Crystal structures of 2-(2-bromo-5-fluorophenyl)-8-ethoxy-3-nitro-2*H*-thiochromene and 2-(2-bromo-5-fluorophenyl)-7-methoxy-3-nitro-2*H*-thiochromene

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Two thiochromene compounds containing Br and F atoms, namely 2-(2-bromo-5-fluorophenyl)-8-ethoxy-3-nitro-2*H*-thiochromene ($C_{17}H_{13}BrFNO_3S$, **A**) and 2-(2-bromo-5-fluorophenyl)-7-methoxy-3-nitro-2*H*-thiochromene ($C_{16}H_{11}BrFNO_3S$, **B**), were prepared *via* the condensation reaction between 2-mercaptobenzaldehyde and nitrostyrene derivatives. In both compounds, the thiochromene plane is almost perpendicular to the phenyl ring. In the structure of **A**, molecules are assembled *via* π–π stacking and C—H···O and C—F···π interactions. In the crystal packing of **B**, molecules are linked by C—H···F, C—H···O, C—H···π and π–π interactions.

1. Chemical context

2*H*-Chromenes (or 2*H*-benzopyrans) are heterocyclic compounds found in many natural plants. This class of molecules shows a wide variety of biological activities, such as anticancer, anti-inflammation and anti-HIV (Horton *et al.*, 2003). Recently, we have shown that 3-nitro-2*H*-chromene can act as a selective mTOR/Pi3K inhibitor, which can lead to a new compound to treat breast cancer (Fouqué *et al.*, 2015). Interestingly, we observed that thiochromene derivatives, where the O atom is replaced by an S atom, can increase significantly the biological activity of these compounds. With the goal in mind to synthesize a chemical library of thiochromene compounds (Nguyen *et al.*, 2016), we have now successfully prepared 2-(2-bromo-5-fluorophenyl)-8-ethoxy-3-nitro-2*H*-thiochromene (**A**) and 2-(2-bromo-5-fluorophenyl)-7-methoxy-3-nitro-2*H*-thiochromene (**B**). Crystal structure determination can help to understand the role of halogenated substituents in the biological activity of these compounds.
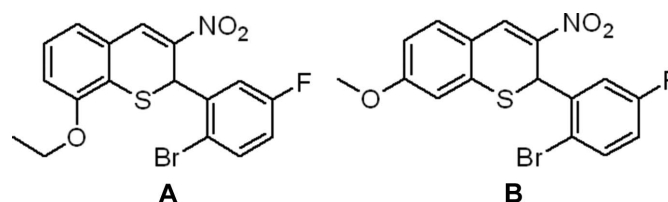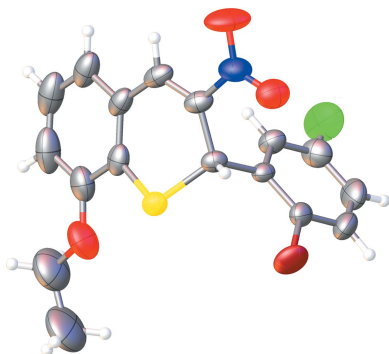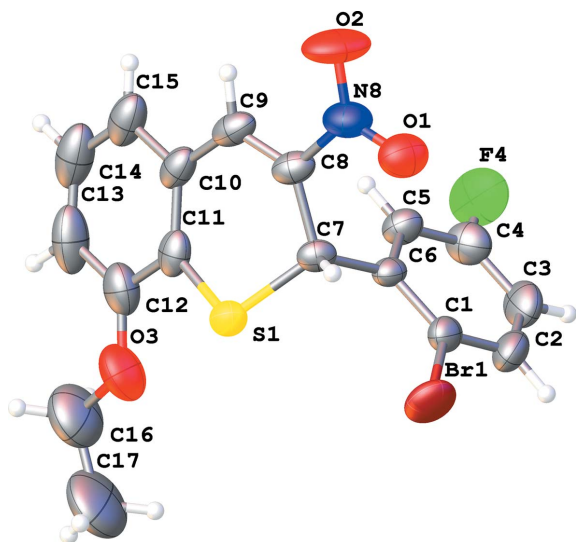

2. Structural commentary

Compound (**A**) crystallizes in the triclinic space group $P\overline{1}$, while compound (**B**) crystallizes in the space group $P2_1/c$, both with one molecule in the asymmetric unit (Figs. 1 and 2). In both compounds, the conformation of the thiochromene ring

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9···O2^i	0.93	2.50	3.419 (7)	168

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

Table 2
Hydrogen-bond geometry (Å, °) for **B**.
$Cg3$ is the centroid of the C10–C15 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9···O1^i	0.93	2.60	3.418 (3)	148
C15—H15···F4^{ii}	0.93	2.54	3.268 (2)	136
C16—C16B···$Cg3^{iii}$	0.96	2.86	3.668 (3)	143

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

Figure 1
The molecular structure of 2-(2-bromo-5-fluorophenyl)-8-ethoxy-3-nitro-2H-thiochromene (**A**), showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.
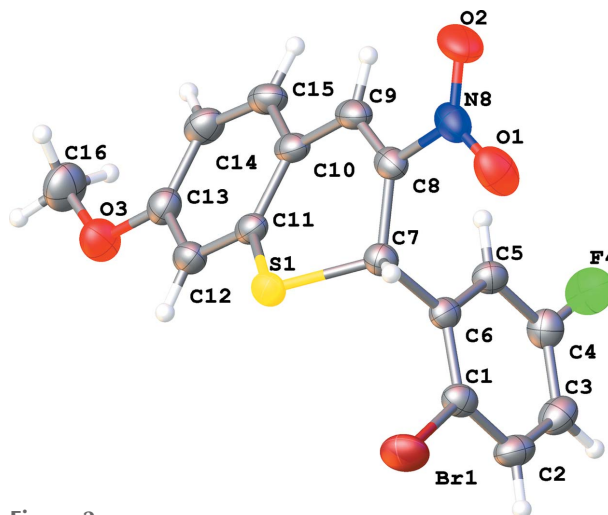
is similar. In **A**, the thiochromene ring makes an angle of 89.3 (2)° with phenyl ring C1–C6, while in **B**, this angle is 86.94 (8)°, which indicates that the 2-bromo-5-fluorophenyl ring is roughly perpendicular to the thiochromene plane. Both 2H-thiopyran rings have a screw-boat conformation, with

Figure 2
The molecular structure of 2-(2-bromo-5-fluorophenyl)-7-methoxy-3-nitro-2H-thiochromene (**B**), showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

atom C7 having the largest deviation from the best plane through atoms S1/C7–C11 [puckering parameters $Q = 0.388$ (4) Å, $\theta = 119.6$ (7)° and $\varphi = 202.2$ (9)° for **A**, and $Q =$
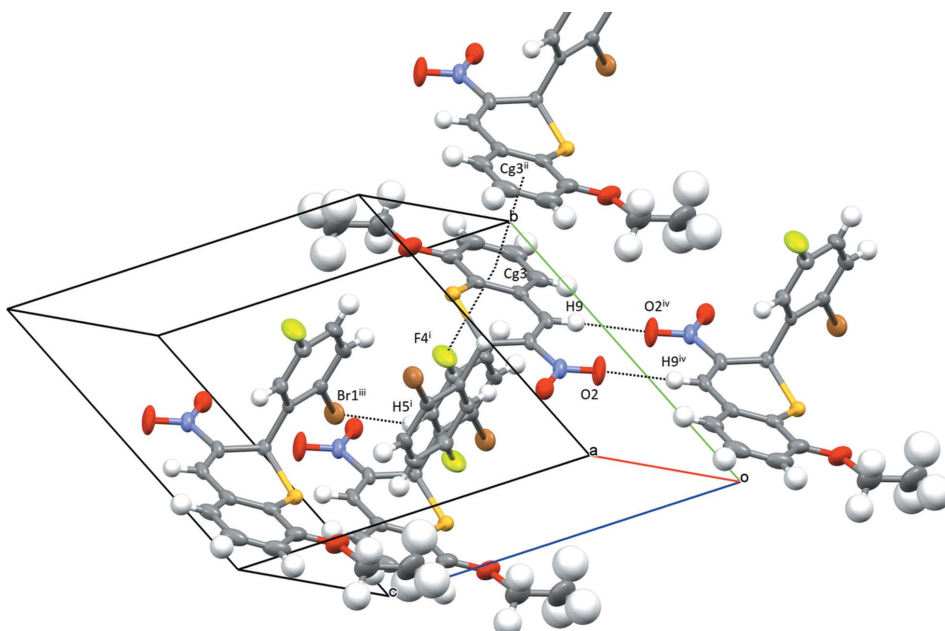
Figure 3
Packing diagram for **A**, showing C—H···O, C—F···π, $\pi-\pi$ and H···Br interactions [symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+2, -z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x, -y+1, -z$]. $Cg3$ is the centroid of the C10–C15 ring.
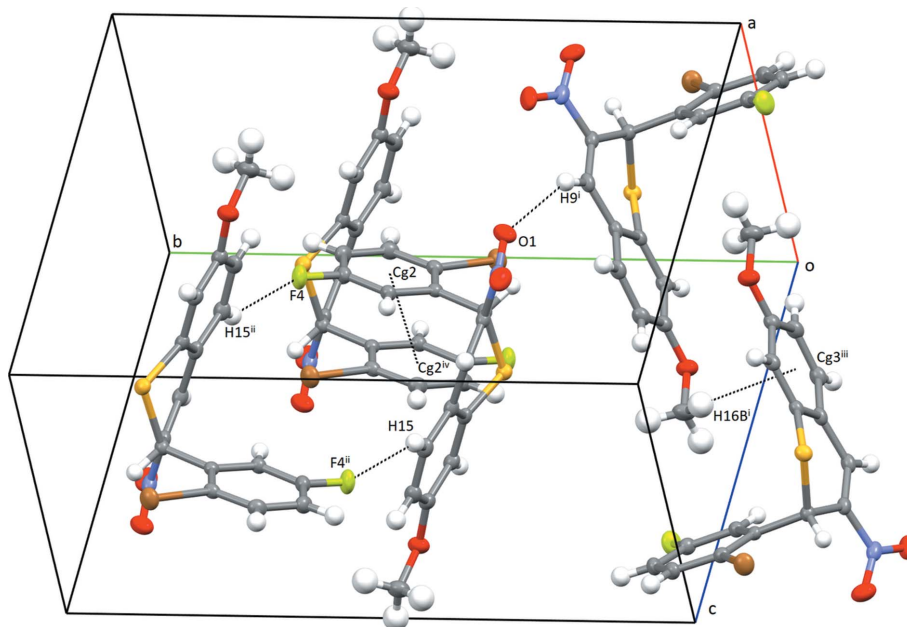
Figure 4
Packing diagram for **B**, showing C—H···O, C—H···F, C—H···π and π–π interactions [symmetry codes: (i) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (ii) $-x + 2$, $-y + 1$, $-z + 2$; (iii) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$; (iv) $-x + 1$, $-y + 1$, $-z + 1$]. $Cg2$ and $Cg3$ are the centroids of the C1–C6 and C10–C15 rings, respectively.

0.5111 (18) Å, θ = 118.2 (2)° and φ = 208.1 (3)° for **B**]. The C—S bond lengths are almost equal [C7—S1 = 1.828 (4) Å and C11—S1 = 1.8307 (19) Å for **A**, and 1.758 (5) and 1.7574 (19) Å for **B**, respectively]. The C11—S1—C7 bond angle is 102.5 (2)° in **A** and 100.47 (9)° in **B**. The N—O bond lengths in compound **B** [1.232 (2) and 1.221 (2) Å] are slightly longer than those in compound **A** [both 1.219 (5) Å]. The nitro group is situated in the thiochromene plane, as illustrated by the torsion angle O2—N8—C8—C9 of 1.3 (7)° in **A** and 9.5 (3)° in **B**.

Table 3
Experimental details.

	A	**B**
Crystal data		
Chemical formula	$C_{17}H_{13}BrFNO_3S$	$C_{16}H_{11}BrFNO_3S$
M_r	410.25	396.23
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	273	273
a, b, c (Å)	7.6695 (12), 10.6867 (18), 12.2767 (19)	7.6231 (4), 17.3484 (8), 11.8345 (6)
α, β, γ (°)	64.686 (4), 80.760 (4), 70.395 (4)	90, 106.016 (2), 90
V (Å^3)	856.7 (2)	1504.35 (13)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.55	2.90
Crystal size (mm)	$0.25 \times 0.2 \times 0.15$	$0.30 \times 0.22 \times 0.11$
Data collection		
Diffractometer	Bruker D8 Quest CMOS	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.621, 0.745	0.599, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12684, 3255, 2291	31660, 3745, 3018
R_{int}	0.037	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.611	0.669
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.128, 1.04	0.029, 0.070, 1.04
No. of reflections	3255	3745
No. of parameters	218	209
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.49	0.52, −0.49

Computer programs: *APEX2* (Bruker, 2013), *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

3. Supramolecular features

In the crystal of **A**, molecules form inversion dimers *via* C—H$\cdots$O hydrogen bonds (Table 1 and Fig. 3) and π–π interactions [$Cg3\cdots Cg3^{i}$ = 3.646 (3) Å; symmetry code: (i) $-x$, $-y + 2$, $-z$; $Cg3$ is the centroid of the C10–C15 ring]. Neighbouring dimers interact through C—F$\cdots\pi$ and short Br1$\cdots$H5^{ii} interactions [F4$\cdots Cg3^{ii}$ = 3.328 (4) Å and Br1$\cdots$H5^{iii} = 2.96 Å; symmetry codes: (ii) $-x$, $-y + 1$, $-z + 1$; (iii) $x + 1$, y, z].

In the crystal of compound **B**, two molecules form dimers through C—H$\cdots$F hydrogen bonds (Table 2 and Fig. 4). These dimers form chains running in the *c* direction through π–π interactions [$Cg2\cdots Cg2^{i}$ = 3.8458 (13) Å; symmetry code: (i) $-x + 2$, $-y + 1$, $-z + 1$; $Cg2$ is the centroid of the C1–C6 ring]. Parallel chains interact *via* C—H$\cdots$O and C—H$\cdots\pi$ interactions.

4. Database survey

The Cambridge Structural Database (CSD, Version 5.40, update of May 2019; Groom *et al.*, 2016) contains seven phenyl-2*H*-thiochromene derivatives, of which three contain halogen atoms [CSD refcodes IFOZIO (Choudhury & Mukherjee, 2013), QAPSAE (Simlandy & Mukherjee, 2017) and WAPCUO (Sangeetha & Sekar, 2017)] and only one structure contains a nitro substituent on the 2*H*-thiochromene ring (NOGDIZ; Le *et al.*, 2019). In all seven structures, the phenyl ring is roughly perpendicular to the thiochromene plane, with dihedral angles between 87.73 and 98.89°. Four of the seven structures display intermolecular interactions between the S atom and a C—H bond. However, in the two structures presented here, this type of interaction has not been observed.

5. Synthesis and crystallization

To a round-bottomed flask was added 2-mercaptobenzaldehyde (1 equiv.), nitrostyrene (1 equiv.) and K_2CO_3 (1 equiv.) in toluene and the reaction mixture was stirred at room temperature for 2 h. After completion of the reaction, the solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica gel (yield 90%). Crystals suitable for single-crystal X-ray diffraction data collection were obtained by slow evaporation from an ethanol solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms bonded to C atoms were placed at calculated positions, with C—H = 0.93–0.98 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ for Csp^2—H and $U_{iso}(H) = 1.5U_{eq}(C)$ for Csp^3—H. A rotating-group model was applied for methyl-group C17 in **A** and C16 in **B**.

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supporting information

Crystal structures of 2-(2-bromo-5-fluorophenyl)-8-ethoxy-3-nitro-2*H*-thiochromene and 2-(2-bromo-5-fluorophenyl)-7-methoxy-3-nitro-2*H*-thiochromene

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

2-(2-Bromo-5-fluorophenyl)-8-ethoxy-3-nitro-2*H*-thiochromene (A)

Crystal data

$C_{17}H_{13}BrFNO_3S$	$Z = 2$
$M_r = 410.25$	$F(000) = 412$
Triclinic, $P\overline{1}$	$D_x = 1.590$ Mg m^{-3}
$a = 7.6695$ (12) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.6867$ (18) Å	Cell parameters from 5933 reflections
$c = 12.2767$ (19) Å	$\theta = 3.0–25.6°$
$\alpha = 64.686$ (4)°	$\mu = 2.55$ mm^{-1}
$\beta = 80.760$ (4)°	$T = 273$ K
$\gamma = 70.395$ (4)°	Triangular-prism, clear light yellow
$V = 856.7$ (2) Å^3	$0.25 \times 0.2 \times 0.15$ mm

Data collection

Bruker D8 Quest CMOS diffractometer	3255 independent reflections
φ and ω scans	2291 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$R_{int} = 0.037$
	$\theta_{max} = 25.7°$, $\theta_{min} = 3.0°$
$T_{min} = 0.621$, $T_{max} = 0.745$	$h = -9 \rightarrow 9$
12684 measured reflections	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: dual
$R[F^2 > 2\sigma(F^2)] = 0.052$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.128$	
$S = 1.04$	H-atom parameters constrained
3255 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 2.0237P]$
218 parameters	where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.53$ e Å^{-3}

$\Delta\rho_{min} = -0.49$ e Å^{-3}

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.78831 (7)	0.45042 (7)	0.29672 (6)	0.0676 (2)
S1	0.34737 (16)	0.76031 (13)	0.17001 (11)	0.0459 (3)
F4	0.1093 (5)	0.3152 (4)	0.5616 (3)	0.0878 (11)
O1	0.4800 (5)	0.3584 (4)	0.1158 (3)	0.0627 (10)
N8	0.3239 (6)	0.4388 (5)	0.0863 (4)	0.0514 (10)
O3	0.1347 (6)	0.9891 (4)	0.2321 (4)	0.0800 (12)
C6	0.4041 (5)	0.4707 (4)	0.3176 (4)	0.0317 (9)
C7	0.3916 (5)	0.5738 (5)	0.1873 (4)	0.0344 (10)
H7	0.5137	0.5464	0.1505	0.041*
O2	0.2238 (6)	0.4176 (5)	0.0326 (4)	0.0877 (14)
C1	0.5698 (6)	0.4073 (5)	0.3787 (4)	0.0398 (10)
C5	0.2496 (6)	0.4375 (5)	0.3831 (4)	0.0430 (11)
H5	0.1353	0.4785	0.3463	0.052*
C8	0.2567 (6)	0.5648 (5)	0.1183 (4)	0.0394 (11)
C9	0.0857 (6)	0.6514 (5)	0.0895 (4)	0.0441 (11)
H9	0.0162	0.6300	0.0480	0.053*
C10	0.0005 (6)	0.7756 (5)	0.1180 (4)	0.0449 (12)
C11	0.1047 (6)	0.8283 (5)	0.1624 (4)	0.0440 (11)
C2	0.5820 (7)	0.3155 (5)	0.4989 (5)	0.0540 (13)
H2	0.6945	0.2760	0.5376	0.065*
C4	0.2649 (7)	0.3447 (6)	0.5014 (4)	0.0538 (13)
C12	0.0194 (8)	0.9462 (6)	0.1916 (5)	0.0588 (14)
C3	0.4268 (8)	0.2827 (6)	0.5611 (5)	0.0593 (14)
H3	0.4323	0.2196	0.6420	0.071*
C15	−0.1906 (7)	0.8446 (6)	0.1038 (5)	0.0612 (15)
H15	−0.2617	0.8100	0.0751	0.073*
C13	−0.1723 (9)	1.0141 (6)	0.1749 (6)	0.0758 (19)
H13	−0.2306	1.0946	0.1932	0.091*
C14	−0.2721 (8)	0.9611 (7)	0.1315 (5)	0.0757 (19)
H14	−0.3987	1.0062	0.1209	0.091*
C16	0.0603 (12)	1.1016 (8)	0.2740 (8)	0.108 (3)
H16A	−0.0355	1.0799	0.3348	0.129*
H16B	0.0066	1.1929	0.2080	0.129*
C17	0.2145 (15)	1.1110 (9)	0.3261 (10)	0.140 (4)
H17A	0.3043	1.1391	0.2639	0.211*
H17B	0.2717	1.0182	0.3877	0.211*
H17C	0.1673	1.1819	0.3604	0.211*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0326 (3)	0.0840 (5)	0.0826 (4)	−0.0170 (3)	−0.0096 (2)	−0.0277 (3)
S1	0.0434 (6)	0.0424 (7)	0.0506 (7)	−0.0164 (5)	−0.0098 (5)	−0.0116 (6)
F4	0.084 (2)	0.116 (3)	0.0506 (19)	−0.054 (2)	0.0178 (17)	−0.0102 (19)
O1	0.056 (2)	0.070 (3)	0.071 (3)	−0.014 (2)	−0.0018 (19)	−0.040 (2)
N8	0.057 (3)	0.069 (3)	0.045 (2)	−0.029 (2)	0.004 (2)	−0.031 (2)
O3	0.094 (3)	0.049 (2)	0.096 (3)	−0.013 (2)	0.003 (2)	−0.036 (2)
C6	0.031 (2)	0.035 (2)	0.034 (2)	−0.0095 (18)	−0.0047 (17)	−0.0171 (19)
C7	0.029 (2)	0.046 (3)	0.034 (2)	−0.0144 (19)	0.0037 (17)	−0.020 (2)
O2	0.078 (3)	0.129 (4)	0.105 (3)	−0.037 (3)	−0.012 (2)	−0.083 (3)
C1	0.038 (2)	0.034 (2)	0.047 (3)	−0.005 (2)	−0.007 (2)	−0.018 (2)
C5	0.038 (2)	0.052 (3)	0.040 (3)	−0.016 (2)	−0.002 (2)	−0.017 (2)
C8	0.037 (2)	0.058 (3)	0.029 (2)	−0.022 (2)	0.0029 (18)	−0.019 (2)
C9	0.039 (2)	0.064 (3)	0.030 (2)	−0.026 (2)	−0.0020 (19)	−0.011 (2)
C10	0.035 (2)	0.051 (3)	0.034 (3)	−0.013 (2)	−0.0046 (19)	−0.002 (2)
C11	0.043 (3)	0.039 (3)	0.031 (2)	−0.008 (2)	0.0030 (19)	−0.002 (2)
C2	0.058 (3)	0.046 (3)	0.050 (3)	−0.004 (3)	−0.023 (3)	−0.013 (2)
C4	0.064 (3)	0.062 (3)	0.040 (3)	−0.030 (3)	0.007 (2)	−0.018 (3)
C12	0.067 (4)	0.039 (3)	0.054 (3)	−0.013 (3)	0.005 (3)	−0.008 (3)
C3	0.083 (4)	0.051 (3)	0.035 (3)	−0.021 (3)	−0.012 (3)	−0.006 (2)
C15	0.043 (3)	0.061 (4)	0.050 (3)	−0.011 (3)	−0.003 (2)	0.002 (3)
C13	0.069 (4)	0.046 (3)	0.069 (4)	0.005 (3)	0.019 (3)	−0.007 (3)
C14	0.048 (3)	0.067 (4)	0.062 (4)	−0.003 (3)	0.006 (3)	0.006 (3)
C16	0.130 (7)	0.070 (5)	0.128 (7)	−0.011 (5)	−0.009 (5)	−0.057 (5)
C17	0.187 (10)	0.072 (5)	0.179 (10)	−0.016 (6)	−0.027 (8)	−0.075 (6)

Geometric parameters (Å, º)

Br1—C1	1.901 (4)	C10—C11	1.400 (7)
S1—C7	1.828 (4)	C10—C15	1.403 (7)
S1—C11	1.758 (5)	C11—C12	1.379 (7)
F4—C4	1.356 (6)	C2—H2	0.9300
O1—N8	1.219 (5)	C2—C3	1.372 (7)
N8—O2	1.219 (5)	C4—C3	1.357 (7)
N8—C8	1.468 (6)	C12—C13	1.408 (8)
O3—C12	1.360 (7)	C3—H3	0.9300
O3—C16	1.418 (8)	C15—H15	0.9300
C6—C7	1.501 (6)	C15—C14	1.353 (9)
C6—C1	1.389 (6)	C13—H13	0.9300
C6—C5	1.381 (6)	C13—C14	1.367 (9)
C7—H7	0.9800	C14—H14	0.9300
C7—C8	1.488 (6)	C16—H16A	0.9700
C1—C2	1.376 (7)	C16—H16B	0.9700
C5—H5	0.9300	C16—C17	1.481 (11)
C5—C4	1.361 (6)	C17—H17A	0.9600
C8—C9	1.325 (6)	C17—H17B	0.9600

C9—H9	0.9300	C17—H17C	0.9600
C9—C10	1.433 (7)		
C11—S1—C7	102.5 (2)	C3—C2—C1	119.4 (5)
O1—N8—C8	117.8 (4)	C3—C2—H2	120.3
O2—N8—O1	122.5 (5)	F4—C4—C5	117.7 (5)
O2—N8—C8	119.8 (4)	F4—C4—C3	119.2 (5)
C12—O3—C16	119.7 (5)	C3—C4—C5	123.1 (5)
C1—C6—C7	121.8 (4)	O3—C12—C11	114.8 (5)
C5—C6—C7	121.3 (4)	O3—C12—C13	125.5 (6)
C5—C6—C1	117.0 (4)	C11—C12—C13	119.6 (6)
S1—C7—H7	106.6	C2—C3—H3	120.9
C6—C7—S1	111.5 (3)	C4—C3—C2	118.2 (5)
C6—C7—H7	106.6	C4—C3—H3	120.9
C8—C7—S1	111.0 (3)	C10—C15—H15	119.8
C8—C7—C6	114.2 (3)	C14—C15—C10	120.4 (6)
C8—C7—H7	106.6	C14—C15—H15	119.8
C6—C1—Br1	119.9 (3)	C12—C13—H13	120.2
C2—C1—Br1	117.9 (3)	C14—C13—C12	119.6 (6)
C2—C1—C6	122.3 (4)	C14—C13—H13	120.2
C6—C5—H5	120.0	C15—C14—C13	121.4 (6)
C4—C5—C6	119.9 (4)	C15—C14—H14	119.3
C4—C5—H5	120.0	C13—C14—H14	119.3
N8—C8—C7	113.7 (4)	O3—C16—H16A	110.3
C9—C8—N8	118.5 (4)	O3—C16—H16B	110.3
C9—C8—C7	127.7 (4)	O3—C16—C17	107.3 (7)
C8—C9—H9	117.8	H16A—C16—H16B	108.5
C8—C9—C10	124.5 (4)	C17—C16—H16A	110.3
C10—C9—H9	117.8	C17—C16—H16B	110.3
C11—C10—C9	120.9 (4)	C16—C17—H17A	109.5
C11—C10—C15	119.0 (5)	C16—C17—H17B	109.5
C15—C10—C9	120.1 (5)	C16—C17—H17C	109.5
C10—C11—S1	122.3 (4)	H17A—C17—H17B	109.5
C12—C11—S1	117.5 (4)	H17A—C17—H17C	109.5
C12—C11—C10	120.0 (5)	H17B—C17—H17C	109.5
C1—C2—H2	120.3		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O2[i]	0.93	2.50	3.419 (7)	168

Symmetry code: (i) −x, −y+1, −z.

2-(2-Bromo-5-fluorophenyl)-7-methoxy-3-nitro-2*H*-thiochromene (B)

Crystal data

C$_{16}$H$_{11}$BrFNO$_3$S
M_r = 396.23
Monoclinic, $P2_1/c$
a = 7.6231 (4) Å
b = 17.3484 (8) Å
c = 11.8345 (6) Å
$β$ = 106.016 (2)°
V = 1504.35 (13) Å^3
Z = 4

$F(000)$ = 792
D_x = 1.749 Mg m^{-3}
Mo *K*α radiation, $λ$ = 0.71073 Å
Cell parameters from 9945 reflections
$θ$ = 3.0–28.3°
$μ$ = 2.90 mm^{-1}
T = 273 K
Block, yellow
0.30 × 0.22 × 0.11 mm

Data collection

Bruker D8 Quest CMOS
 diffractometer
$φ$ and $ω$ scans
Absorption correction: multi-scan
 (SADABS; Bruker, 2016)
T_{min} = 0.599, T_{max} = 0.746
31660 measured reflections

3745 independent reflections
3018 reflections with $I > 2σ(I)$
R_{int} = 0.032
$θ_{max}$ = 28.4°, $θ_{min}$ = 3.0°
h = −10→10
k = −23→23
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2σ(F^2)]$ = 0.029
$wR(F^2)$ = 0.070
S = 1.04
3745 reflections
209 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from
 neighbouring sites
H-atom parameters constrained
$w = 1/[σ^2(F_o^2) + (0.0274P)^2 + 0.9845P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(Δ/σ)_{max}$ = 0.001
$Δρ_{max}$ = 0.52 e Å^{-3}
$Δρ_{min}$ = −0.49 e Å^{-3}

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.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.57090 (3)	0.36398 (2)	0.38157 (2)	0.04708 (9)
S1	0.52686 (6)	0.31114 (3)	0.66185 (4)	0.03212 (11)
F4	1.0275 (2)	0.57875 (8)	0.73645 (12)	0.0538 (4)
O3	0.2529 (2)	0.42250 (10)	0.96347 (13)	0.0458 (4)
O2	1.1678 (2)	0.23148 (10)	0.82659 (17)	0.0550 (4)
O1	1.0798 (2)	0.26267 (11)	0.64265 (15)	0.0545 (4)
N8	1.0577 (2)	0.26017 (10)	0.74190 (18)	0.0383 (4)
C6	0.7901 (2)	0.40495 (10)	0.61148 (16)	0.0265 (4)
C1	0.7106 (3)	0.43164 (11)	0.49777 (16)	0.0306 (4)
C8	0.8921 (3)	0.29553 (11)	0.75735 (17)	0.0307 (4)

C7	0.7581 (3)	0.32337 (11)	0.64724 (16)	0.0289 (4)
H7	0.7692	0.2893	0.5835	0.035*
C11	0.5550 (3)	0.34811 (11)	0.80401 (16)	0.0288 (4)
C12	0.4044 (3)	0.37801 (11)	0.83133 (17)	0.0325 (4)
H12	0.2966	0.3854	0.7721	0.039*
C10	0.7218 (3)	0.33978 (11)	0.89180 (17)	0.0311 (4)
C5	0.8972 (3)	0.45668 (11)	0.69165 (16)	0.0300 (4)
H5	0.9539	0.4411	0.7682	0.036*
C2	0.7313 (3)	0.50680 (13)	0.46588 (18)	0.0375 (5)
H2	0.6742	0.5232	0.3898	0.045*
C9	0.8784 (3)	0.30534 (11)	0.86622 (17)	0.0338 (4)
H9	0.9746	0.2892	0.9287	0.041*
C4	0.9184 (3)	0.53081 (12)	0.65674 (18)	0.0349 (4)
C14	0.5759 (3)	0.39037 (13)	1.03475 (18)	0.0385 (5)
H14	0.5829	0.4043	1.1118	0.046*
C15	0.7271 (3)	0.36263 (12)	1.00596 (17)	0.0361 (4)
H15	0.8368	0.3589	1.0646	0.043*
C13	0.4121 (3)	0.39734 (12)	0.94672 (18)	0.0347 (4)
C3	0.8361 (3)	0.55789 (12)	0.54603 (19)	0.0386 (5)
H3	0.8503	0.6088	0.5256	0.046*
C16	0.2464 (4)	0.43592 (16)	1.0811 (2)	0.0534 (6)
H16A	0.1254	0.4515	1.0807	0.080*
H16B	0.3313	0.4759	1.1157	0.080*
H16C	0.2781	0.3894	1.1261	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.05237 (15)	0.05020 (14)	0.03012 (11)	−0.00306 (11)	−0.00293 (9)	−0.00516 (9)
S1	0.0285 (2)	0.0376 (3)	0.0274 (2)	−0.0057 (2)	0.00289 (18)	−0.00232 (19)
F4	0.0685 (9)	0.0376 (7)	0.0489 (8)	−0.0167 (7)	0.0057 (7)	−0.0092 (6)
O3	0.0422 (9)	0.0591 (10)	0.0385 (8)	0.0009 (7)	0.0153 (7)	−0.0034 (7)
O2	0.0376 (9)	0.0477 (10)	0.0733 (12)	0.0126 (7)	0.0044 (8)	0.0180 (9)
O1	0.0390 (9)	0.0724 (12)	0.0530 (10)	0.0034 (8)	0.0143 (8)	−0.0143 (9)
N8	0.0301 (9)	0.0276 (8)	0.0544 (11)	−0.0014 (7)	0.0066 (8)	−0.0011 (8)
C6	0.0260 (9)	0.0271 (9)	0.0274 (9)	0.0028 (7)	0.0091 (7)	0.0009 (7)
C1	0.0301 (9)	0.0346 (10)	0.0264 (9)	0.0027 (8)	0.0068 (7)	−0.0023 (8)
C8	0.0278 (9)	0.0244 (9)	0.0371 (10)	−0.0008 (7)	0.0044 (8)	0.0026 (8)
C7	0.0290 (9)	0.0277 (9)	0.0287 (9)	0.0002 (8)	0.0059 (7)	−0.0012 (7)
C11	0.0319 (10)	0.0275 (9)	0.0250 (9)	−0.0046 (7)	0.0046 (7)	0.0031 (7)
C12	0.0302 (9)	0.0353 (10)	0.0291 (9)	−0.0052 (8)	0.0032 (8)	0.0031 (8)
C10	0.0339 (10)	0.0275 (9)	0.0281 (9)	−0.0027 (8)	0.0019 (8)	0.0059 (7)
C5	0.0326 (10)	0.0312 (10)	0.0257 (9)	0.0012 (8)	0.0070 (7)	−0.0004 (8)
C2	0.0422 (11)	0.0393 (11)	0.0309 (10)	0.0086 (9)	0.0099 (9)	0.0083 (9)
C9	0.0318 (10)	0.0301 (10)	0.0341 (10)	−0.0011 (8)	0.0000 (8)	0.0073 (8)
C4	0.0378 (11)	0.0312 (10)	0.0362 (10)	−0.0032 (8)	0.0114 (8)	−0.0058 (8)
C14	0.0479 (12)	0.0390 (11)	0.0272 (10)	−0.0054 (10)	0.0081 (9)	−0.0003 (8)
C15	0.0381 (11)	0.0369 (11)	0.0273 (9)	−0.0032 (9)	−0.0010 (8)	0.0042 (8)

C13	0.0370 (11)	0.0341 (10)	0.0341 (10)	−0.0042 (9)	0.0115 (8)	0.0020 (8)
C3	0.0469 (12)	0.0295 (10)	0.0421 (11)	0.0029 (9)	0.0169 (10)	0.0051 (9)
C16	0.0579 (15)	0.0655 (16)	0.0437 (13)	−0.0029 (13)	0.0256 (12)	−0.0042 (12)

Geometric parameters (Å, º)

Br1—C1	1.8961 (19)	C12—H12	0.9300
S1—C7	1.8307 (19)	C12—C13	1.392 (3)
S1—C11	1.7574 (19)	C10—C9	1.440 (3)
F4—C4	1.357 (2)	C10—C15	1.398 (3)
O3—C13	1.355 (3)	C5—H5	0.9300
O3—C16	1.426 (3)	C5—C4	1.374 (3)
O2—N8	1.221 (2)	C2—H2	0.9300
O1—N8	1.232 (2)	C2—C3	1.380 (3)
N8—C8	1.460 (3)	C9—H9	0.9300
C6—C1	1.394 (3)	C4—C3	1.370 (3)
C6—C7	1.516 (3)	C14—H14	0.9300
C6—C5	1.395 (3)	C14—C15	1.376 (3)
C1—C2	1.379 (3)	C14—C13	1.393 (3)
C8—C7	1.497 (3)	C15—H15	0.9300
C8—C9	1.332 (3)	C3—H3	0.9300
C7—H7	0.9800	C16—H16A	0.9600
C11—C12	1.377 (3)	C16—H16B	0.9600
C11—C10	1.410 (3)	C16—H16C	0.9600
C11—S1—C7	100.47 (9)	C4—C5—C6	119.55 (18)
C13—O3—C16	117.99 (18)	C4—C5—H5	120.2
O2—N8—O1	123.58 (19)	C1—C2—H2	119.8
O2—N8—C8	119.36 (19)	C1—C2—C3	120.50 (19)
O1—N8—C8	117.04 (17)	C3—C2—H2	119.8
C1—C6—C7	121.27 (17)	C8—C9—C10	123.18 (18)
C1—C6—C5	117.40 (17)	C8—C9—H9	118.4
C5—C6—C7	121.32 (16)	C10—C9—H9	118.4
C6—C1—Br1	120.14 (15)	F4—C4—C5	117.72 (18)
C2—C1—Br1	118.09 (15)	F4—C4—C3	119.08 (19)
C2—C1—C6	121.77 (18)	C3—C4—C5	123.20 (19)
N8—C8—C7	115.63 (17)	C15—C14—H14	120.5
C9—C8—N8	118.44 (18)	C15—C14—C13	118.98 (19)
C9—C8—C7	125.74 (18)	C13—C14—H14	120.5
S1—C7—H7	107.0	C10—C15—H15	118.8
C6—C7—S1	111.58 (13)	C14—C15—C10	122.39 (19)
C6—C7—H7	107.0	C14—C15—H15	118.8
C8—C7—S1	108.90 (13)	O3—C13—C12	115.12 (18)
C8—C7—C6	114.88 (15)	O3—C13—C14	124.95 (19)
C8—C7—H7	107.0	C12—C13—C14	119.93 (19)
C12—C11—S1	118.22 (14)	C2—C3—H3	121.2
C12—C11—C10	120.41 (18)	C4—C3—C2	117.55 (19)
C10—C11—S1	121.01 (15)	C4—C3—H3	121.2

C11—C12—H12	119.7	O3—C16—H16A	109.5
C11—C12—C13	120.61 (18)	O3—C16—H16B	109.5
C13—C12—H12	119.7	O3—C16—H16C	109.5
C11—C10—C9	121.27 (18)	H16A—C16—H16B	109.5
C15—C10—C11	117.59 (19)	H16A—C16—H16C	109.5
C15—C10—C9	121.07 (18)	H16B—C16—H16C	109.5
C6—C5—H5	120.2		

Hydrogen-bond geometry (Å, º)

*Cg*3 is the centroid of the C10–C15 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C9—H9⋯O1[i]	0.93	2.60	3.418 (3)	148
C15—H15⋯F4[ii]	0.93	2.54	3.268 (2)	136
C16—C16B⋯*Cg*3[iii]	0.96	2.86	3.668 (3)	143

Symmetry codes: (i) x, $-y+1/2$, $z+1/2$; (ii) $-x+2$, $-y+1$, $-z+2$; (iii) $-x+1$, $-y+1$, $-z+2$.