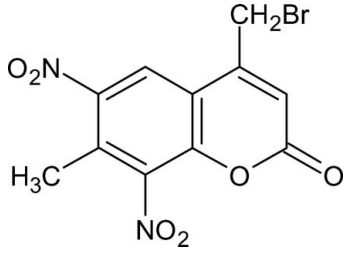
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.010 Å; R factor = 0.060; wR factor = 0.171; data-to-parameter ratio = 12.1.

The crystal structure of the title compound, $C_{11}H_7BrN_2O_6$, establishes the substitution positions of the nitro groups from the nitration reaction of 7-methyl-4-bromomethyl coumarin. The mean planes of the nitro groups form dihedral angles of 43.9 (8) and 52.7 (10)° with the essentially planar [maximum deviation 0.031 (6) Å] benzopyran ring system.

Related literature

For background information on the nitration of coumarin compounds, see: Kulkarni *et al.* (1983); Clayton *et al.* (1910). For a related structure, see: Vasudevan *et al.* (1990). For *ab initio* calculations on 6-methyl-4-bromomethylcoumarins, see: Sortur *et al.* (2006).



Experimental

Crystal data

$C_{11}H_7BrN_2O_6$ M_r = 343.09
Orthorhombic, *Pbca*
a = 8.122 (2) Å
b = 11.091 (4) Å
c = 27.723 (6) Å
V = 2497.3 (12) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.32 mm^{-1}
T = 294 K
0.2 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.520, T_{max} = 0.72
2196 measured reflections
2196 independent reflections
1148 reflections with $I > 2\sigma(I)$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.171
S = 1.05
2196 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2864).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Clayton, A. (1910). *J. Chem. Soc.* **97**, 1397–1408.
Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Kulkarni, M. V., Pujar, B. G. & Patil, V. D. (1983). *Arch. Pharm.* **316**, 15–21.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sortur, V., Yenagi, J., Tonannavar, J., Jadhav, V. B. & Kulkarni, M. V. (2006). *Spectrochim. Acta A*, **64**, 301–307.
Vasudevan, K. T., Puttaraja, & Kulkarni, M. V. (1990). *Acta Cryst.* C**46**, 2129–2131.

supporting information

Acta Cryst. (2009). E**65**, o2446 [doi:10.1107/S160053680903596X]

4-Bromomethyl-7-methyl-6,8-dinitrocoumarin

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S1. Comment

The molecular structure of the title compound is shown in Fig. 1. The bromomethyl group is twisted is out of the plane of the benzopyran ring as described by the torsion angle of 104.6 (7)° for C2-C3-C10-Br. This is in agreement with the ab initio calculations on 6-methyl-4- bromomethylcoumarins (Sortur *et al.*, 2006). Positions C-6 and C-8 (refers to positions from systematic naming scheme) become activated due to the electron donating methyl group at C-7 and hence nitration occurs at C-6 and C-8 consistent with the title compound which is also in agreement with earlier reports (Clayton, 1910; Kulkarni *et al.*, 1983).

S2. Experimental

5.06 g of 7-methyl-4-bromomethyl coumarin (0.02 mol) was dissolved in conc. sulfuric acid (10 ml) and treated with a nitrating mixture 15 ml (10 ml H_2SO_4 + 5 ml HNO_3) at ice bath temperatures (273-278K). The reaction mixture was then allowed to stand at room temperature for two hours and the reaction mixture was poured over crushed ice. The separated solid was washed with excess of water, dried and recrystallized from glacial acetic acid. Crystals suitable for diffraction studies were grown by slow evaporation of an ethanol solution of the title compound.

S3. Refinement

Hydrogen atoms were positioned geometrically with C—H = 0.93-0.97 A° and included in the refinment in a riding-model approximation with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl C atoms.

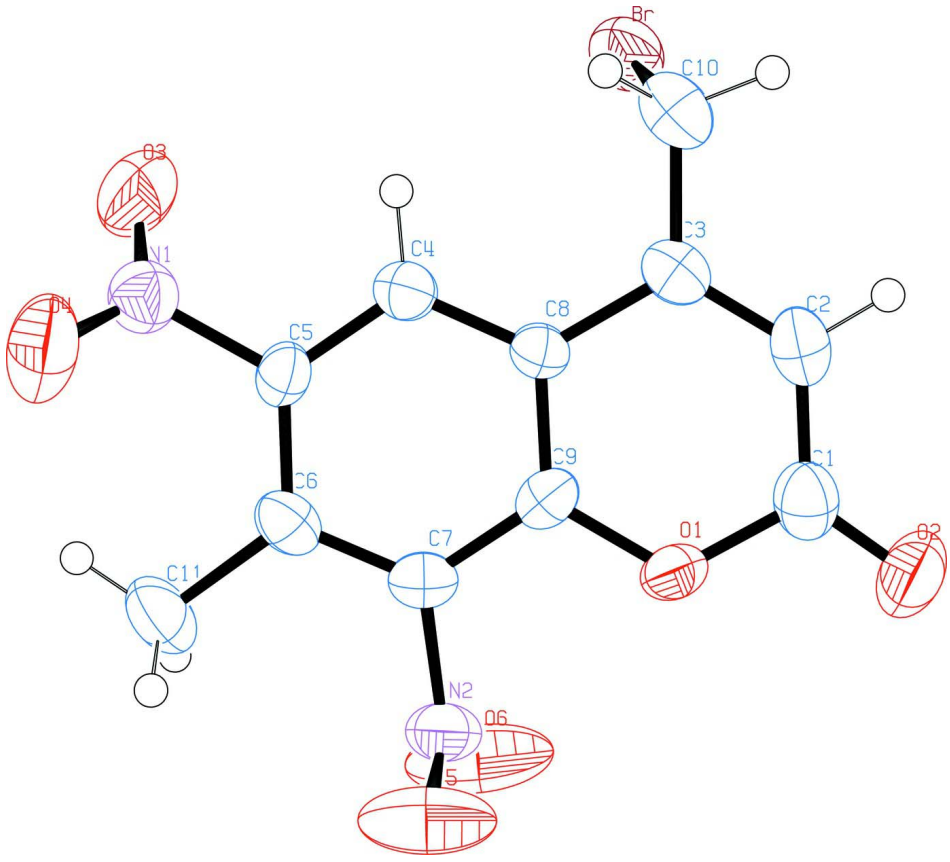

Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering.

4-Bromomethyl-7-methyl-6,8-dinitrocoumarin

Crystal data

$C_{11}H_7BrN_2O_6$
$M_r = 343.09$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 8.122\ (2)$ Å
$b = 11.091\ (4)$ Å
$c = 27.723\ (6)$ Å
$V = 2497.3\ (12)$ Å^3
$Z = 8$
$F(000) = 1360$
$D_x = 1.825$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 3.32$ mm^{-1}
$T = 294$ K
Plate, colourless
0.2 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.520$, $T_{max} = 0.72$
2196 measured reflections
2196 independent reflections
1148 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.9°$
$h = 0 \rightarrow 9$

$k = 0 \rightarrow 13$
$l = 0 \rightarrow 32$

2 standard reflections every 60 min
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.171$
$S = 1.05$
2196 reflections
182 parameters

0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 11.8667P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ 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}
C1	0.7703 (11)	0.2886 (7)	0.6819 (3)	0.047 (2)
C2	0.9438 (10)	0.2873 (7)	0.6922 (3)	0.045 (2)
H3	0.9856	0.3447	0.7134	0.054*
C3	1.0484 (9)	0.2073 (6)	0.6727 (3)	0.0380 (18)
C4	1.0779 (9)	0.0341 (6)	0.6146 (3)	0.0364 (18)
H5	1.1898	0.0281	0.6213	0.044*
C5	1.0085 (9)	−0.0431 (6)	0.5812 (2)	0.0348 (17)
C6	0.8400 (9)	−0.0445 (6)	0.5709 (3)	0.0395 (19)
C7	0.7498 (9)	0.0406 (6)	0.5954 (2)	0.0358 (16)
C8	0.9860 (8)	0.1194 (6)	0.6381 (3)	0.0326 (17)
C9	0.8194 (9)	0.1222 (6)	0.6280 (3)	0.0339 (17)
C10	1.2259 (10)	0.2058 (7)	0.6867 (3)	0.049 (2)
H11A	1.2542	0.2804	0.7030	0.059*
H11B	1.2942	0.1987	0.6581	0.059*
C11	0.7574 (12)	−0.1318 (7)	0.5373 (3)	0.057 (2)
H12A	0.8385	−0.1842	0.5234	0.085*
H12B	0.7020	−0.0882	0.5122	0.085*
H12C	0.6787	−0.1790	0.5550	0.085*
N1	1.1229 (9)	−0.1278 (6)	0.5564 (3)	0.0483 (17)
N2	0.5699 (8)	0.0459 (6)	0.5897 (3)	0.0477 (17)
O1	0.7146 (6)	0.2044 (4)	0.64815 (18)	0.0406 (13)
O2	0.6689 (8)	0.3553 (6)	0.6980 (2)	0.0649 (18)
O3	1.2252 (9)	−0.1757 (6)	0.5791 (3)	0.085 (2)
O4	1.1032 (9)	−0.1384 (6)	0.5134 (3)	0.079 (2)
O5	0.5137 (9)	0.0940 (7)	0.5564 (3)	0.099 (3)

O6	0.4882 (8)	0.0020 (9)	0.6212 (3)	0.113 (3)
Br	1.26518 (11)	0.06847 (7)	0.72976 (3)	0.0597 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.061 (6)	0.043 (4)	0.037 (4)	0.004 (5)	−0.002 (5)	−0.002 (4)
C2	0.060 (6)	0.036 (4)	0.040 (4)	−0.001 (4)	−0.002 (4)	−0.006 (4)
C3	0.040 (4)	0.039 (4)	0.034 (4)	−0.008 (4)	−0.002 (3)	0.004 (3)
C4	0.034 (4)	0.038 (4)	0.038 (4)	0.000 (3)	−0.004 (3)	−0.001 (3)
C5	0.039 (4)	0.036 (4)	0.029 (4)	0.007 (3)	0.003 (3)	−0.002 (3)
C6	0.045 (5)	0.040 (4)	0.034 (4)	−0.003 (4)	−0.009 (4)	0.001 (3)
C7	0.030 (4)	0.039 (4)	0.039 (4)	−0.002 (4)	−0.002 (4)	0.006 (3)
C8	0.028 (4)	0.034 (4)	0.036 (4)	−0.004 (3)	0.000 (3)	−0.003 (3)
C9	0.033 (4)	0.037 (4)	0.032 (4)	0.007 (3)	0.004 (3)	0.005 (3)
C10	0.056 (6)	0.048 (4)	0.044 (4)	−0.013 (4)	−0.004 (4)	−0.001 (4)
C11	0.072 (6)	0.040 (4)	0.058 (5)	−0.001 (5)	−0.024 (5)	−0.011 (4)
N1	0.049 (5)	0.049 (4)	0.045 (5)	0.001 (4)	0.001 (4)	−0.001 (4)
N2	0.037 (4)	0.046 (4)	0.058 (5)	0.001 (3)	−0.012 (4)	0.001 (4)
O1	0.031 (3)	0.049 (3)	0.042 (3)	0.010 (2)	−0.003 (2)	−0.002 (3)
O2	0.071 (4)	0.063 (4)	0.061 (4)	0.026 (4)	0.003 (3)	−0.013 (3)
O3	0.074 (5)	0.092 (5)	0.088 (5)	0.039 (4)	−0.010 (4)	−0.023 (4)
O4	0.102 (6)	0.076 (4)	0.059 (5)	0.023 (4)	0.012 (4)	−0.014 (4)
O5	0.060 (5)	0.130 (7)	0.108 (6)	0.004 (4)	−0.033 (5)	0.048 (5)
O6	0.038 (4)	0.160 (8)	0.141 (8)	−0.011 (5)	−0.002 (5)	0.073 (7)
Br	0.0621 (6)	0.0560 (5)	0.0611 (6)	0.0056 (5)	−0.0181 (5)	−0.0042 (4)

Geometric parameters (Å, º)

C1—O2	1.194 (9)	C7—C9	1.397 (10)
C1—O1	1.398 (9)	C7—N2	1.471 (10)
C1—C2	1.438 (11)	C8—C9	1.382 (9)
C2—C3	1.342 (10)	C9—O1	1.368 (8)
C2—H3	0.9300	C10—H11A	0.9700
C3—C8	1.458 (10)	C10—H11B	0.9700
C3—C10	1.494 (11)	C11—H12A	0.9600
C4—C8	1.370 (10)	C11—H12B	0.9600
C4—C5	1.383 (9)	C11—H12C	0.9600
C4—H5	0.9300	N1—O3	1.169 (9)
C5—C6	1.398 (10)	N1—O4	1.210 (9)
C5—N1	1.488 (10)	N2—O5	1.160 (8)
C6—C7	1.375 (10)	N2—O6	1.201 (9)
C6—C11	1.501 (10)		
O2—C1—O1	116.2 (8)	C9—C8—C3	117.3 (7)
O2—C1—C2	127.4 (8)	O1—C9—C8	122.8 (7)
O1—C1—C2	116.3 (7)	O1—C9—C7	116.4 (6)
C3—C2—C1	123.1 (7)	C8—C9—C7	120.9 (7)

C3—C2—H3	118.4	C3—C10—Br	108.9 (5)
C1—C2—H3	118.4	C3—C10—H11A	109.9
C2—C3—C8	119.2 (7)	Br—C10—H11A	109.9
C2—C3—C10	120.9 (7)	C3—C10—H11B	109.9
C8—C3—C10	120.0 (7)	Br—C10—H11B	109.9
C8—C4—C5	121.6 (7)	H11A—C10—H11B	108.3
C8—C4—H5	119.2	C6—C11—H12A	109.5
C5—C4—H5	119.2	C6—C11—H12B	109.5
C4—C5—C6	122.9 (7)	H12A—C11—H12B	109.5
C4—C5—N1	116.5 (7)	C6—C11—H12C	109.5
C6—C5—N1	120.7 (7)	H12A—C11—H12C	109.5
C7—C6—C5	114.4 (7)	H12B—C11—H12C	109.5
C7—C6—C11	120.8 (7)	O3—N1—O4	125.5 (8)
C5—C6—C11	124.8 (7)	O3—N1—C5	118.9 (7)
C6—C7—C9	123.3 (7)	O4—N1—C5	115.6 (7)
C6—C7—N2	120.2 (7)	O5—N2—O6	123.2 (8)
C9—C7—N2	116.5 (6)	O5—N2—C7	119.7 (8)
C4—C8—C9	116.9 (7)	O6—N2—C7	117.0 (7)
C4—C8—C3	125.8 (7)	C9—O1—C1	121.2 (6)

O2—C1—C2—C3	179.1 (8)	C3—C8—C9—O1	1.3 (10)
O1—C1—C2—C3	−2.9 (11)	C4—C8—C9—C7	0.4 (11)
C1—C2—C3—C8	2.1 (11)	C3—C8—C9—C7	−179.7 (6)
C1—C2—C3—C10	−176.6 (7)	C6—C7—C9—O1	177.6 (6)
C8—C4—C5—C6	−3.6 (11)	N2—C7—C9—O1	−4.9 (9)
C8—C4—C5—N1	177.2 (7)	C6—C7—C9—C8	−1.5 (11)
C4—C5—C6—C7	2.5 (11)	N2—C7—C9—C8	176.0 (7)
N1—C5—C6—C7	−178.4 (6)	C2—C3—C10—Br	104.6 (7)
C4—C5—C6—C11	−175.8 (7)	C8—C3—C10—Br	−74.1 (7)
N1—C5—C6—C11	3.3 (11)	C4—C5—N1—O3	41.9 (11)
C5—C6—C7—C9	0.0 (10)	C6—C5—N1—O3	−137.3 (8)
C11—C6—C7—C9	178.4 (7)	C4—C5—N1—O4	−136.2 (8)
C5—C6—C7—N2	−177.3 (6)	C6—C5—N1—O4	44.6 (10)
C11—C6—C7—N2	1.0 (11)	C6—C7—N2—O5	−81.1 (10)
C5—C4—C8—C9	2.0 (11)	C9—C7—N2—O5	101.4 (9)
C5—C4—C8—C3	−177.9 (7)	C6—C7—N2—O6	101.1 (10)
C2—C3—C8—C4	178.7 (7)	C9—C7—N2—O6	−76.4 (10)
C10—C3—C8—C4	−2.6 (11)	C8—C9—O1—C1	−2.2 (10)
C2—C3—C8—C9	−1.2 (10)	C7—C9—O1—C1	178.7 (6)
C10—C3—C8—C9	177.5 (7)	O2—C1—O1—C9	−178.9 (7)
C4—C8—C9—O1	−178.6 (6)	C2—C1—O1—C9	2.9 (10)