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ISSN 2414-3146

(6-Bromo-2-oxo-2*H*-chromen-4-yl)methyl diethylcarbamodithioate

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Received 27 December 2015
Accepted 4 January 2016

Edited by R. J. Butcher, Howard University, USA

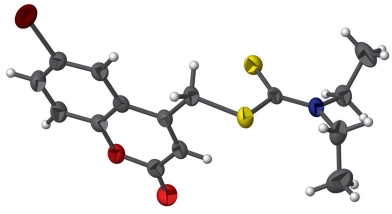
Keywords: crystal structure; coumarin structures; 2*H*-chromene ring systems; dithiocarbamates..

CCDC reference: 1445314

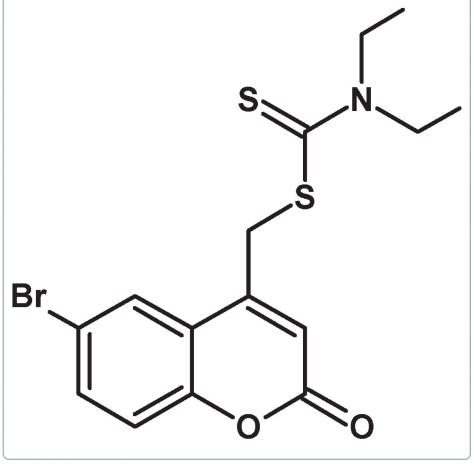
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{15}H_{16}BrNO_2S_2$, the 2*H*-chromene ring system is nearly planar, with a maximum deviation of 0.0182 (22) Å. In the crystal, π–π interactions between pyran and benzene rings of chromene [shortest centroid–centroid distance = 3.7588 (14) Å] occur.

3D view



Chemical scheme



Structure description

Coumarin derivatives are an interesting class of heterocyclic system since the coumarin ring is an essential core moiety in a variety of natural and synthetic biologically active compounds. Coumarin and its derivatives are a group of lactones derived from phenols. Alternately stated, a coumarin ring system is formed by the fusion of benzene and 1,2-pyrone ring. The structure of benzopyrone has many advantages including high fluorescence quantum yield, large Stokes shift, excellent light stability, and low toxicity (Zhou *et al.*, 2010; Sato *et al.*, 2008; Singh *et al.*, 2011). A series of dithiocarbamate compounds have been synthesized and found to possess *in vitro* and *in vivo* antitumor activity (Li *et al.*, 2004; Guo *et al.*, 2004). In an effort to look for the possible non-classical antifolates acting as antitumor agents, we were interested in the incorporation of the dithiocarbamate moiety with coumarin. Herein we report the synthesis, and structural characterization of (6-bromo-2-oxo-2*H*-chromen-4-yl)methyl diethylcarbamodithioate.

The asymmetric unit of (6-bromo-2-oxo-2*H*-chromen-4-yl)methyl diethylcarbamodithioate is shown in Fig. 1. The 2*H*-chromene ring system (O4/C7–C15) is nearly planar, with a maximum deviation of 0.018 (2) Å for atom C13. In the crystal, π–π interactions between pyran (O4/C9/C10/C13–C15) and benzene rings of chromene [shortest centroid–centroid distance = 3.7588 (14) Å] occur.

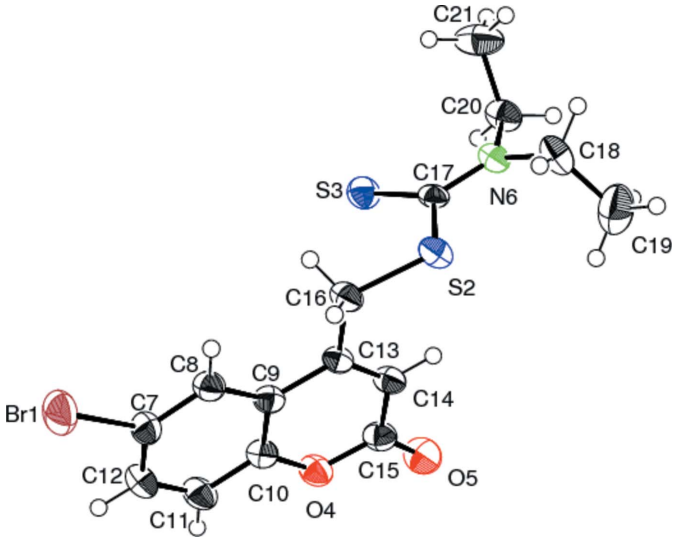


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

Synthesis and crystallization

All the chemicals used were of analytical reagent grade and were used directly without further purification. The title compound was synthesized according to the reported method (Kumar *et al.*, 2012). The compound was recrystallized from an ethanol–chloroform mixture (*v*/*v* = 2/1) by slow evaporation at room temperature. Yield = 72%, m.p. 401–403 K; IR (KBr, cm^{-1}): 985, 1141, 1201, 1410, 1492, and 1730. GCMS: *m*/*e*: 386. 1H NMR (400 MHz, $CDCl_3$, δ, p.p.m): 7.74 (*s*, 1H, Ar—H), 7.51 (*dd*, 1H, Ar—H), 7.31 (*t*, 1H, Ar—H), 6.62 (*s*, 1H, Ar—H), 4.72 (*s*, 2H, CH_2), 4.07 (*q*, 2H, CH_2), 3.80 (*q*, 2H, CH_2), 1.34 (*q*, 6H, CH_3). Elemental analysis for $C_{15}H_{16}BrNO_2S_2$: C, 46.63; H, 4.17; N, 3.63 (calculated); C, 46.67; H, 4.12; N, 3.68(found).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{16}BrNO_2S_2$
M_r	386.32
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, *b*, *c* (Å)	7.8958 (2), 8.0536 (2), 25.2735 (8)
β (°)	97.909 (2)
V (Å^3)	1591.84 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.85
Crystal size (mm)	0.24 × 0.20 × 0.12
Data collection	
Diffractometer	Bruker *SMART* CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2007)
T_{min}, T_{max}	0.770, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12640, 2806, 2419
R_{int}	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.074, 1.04
No. of reflections	2806
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, −0.44

Computer programs: *SMART* (Bruker, 2001), *SAINT* (Bruker, 2001), *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *SHELXL2014*/7.

Acknowledgements

The authors thank to Universities Sophisticated Instrumental Centre, Karnatak University, Dharwad for CCD X-ray facilities, X-ray data collection.

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full crystallographic data

IUCrData (2016). **1**, x160015 [doi:10.1107/S2414314616000158]

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Crystal data

$C_{15}H_{16}BrNO_2S_2$
M_r = 386.32
Monoclinic, $P2_1/n$
a = 7.8958 (2) Å
b = 8.0536 (2) Å
c = 25.2735 (8) Å
β = 97.909 (2)°
V = 1591.84 (8) Å^3
Z = 4
F(000) = 784
D_x = 1.612 Mg m^{-3}
Melting point: 401 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2806 reflections
θ = 2.8–25.0°
μ = 2.85 mm^{-1}
T = 296 K
Plate, colourless
0.24 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.770, T_{max} = 1.000
12640 measured reflections
2806 independent reflections
2419 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 25.0°, θ_{min} = 2.8°
h = −9→9
k = −9→9
l = −30→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.074
S = 1.04
2806 reflections
191 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.9395P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Extinction correction: *SHELXL2014*/7 (Sheldrick 2015, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0078 (6)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.59128 (4)	1.00761 (4)	1.10054 (2)	0.05696 (14)
S2	0.97175 (8)	0.75097 (8)	0.86560 (2)	0.03566 (17)
S3	0.60724 (8)	0.65728 (8)	0.82431 (3)	0.03919 (18)
O4	0.7447 (2)	0.3444 (2)	1.01068 (7)	0.0385 (4)
O5	0.8515 (3)	0.1807 (2)	0.95411 (8)	0.0511 (5)
N6	0.8656 (2)	0.6584 (2)	0.76765 (8)	0.0327 (4)
C7	0.6395 (3)	0.8010 (3)	1.06954 (10)	0.0366 (6)
C8	0.7109 (3)	0.7968 (3)	1.02306 (10)	0.0336 (5)
H8	0.7347	0.8951	1.0062	0.040*
C9	0.7477 (3)	0.6432 (3)	1.00118 (9)	0.0306 (5)
C10	0.7105 (3)	0.5005 (3)	1.02818 (10)	0.0324 (5)
C11	0.6357 (3)	0.5063 (3)	1.07453 (11)	0.0409 (6)
H11	0.6103	0.4087	1.0915	0.049*
C12	0.5995 (3)	0.6573 (3)	1.09518 (11)	0.0430 (6)
H12	0.5485	0.6632	1.1262	0.052*
C13	0.8253 (3)	0.6230 (3)	0.95250 (9)	0.0291 (5)
C14	0.8597 (3)	0.4683 (3)	0.93707 (10)	0.0332 (5)
H14	0.9110	0.4555	0.9063	0.040*
C15	0.8213 (3)	0.3214 (3)	0.96566 (10)	0.0362 (6)
C16	0.8615 (3)	0.7774 (3)	0.92238 (10)	0.0340 (5)
H16A	0.9283	0.8521	0.9472	0.041*
H16B	0.7534	0.8318	0.9105	0.041*
C17	0.8095 (3)	0.6840 (3)	0.81439 (9)	0.0285 (5)
C18	1.0413 (3)	0.6957 (4)	0.75752 (11)	0.0465 (7)
H18A	1.0886	0.7822	0.7819	0.056*
H18B	1.0373	0.7380	0.7214	0.056*
C19	1.1578 (4)	0.5469 (5)	0.76417 (16)	0.0681 (9)
H19A	1.2698	0.5783	0.7571	0.102*
H19B	1.1645	0.5058	0.8001	0.102*
H19C	1.1132	0.4616	0.7396	0.102*
C20	0.7533 (3)	0.5899 (3)	0.72156 (10)	0.0406 (6)
H20A	0.6700	0.5172	0.7344	0.049*
H20B	0.8214	0.5234	0.7004	0.049*
C21	0.6610 (5)	0.7204 (4)	0.68662 (12)	0.0607 (8)
H21A	0.5900	0.6684	0.6574	0.091*
H21B	0.5911	0.7851	0.7070	0.091*
H21C	0.7426	0.7914	0.6730	0.091*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0733 (2)	0.04765 (19)	0.0528 (2)	0.00713 (14)	0.01885 (16)	−0.01305 (14)
S2	0.0369 (3)	0.0427 (4)	0.0276 (3)	−0.0064 (3)	0.0053 (2)	0.0020 (3)
S3	0.0343 (3)	0.0448 (4)	0.0391 (4)	−0.0033 (3)	0.0073 (3)	0.0049 (3)
O4	0.0511 (10)	0.0296 (9)	0.0359 (10)	−0.0034 (7)	0.0102 (8)	0.0035 (7)

O5	0.0772 (13)	0.0281 (10)	0.0493 (12)	0.0013 (9)	0.0127 (10)	−0.0027 (8)
N6	0.0408 (11)	0.0318 (10)	0.0262 (11)	−0.0029 (8)	0.0070 (8)	0.0011 (8)
C7	0.0394 (13)	0.0387 (13)	0.0318 (14)	0.0032 (10)	0.0054 (10)	−0.0051 (11)
C8	0.0378 (13)	0.0321 (13)	0.0309 (14)	−0.0005 (10)	0.0045 (10)	0.0021 (10)
C9	0.0301 (11)	0.0329 (12)	0.0278 (13)	−0.0012 (9)	0.0006 (9)	0.0020 (10)
C10	0.0349 (12)	0.0314 (12)	0.0304 (13)	−0.0017 (9)	0.0024 (10)	0.0013 (10)
C11	0.0472 (15)	0.0410 (15)	0.0367 (15)	−0.0059 (11)	0.0137 (12)	0.0087 (12)
C12	0.0481 (15)	0.0519 (16)	0.0315 (14)	0.0010 (12)	0.0147 (12)	0.0030 (12)
C13	0.0314 (11)	0.0313 (12)	0.0239 (12)	−0.0020 (9)	0.0007 (9)	0.0003 (10)
C14	0.0412 (13)	0.0324 (13)	0.0252 (12)	−0.0011 (10)	0.0019 (10)	0.0007 (10)
C15	0.0429 (14)	0.0326 (14)	0.0317 (14)	−0.0018 (10)	−0.0001 (11)	−0.0008 (11)
C16	0.0465 (14)	0.0293 (12)	0.0269 (13)	−0.0020 (10)	0.0075 (10)	0.0012 (10)
C17	0.0402 (13)	0.0214 (10)	0.0237 (12)	0.0005 (9)	0.0042 (10)	0.0060 (9)
C18	0.0487 (15)	0.0560 (17)	0.0384 (16)	−0.0092 (13)	0.0190 (12)	−0.0017 (13)
C19	0.0454 (17)	0.084 (2)	0.076 (2)	0.0058 (16)	0.0126 (16)	−0.016 (2)
C20	0.0592 (16)	0.0317 (13)	0.0305 (14)	−0.0043 (11)	0.0043 (11)	−0.0047 (11)
C21	0.090 (2)	0.0470 (17)	0.0392 (17)	−0.0020 (15)	−0.0134 (15)	0.0049 (14)

Geometric parameters (Å, º)

Br1—C7	1.900 (2)	C12—H12	0.9300
S2—C17	1.775 (2)	C13—C14	1.344 (3)
S2—C16	1.791 (2)	C13—C16	1.506 (3)
S3—C17	1.664 (2)	C14—C15	1.440 (3)
O4—C10	1.371 (3)	C14—H14	0.9300
O4—C15	1.372 (3)	C16—H16A	0.9700
O5—C15	1.203 (3)	C16—H16B	0.9700
N6—C17	1.333 (3)	C18—C19	1.506 (4)
N6—C20	1.471 (3)	C18—H18A	0.9700
N6—C18	1.476 (3)	C18—H18B	0.9700
C7—C8	1.372 (3)	C19—H19A	0.9600
C7—C12	1.384 (4)	C19—H19B	0.9600
C8—C9	1.402 (3)	C19—H19C	0.9600
C8—H8	0.9300	C20—C21	1.496 (4)
C9—C10	1.389 (3)	C20—H20A	0.9700
C9—C13	1.457 (3)	C20—H20B	0.9700
C10—C11	1.383 (4)	C21—H21A	0.9600
C11—C12	1.369 (4)	C21—H21B	0.9600
C11—H11	0.9300	C21—H21C	0.9600
C17—S2—C16	103.82 (11)	C13—C16—H16A	108.0
C10—O4—C15	121.33 (18)	S2—C16—H16A	108.0
C17—N6—C20	121.4 (2)	C13—C16—H16B	108.0
C17—N6—C18	123.9 (2)	S2—C16—H16B	108.0
C20—N6—C18	114.7 (2)	H16A—C16—H16B	107.3
C8—C7—C12	121.9 (2)	N6—C17—S3	123.80 (18)
C8—C7—Br1	120.24 (19)	N6—C17—S2	113.48 (17)
C12—C7—Br1	117.90 (19)	S3—C17—S2	122.72 (14)

C7—C8—C9	119.4 (2)	N6—C18—C19	113.1 (2)
C7—C8—H8	120.3	N6—C18—H18A	109.0
C9—C8—H8	120.3	C19—C18—H18A	109.0
C10—C9—C8	117.9 (2)	N6—C18—H18B	109.0
C10—C9—C13	117.7 (2)	C19—C18—H18B	109.0
C8—C9—C13	124.4 (2)	H18A—C18—H18B	107.8
O4—C10—C11	115.5 (2)	C18—C19—H19A	109.5
O4—C10—C9	122.4 (2)	C18—C19—H19B	109.5
C11—C10—C9	122.1 (2)	H19A—C19—H19B	109.5
C12—C11—C10	119.3 (2)	C18—C19—H19C	109.5
C12—C11—H11	120.4	H19A—C19—H19C	109.5
C10—C11—H11	120.4	H19B—C19—H19C	109.5
C11—C12—C7	119.4 (2)	N6—C20—C21	113.3 (2)
C11—C12—H12	120.3	N6—C20—H20A	108.9
C7—C12—H12	120.3	C21—C20—H20A	108.9
C14—C13—C9	118.3 (2)	N6—C20—H20B	108.9
C14—C13—C16	124.0 (2)	C21—C20—H20B	108.9
C9—C13—C16	117.8 (2)	H20A—C20—H20B	107.7
C13—C14—C15	123.4 (2)	C20—C21—H21A	109.5
C13—C14—H14	118.3	C20—C21—H21B	109.5
C15—C14—H14	118.3	H21A—C21—H21B	109.5
O5—C15—O4	117.0 (2)	C20—C21—H21C	109.5
O5—C15—C14	126.2 (2)	H21A—C21—H21C	109.5
O4—C15—C14	116.9 (2)	H21B—C21—H21C	109.5
C13—C16—S2	116.99 (17)		