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Crystal structures of the Schiff base derivatives (*E*)-*N*′-[(1*H*-indol-3-yl)methylidene]isonicotinohydrazide ethanol monosolvate and (*E*)-*N*-methyl-2-[1-(2-oxo-2*H*-chromen-3-yl)ethylidene]hydrazinecarbothioamide

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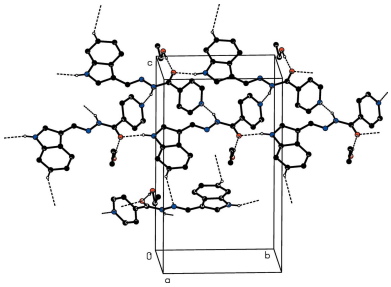
The crystal structures of two title Schiff base derivatives, $C_{15}H_{12}N_4O\cdot C_2H_6O$ (**1·EtOH**) and $C_{13}H_{13}N_3O_2S$ (**2**), were determined at 110 and 100 K, respectively. In the crystal of compound **1·EtOH**, the (*E*)-*N*′-[(1*H*-indol-3-yl)-methylidene]isonicotinohydrazide and ethanol molecules are linked by O—H···O, N—H···O and N—H···N hydrogen bonds, forming a tape structure running along the *b*-axis direction. The tapes are weakly linked *via* a C—H···N interaction. In the crystal of compound **2**, (*E*)-*N*-methyl-2-[1-(2-oxo-2*H*-chromen-3-yl)ethylidene]hydrazinecarbothioamide molecules are linked *via* N—H···O and C—H···O hydrogen bonds, forming a helical chain along the *b*-axis direction. The chains are further linked into a layer expanding parallel to (102) through C—H···S interactions.

1. Chemical context

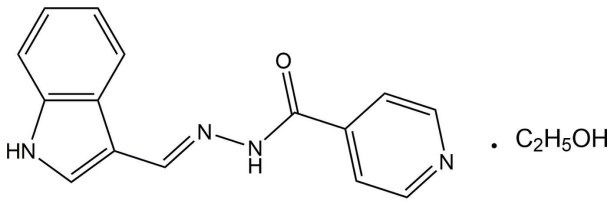
Schiff base derivatives are a biologically versatile class of compounds possessing diverse activities, such as anti-oxidant (Haribabu, Subhashree *et al.*, 2015, 2016), anti-inflammatory (Alam *et al.*, 2012), anti-cancer (Creaven *et al.*, 2010; Haribabu, Jeyalakshmi *et al.*, 2015, 2016), anti-bacterial (Sondhi *et al.*, 2006), anti-fungal (Jarrahpour *et al.*, 2007), anti-convulsant (Bhat & Al-Omar, 2011). Schiff bases have gained special attention in pharmacophore research and in the development of several bioactive lead molecules. They are widely used as catalysts, corrosion inhibitors and intermediates in organic synthesis, and also play a potential role in the development of coordination chemistry (Muralisankar *et al.*, 2016). As part of our studies in this area, we have synthesized the title Schiff base compounds, **1·EtOH** and **2**, and determined their crystal structures.



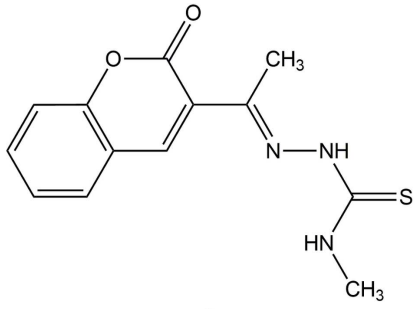
2. Structural commentary

The molecular structures ((Figs. 1 and 2) of both **1** and **2** are non-planar, as evidenced by the torsion angles N3—C10—C11—C12 [42.5 (3)°] in **1** and C1—C2—C10—N1 [−152.0 (2)°] in **2**. The mean plane of the central chain C9/N2/N3/C10/O1 in **1** makes dihedral angles of 6.91 (12) and

42.71 (13)°, respectively, with the C1–C8/N1 ring system and the pyridine C11–C15/N4 ring. In molecule **2**, the dihedral angle between the C1–C9/O1 ring system and the mean plane of the C10/N1/N2/C12/N3/C13 chain is 30.36 (9)°.



1·EtOH



2

3. Supramolecular features

The crystal packing of **1·EtOH** features O—H···O, N—H···O and N—H···N hydrogen bonds (Table 1), which link the molecules into a tape structure running along the *b*-axis direction (Fig. 3). The tapes are weakly linked *via* a C—H···N interaction (Table 1). In the N—H···O and N—H···N hydrogen bonds, atoms N1 and N3 act as donors to atoms O1 and N4, respectively, generating *C*(9) and *C*(7) chain motifs. The C—H···N interaction generates a *C*(8) chain. Atom O1*S* of the ethanol molecule acts as a donor in forming the O—H···O hydrogen bond with atom O1, which acts as a double acceptor.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88	2.05	2.871 (3)	156
N3—H3···N4^{ii}	0.88	2.14	2.979 (3)	159
C5—H5···N2^{iii}	0.95	2.62	3.236 (3)	123
O1*S*—H1*S*···O1	0.84	1.90	2.742 (3)	177

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

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	0.88	2.39	3.269 (3)	175
C11—H11*A*···O2^{i}	0.98	2.47	3.109 (3)	123
C7—H7···S1^{ii}	0.95	2.85	3.711 (3)	151
C11—H11*B*···S1^{iii}	0.98	2.87	3.728 (3)	146

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

In **2**, the crystal packing features N—H···O, C—H···O and C—H···S interactions (Table 2). The molecules are linked *via* N—H···O and C—H···O hydrogen bonds, forming a helical chain along the *b*-axis direction (Fig. 4). The chains are further linked *via* C—H···S interactions, forming a layer expanding parallel to (102). Atoms N2 and C11 act as donors to the double acceptor O2, generating *C*(7) and *C*(6) chains, respectively. As a result of these two hydrogen bonds, an $R_2^1(7)$ ring motif is generated. In the C—H···S interactions, atoms C7 and C11 act as donors to the double acceptor S1, generating *C*(11) and *C*(7) chains, respectively.

4. Database survey

A search of the Cambridge Structural Database (Groom *et al.*, 2016) for the substructures **1** and **2** revealed several related Schiff base derivatives, including those with refcodes ADEKAW, ACIPIN, ADEZAL02 and APAQEP reported by

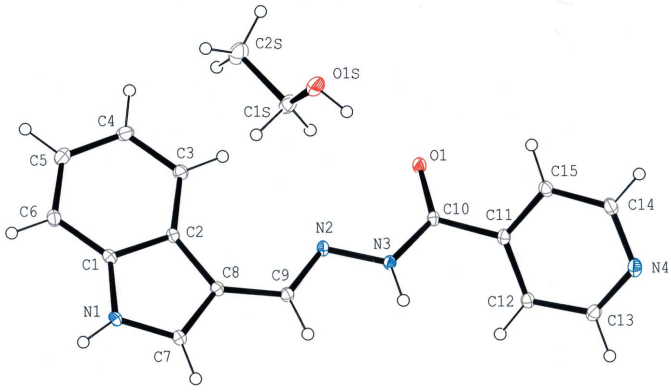


Figure 1
The molecular structure of compound **1·EtOH**, with the atom labelling. Displacement ellipsoids of non-H atoms are drawn at 30% probability level.

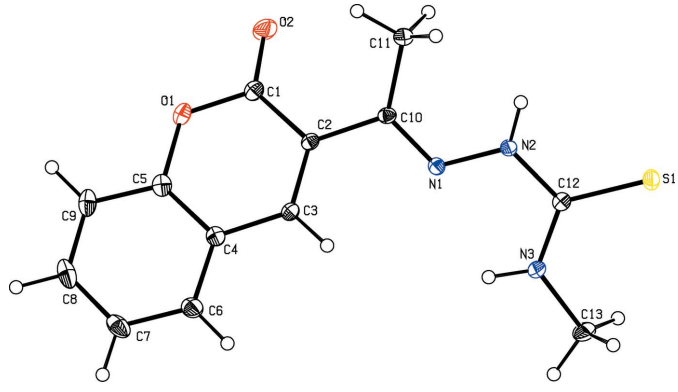


Figure 2
The molecular structure of compound **2**, with the atom labelling. Displacement ellipsoids of non-H atoms are drawn at 30% probability level.

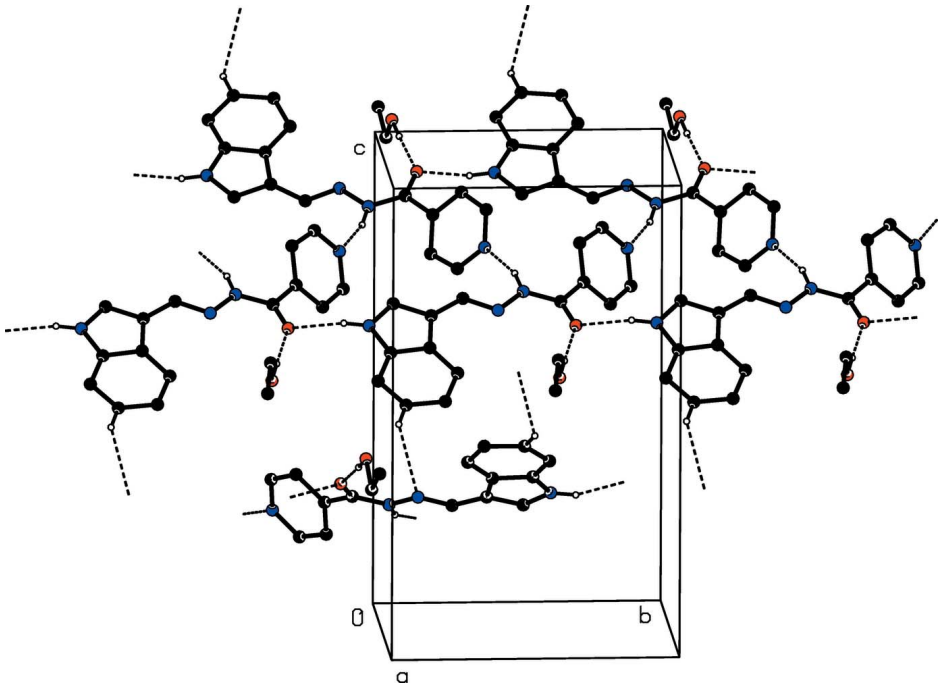


Figure 3
A packing diagram of compound **1·EtOH**, viewed along the *a* axis, showing the O—H···O, N—H···O, N—H···N and C—H···N interactions (dashed lines). For clarity, H atoms not involved in these interactions have been omitted.

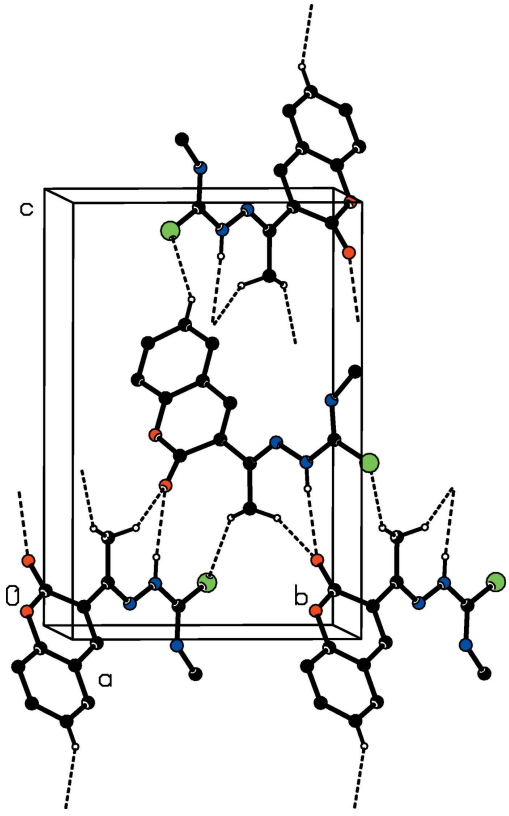


Figure 4
A crystal packing view of **2** along the *a* axis, showing the intermolecular hydrogen-bonded network formed by N—H···O, C—H···O and C—H···S interactions (dashed lines). For clarity, H atoms not involved in these interactions have been omitted.

Qiu *et al.* (2006), Lobana *et al.* (2012), Ilies *et al.* (2013) and Chainok *et al.* (2016), respectively.

5. Synthesis and crystallization

Compound **1** was synthesized by condensing equimolar amounts of 1*H*-indole-3-carbaldehyde (145 mg, 1 mmol) with nicotinic acid hydrazide (137 mg, 1 mmol) in ethanol. The reaction mixture was then refluxed on a water bath for 5 h and poured into crushed ice. The corresponding solid Schiff base that formed was filtered, washed several times with distilled water and dried under vacuum. The compound was recrystallized from an ethanol–chloroform (1:3) solvent mixture, yielding the ethanol solvate compound, **1·EtOH**. Similarly, compound **2** was synthesized from equimolar amounts of 3-acetyl-2*H*-chromen-2-one (188 mg, 1 mmol) with *N*-methylhydrazinecarbothioamide (105 mg, 1 mmol) in ethanol. Compound **2** was also recrystallized from an ethanol–chloroform (1:3) solvent mixture.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were refined as riding with N—H = 0.88, C—H = 0.95 or 0.98 Å and U_{iso}(H) = 1.2 or 1.5U_{eq}(parent atom). For **1·EtOH**, the methylene H atoms of the ethanol solvent molecule were refined independently under strong bond-length and angle restraints using *DFIX* to avoid a large residual electron-density peak near the methylene C atom caused by the usual riding treatment of the H

Table 3
Experimental details.

	1·EtOH	**2**
Crystal data		
Chemical formula	$C_{15}H_{12}N_4O·C_2H_6O$	$C_{13}H_{13}N_3O_2S$
M_r	310.35	275.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
Temperature (K)	110	100
a, b, c (Å)	9.4692 (18), 9.9821 (19), 16.682 (3)	9.289 (4), 9.616 (4), 14.474 (6)
α, β, γ (°)	90, 90, 90	90, 90.825 (4), 90
V (Å^3)	1576.9 (5)	1292.8 (9)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.25
Crystal size (mm)	0.50 × 0.37 × 0.13	0.49 × 0.46 × 0.31
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*TWINABS*; Bruker, 2012)
T_{min}, T_{max}	0.618, 0.681	0.534, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39878, 3616, 3527	5480, 2902, 2285
R_{int}	0.054	0.044
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.651	0.651
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.119, 0.98	0.048, 0.116, 1.10
No. of reflections	3616	2902
No. of parameters	216	174
No. of restraints	3	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.50, −0.36	0.30, −0.35
Absolute structure	Flack x determined using 1491 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	–
Absolute structure parameter	−0.2 (3)	–

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS2014* and *SHELXS2013* (Sheldrick, 2008), *SHELXL2013* and *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2015).

atoms. In **2**, *TWINABS* was employed to correct the data for absorption effects, as well as to separate hkl files for the domains with major and minor components; the twin ratio was observed to be 91:9. In the refinement, only the data of the major domain were used.

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supporting information

Acta Cryst. (2017). E**73**, 594-597 [https://doi.org/10.1107/S205698901700411X]

Crystal structures of the Schiff base derivatives (*E*)-*N*′-[(1*H*-indol-3-yl)methylidene]isonicotinohydrazide ethanol monosolvate and (*E*)-*N*-methyl-2-[1-(2-oxo-2*H*-chromen-3-yl)ethylidene]hydrazinecarbothioamide

Sivaraj Saranya, Jebiti Haribabu, Nattamai S. P. Bhuvanesh, Ramasamy Karvembu and Dasararaju Gayathri

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013). Program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008) for 1.EtOH; *SHELXS2013* (Sheldrick, 2008) for (2). Program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015) for 1.EtOH; *SHELXL2013* (Sheldrick, 2008) for (2). For both compounds, molecular graphics: *PLATON* (Spek, 2015). Software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2015) for 1.EtOH; *SHELXL2013* (Sheldrick, 2015) and *PLATON* (Spek, 2015) for (2).

(1.EtOH) (*E*)-*N*′-[(1*H*-Indol-3-yl)methylidene]isonicotinohydrazide ethanol monosolvate

Crystal data

$C_{15}H_{12}N_4O\cdot C_2H_6O$
$M_r = 310.35$
Orthorhombic, $P2_12_12_1$
$a = 9.4692$ (18) Å
$b = 9.9821$ (19) Å
$c = 16.682$ (3) Å
$V = 1576.9$ (5) Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.307$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9846 reflections
$\theta = 2.4$–27.5°
$\mu = 0.09$ mm^{-1}
$T = 110$ K
Block, colorless
0.50 × 0.37 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
$T_{min} = 0.618$, $T_{max} = 0.681$
39878 measured reflections
3616 independent reflections
3527 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.4°$
$h = -12\rightarrow12$
$k = -12\rightarrow12$
$l = -21\rightarrow21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.119$
$S = 0.98$
3616 reflections
216 parameters
3 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.9574P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 1.50$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Absolute structure: Flack *x* determined using 1491 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.2 (3)

Special details

Experimental. SADABS-2014/3 (Bruker, 2014) was used for absorption correction. wR2(int) was 0.1205 before and 0.0824 after correction. The Ratio of minimum to maximum transmission is 0.9082. The $\lambda/2$ correction factor is not present.

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.

Refinement. 1. Fixed Uiso; at 1.2 times of: all C(H) groups, all N(H) groups and at 1.5 times of: C2S(H2SA, H2SB, H2SC) and O(H) groups 2. a. Aromatic/amide H refined with riding coordinates: N1(H1), N3(H3), C3(H3A), C4(H4), C5(H5), C6(H6), C7(H7), C9(H9), C12(H12), C13(H13), C14(H14), C15(H15) b. Idealised Me refined as rotating group: C11(H11A, H11B, H11C) 3. Strong restraints with DFIX were employed for methylene hydrogen atoms of the ethanol solvent molecule.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.41425 (19)	0.67417 (16)	0.63518 (11)	0.0184 (4)
N1	0.4971 (2)	−0.05011 (19)	0.64904 (12)	0.0157 (4)
H1	0.492857	−0.137698	0.654508	0.019*
N2	0.3980 (2)	0.40446 (18)	0.66721 (11)	0.0140 (4)
N3	0.2999 (2)	0.49844 (19)	0.69437 (12)	0.0137 (4)
H3	0.228694	0.472947	0.724635	0.016*
N4	−0.0322 (2)	0.8812 (2)	0.74337 (13)	0.0195 (4)
C1	0.5943 (2)	0.0185 (2)	0.60295 (13)	0.0143 (4)
C2	0.5644 (2)	0.1570 (2)	0.60882 (13)	0.0135 (4)
C3	0.6449 (3)	0.2483 (2)	0.56436 (14)	0.0166 (5)
H3A	0.625228	0.341561	0.566138	0.020*
C4	0.7543 (3)	0.1987 (3)	0.51768 (15)	0.0201 (5)
H4	0.809673	0.259218	0.486964	0.024*
C5	0.7852 (3)	0.0605 (3)	0.51472 (15)	0.0204 (5)
H5	0.862792	0.030250	0.483480	0.024*
C6	0.7048 (3)	−0.0316 (2)	0.55637 (14)	0.0185 (5)
H6	0.723861	−0.124959	0.553456	0.022*
C7	0.4091 (2)	0.0393 (2)	0.68452 (14)	0.0156 (4)
H7	0.333452	0.016491	0.719368	0.019*
C8	0.4453 (2)	0.1688 (2)	0.66264 (13)	0.0140 (4)
C9	0.3669 (2)	0.2839 (2)	0.68918 (13)	0.0142 (4)
H9	0.289165	0.270747	0.724287	0.017*
C10	0.3146 (2)	0.6275 (2)	0.67420 (13)	0.0133 (4)
C11	0.1947 (2)	0.7155 (2)	0.70049 (14)	0.0139 (4)
C12	0.1325 (2)	0.7050 (2)	0.77589 (14)	0.0156 (4)
H12	0.165590	0.641316	0.813786	0.019*

C13	0.0204 (2)	0.7902 (2)	0.79444 (14)	0.0185 (5)
H13	−0.021080	0.783377	0.846143	0.022*
C14	0.0301 (3)	0.8902 (2)	0.67103 (15)	0.0196 (5)
H14	−0.005725	0.954149	0.634104	0.023*
C15	0.1435 (2)	0.8117 (2)	0.64711 (15)	0.0168 (5)
H15	0.185233	0.823122	0.595771	0.020*
O1S	0.6541 (2)	0.6025 (2)	0.55370 (12)	0.0279 (4)
H1S	0.582293	0.623623	0.580387	0.042*
C1S	0.7704 (3)	0.5902 (2)	0.60520 (14)	0.0246 (5)
H1SA	0.757 (3)	0.4957 (4)	0.6166 (9)	0.037*
H1SB	0.776 (4)	0.6301 (9)	0.6581 (2)	0.037*
C2S	0.9016 (3)	0.5715 (3)	0.5560 (2)	0.0314 (6)
H2SA	0.889630	0.494186	0.520487	0.047*
H2SB	0.982242	0.556124	0.591660	0.047*
H2SC	0.918511	0.652049	0.523841	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0179 (8)	0.0109 (7)	0.0262 (8)	−0.0002 (6)	0.0061 (7)	−0.0001 (6)
N1	0.0189 (9)	0.0099 (8)	0.0183 (9)	−0.0004 (7)	0.0013 (7)	0.0009 (7)
N2	0.0137 (8)	0.0113 (8)	0.0169 (9)	0.0022 (7)	0.0002 (7)	−0.0012 (7)
N3	0.0120 (8)	0.0116 (8)	0.0177 (9)	0.0004 (7)	0.0025 (7)	−0.0003 (7)
N4	0.0150 (9)	0.0153 (9)	0.0282 (10)	0.0019 (8)	0.0009 (8)	−0.0020 (8)
C1	0.0156 (10)	0.0125 (10)	0.0147 (9)	−0.0009 (8)	−0.0034 (8)	0.0008 (8)
C2	0.0138 (10)	0.0122 (10)	0.0143 (9)	0.0011 (7)	−0.0018 (8)	−0.0001 (8)
C3	0.0182 (11)	0.0137 (10)	0.0178 (10)	−0.0015 (8)	0.0003 (9)	−0.0003 (8)
C4	0.0207 (11)	0.0219 (12)	0.0177 (10)	−0.0021 (10)	0.0046 (9)	0.0005 (9)
C5	0.0181 (11)	0.0250 (13)	0.0180 (10)	0.0025 (9)	0.0018 (9)	−0.0022 (9)
C6	0.0213 (11)	0.0158 (10)	0.0184 (11)	0.0043 (9)	−0.0012 (9)	−0.0016 (9)
C7	0.0168 (10)	0.0130 (10)	0.0171 (10)	0.0004 (8)	−0.0004 (8)	0.0005 (8)
C8	0.0139 (10)	0.0129 (10)	0.0153 (9)	−0.0004 (8)	−0.0011 (8)	0.0005 (8)
C9	0.0133 (9)	0.0135 (10)	0.0157 (10)	0.0000 (8)	0.0002 (8)	0.0003 (8)
C10	0.0138 (10)	0.0118 (9)	0.0143 (10)	0.0014 (8)	−0.0011 (8)	−0.0020 (8)
C11	0.0126 (9)	0.0110 (9)	0.0181 (10)	−0.0012 (8)	−0.0006 (8)	−0.0029 (8)
C12	0.0151 (10)	0.0134 (10)	0.0183 (10)	0.0001 (8)	−0.0004 (8)	−0.0007 (8)
C13	0.0165 (10)	0.0186 (10)	0.0204 (11)	−0.0007 (9)	0.0032 (9)	−0.0021 (9)
C14	0.0180 (10)	0.0144 (10)	0.0263 (11)	0.0018 (9)	−0.0003 (9)	0.0028 (9)
C15	0.0162 (10)	0.0132 (10)	0.0212 (11)	−0.0007 (8)	0.0006 (9)	0.0011 (8)
O1S	0.0224 (9)	0.0324 (10)	0.0288 (10)	0.0047 (8)	0.0065 (7)	−0.0004 (8)
C1S	0.0269 (13)	0.0223 (12)	0.0246 (12)	−0.0020 (10)	0.0061 (10)	−0.0072 (10)
C2S	0.0208 (12)	0.0312 (14)	0.0423 (16)	−0.0029 (11)	0.0077 (12)	−0.0042 (12)

Geometric parameters (Å, º)

O1—C10	1.238 (3)	C7—C8	1.386 (3)
N1—C7	1.357 (3)	C7—H7	0.9500
N1—C1	1.381 (3)	C8—C9	1.437 (3)

N1—H1	0.8800	C9—H9	0.9500
N2—C9	1.292 (3)	C10—C11	1.501 (3)
N2—N3	1.396 (3)	C11—C12	1.393 (3)
N3—C10	1.339 (3)	C11—C15	1.396 (3)
N3—H3	0.8800	C12—C13	1.395 (3)
N4—C13	1.341 (3)	C12—H12	0.9500
N4—C14	1.346 (3)	C13—H13	0.9500
C1—C6	1.397 (3)	C14—C15	1.388 (3)
C1—C2	1.414 (3)	C14—H14	0.9500
C2—C3	1.401 (3)	C15—H15	0.9500
C2—C8	1.446 (3)	O1S—C1S	1.402 (3)
C3—C4	1.387 (3)	O1S—H1S	0.8400
C3—H3A	0.9500	C1S—C2S	1.500 (4)
C4—C5	1.411 (4)	C1S—H1SA	0.9700 (2)
C4—H4	0.9500	C1S—H1SB	0.9700 (2)
C5—C6	1.381 (3)	C2S—H2SA	0.9800
C5—H5	0.9500	C2S—H2SB	0.9800
C6—H6	0.9500	C2S—H2SC	0.9800

C7—N1—C1	109.00 (18)	N2—C9—H9	118.7
C7—N1—H1	125.5	C8—C9—H9	118.7
C1—N1—H1	125.5	O1—C10—N3	125.0 (2)
C9—N2—N3	112.49 (18)	O1—C10—C11	120.7 (2)
C10—N3—N2	119.74 (19)	N3—C10—C11	114.30 (19)
C10—N3—H3	120.1	C12—C11—C15	118.7 (2)
N2—N3—H3	120.1	C12—C11—C10	122.7 (2)
C13—N4—C14	116.9 (2)	C15—C11—C10	118.6 (2)
N1—C1—C6	129.1 (2)	C11—C12—C13	118.5 (2)
N1—C1—C2	108.2 (2)	C11—C12—H12	120.8
C6—C1—C2	122.6 (2)	C13—C12—H12	120.8
C3—C2—C1	119.3 (2)	N4—C13—C12	123.6 (2)
C3—C2—C8	134.4 (2)	N4—C13—H13	118.2
C1—C2—C8	106.20 (19)	C12—C13—H13	118.2
C4—C3—C2	118.1 (2)	N4—C14—C15	124.0 (2)
C4—C3—H3A	120.9	N4—C14—H14	118.0
C2—C3—H3A	120.9	C15—C14—H14	118.0
C3—C4—C5	121.6 (2)	C14—C15—C11	118.3 (2)
C3—C4—H4	119.2	C14—C15—H15	120.9
C5—C4—H4	119.2	C11—C15—H15	120.9
C6—C5—C4	121.3 (2)	C1S—O1S—H1S	109.5
C6—C5—H5	119.4	O1S—C1S—C2S	109.0 (2)
C4—C5—H5	119.4	O1S—C1S—H1SA	96.0 (14)
C5—C6—C1	117.0 (2)	C2S—C1S—H1SA	95.2 (13)
C5—C6—H6	121.5	O1S—C1S—H1SB	124.6 (19)
C1—C6—H6	121.5	C2S—C1S—H1SB	120 (2)
N1—C7—C8	110.3 (2)	H1SA—C1S—H1SB	103.2 (9)
N1—C7—H7	124.9	C1S—C2S—H2SA	109.5
C8—C7—H7	124.9	C1S—C2S—H2SB	109.5

C7—C8—C9	122.4 (2)	H2SA—C2S—H2SB	109.5
C7—C8—C2	106.3 (2)	C1S—C2S—H2SC	109.5
C9—C8—C2	131.2 (2)	H2SA—C2S—H2SC	109.5
N2—C9—C8	122.6 (2)	H2SB—C2S—H2SC	109.5
C9—N2—N3—C10	−177.7 (2)	C3—C2—C8—C9	0.1 (4)
C7—N1—C1—C6	179.6 (2)	C1—C2—C8—C9	−178.0 (2)
C7—N1—C1—C2	−1.0 (3)	N3—N2—C9—C8	174.45 (19)
N1—C1—C2—C3	−177.2 (2)	C7—C8—C9—N2	−178.1 (2)
C6—C1—C2—C3	2.2 (3)	C2—C8—C9—N2	−1.6 (4)
N1—C1—C2—C8	1.3 (2)	N2—N3—C10—O1	−3.5 (3)
C6—C1—C2—C8	−179.3 (2)	N2—N3—C10—C11	174.32 (18)
C1—C2—C3—C4	−1.8 (3)	O1—C10—C11—C12	−139.5 (2)
C8—C2—C3—C4	−179.8 (2)	N3—C10—C11—C12	42.5 (3)
C2—C3—C4—C5	−0.3 (4)	O1—C10—C11—C15	40.6 (3)
C3—C4—C5—C6	2.0 (4)	N3—C10—C11—C15	−137.4 (2)
C4—C5—C6—C1	−1.6 (4)	C15—C11—C12—C13	0.7 (3)
N1—C1—C6—C5	178.8 (2)	C10—C11—C12—C13	−179.2 (2)
C2—C1—C6—C5	−0.5 (3)	C14—N4—C13—C12	−1.1 (3)
C1—N1—C7—C8	0.2 (3)	C11—C12—C13—N4	0.7 (4)
N1—C7—C8—C9	177.8 (2)	C13—N4—C14—C15	0.0 (4)
N1—C7—C8—C2	0.6 (3)	N4—C14—C15—C11	1.4 (4)
C3—C2—C8—C7	177.1 (2)	C12—C11—C15—C14	−1.7 (3)
C1—C2—C8—C7	−1.1 (2)	C10—C11—C15—C14	178.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88	2.05	2.871 (3)	156
N3—H3···N4^{ii}	0.88	2.14	2.979 (3)	159
C5—H5···N2^{iii}	0.95	2.62	3.236 (3)	123
O1*S*—H1*S*···O1	0.84	1.90	2.742 (3)	177

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

(2) (*E*)-*N*′-Methyl-2-[1-(2-oxo-2*H*-chromen-3-yl)ethylidene]hydrazinecarbothioamide

Crystal data

$C_{13}H_{13}N_3O_2S$
M_r = 275.32
Monoclinic, $P2_1/c$
a = 9.289 (4) Å
b = 9.616 (4) Å
c = 14.474 (6) Å
β = 90.825 (4)°
V = 1292.8 (9) Å^3
Z = 4
$F(000)$ = 576
D_x = 1.415 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4293 reflections
θ = 2.2–27.3°
μ = 0.25 mm^{-1}
T = 100 K
Block, yellow
0.49 × 0.46 × 0.31 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*TWINABS*; Bruker, 2012)
T_{min} = 0.534, T_{max} = 0.746
5480 measured reflections

2902 independent reflections
2285 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 27.6°, θ_{min} = 2.2°
h = −12→12
k = −12→12
l = 0→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.116
S = 1.10
2902 reflections
174 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

Experimental. For component 1: wR2(int) was 0.1337 before and 0.0605 after correction. The ratio of minimum to maximum transmission is 0.72. The $\lambda/2$ correction factor is not present
Final HKLF 4 output contains 20988 reflections, Rint = 0.0871 (9738 with I > 3sig(I), Rint = 0.0747)
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.
Refinement. The absorption correction program TWINABS2 was employed to correct the data for absorption effects, as well as to separate hkl files for the domains with major component, which was used for further analysis.
1. Fixed Uiso; at 1.2 times of: All C(H) groups, all N(H) groups at 1.5 times of: all C(H, H, H) groups 2. a. Aromatic/amide H refined with riding coordinates: N2(H2), N3(H3), C3(H3A), C6(H6), C7(H7), C8(H8), C9(H9) b. Idealised Me refined as rotating group: C11(H11A, H11B, H11C), C13(H13A, H13B, H13C)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.80937 (6)	1.04558 (5)	0.39682 (4)	0.02114 (16)
O1	0.21617 (15)	0.36330 (14)	0.44249 (10)	0.0215 (3)
O2	0.37162 (18)	0.38370 (16)	0.33164 (11)	0.0314 (4)
N1	0.52878 (17)	0.75100 (17)	0.43518 (11)	0.0160 (4)
N2	0.61381 (18)	0.84670 (17)	0.39257 (11)	0.0173 (4)
H2	0.6171	0.8510	0.3319	0.021*
N3	0.67181 (19)	0.92800 (18)	0.53607 (11)	0.0197 (4)
H3	0.6007	0.8755	0.5554	0.024*
C1	0.3192 (2)	0.4382 (2)	0.39822 (14)	0.0200 (4)
C2	0.3575 (2)	0.5745 (2)	0.43650 (13)	0.0158 (4)
C3	0.3017 (2)	0.6138 (2)	0.51797 (13)	0.0164 (4)
H3A	0.3296	0.7005	0.5441	0.020*
C4	0.2019 (2)	0.5287 (2)	0.56577 (13)	0.0182 (4)
C5	0.1581 (2)	0.4043 (2)	0.52496 (14)	0.0193 (4)
C6	0.1375 (2)	0.5677 (2)	0.64904 (14)	0.0256 (5)

H6	0.1641	0.6528	0.6780	0.031*
C7	0.0363 (2)	0.4834 (3)	0.68876 (15)	0.0311 (6)
H7	−0.0071	0.5099	0.7452	0.037*
C8	−0.0026 (2)	0.3591 (3)	0.64601 (16)	0.0310 (6)
H8	−0.0720	0.3010	0.6743	0.037*
C9	0.0567 (2)	0.3179 (2)	0.56388 (15)	0.0256 (5)
H9	0.0289	0.2332	0.5349	0.031*
C10	0.4546 (2)	0.6670 (2)	0.38477 (13)	0.0164 (4)
C11	0.4552 (3)	0.6675 (3)	0.28152 (14)	0.0309 (6)
H11A	0.4431	0.7630	0.2590	0.046*
H11B	0.3760	0.6097	0.2579	0.046*
H11C	0.5470	0.6302	0.2599	0.046*
C12	0.6937 (2)	0.9357 (2)	0.44612 (13)	0.0159 (4)
C13	0.7581 (2)	1.0010 (2)	0.60437 (14)	0.0273 (5)
H13A	0.8603	0.9825	0.5938	0.041*
H13B	0.7326	0.9689	0.6663	0.041*
H13C	0.7399	1.1011	0.5994	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0185 (3)	0.0218 (3)	0.0231 (3)	−0.0043 (2)	0.0011 (2)	0.0012 (2)
O1	0.0192 (8)	0.0158 (7)	0.0295 (8)	−0.0012 (6)	−0.0026 (6)	−0.0015 (6)
O2	0.0320 (9)	0.0280 (9)	0.0343 (9)	−0.0001 (7)	0.0055 (7)	−0.0140 (7)
N1	0.0141 (8)	0.0183 (9)	0.0155 (8)	0.0000 (7)	−0.0004 (6)	0.0013 (6)
N2	0.0162 (8)	0.0225 (9)	0.0130 (8)	−0.0038 (7)	−0.0018 (6)	0.0010 (7)
N3	0.0206 (9)	0.0219 (9)	0.0164 (9)	−0.0043 (7)	−0.0021 (7)	−0.0015 (7)
C1	0.0168 (10)	0.0206 (11)	0.0226 (11)	0.0015 (9)	−0.0033 (8)	−0.0010 (9)
C2	0.0133 (9)	0.0178 (10)	0.0161 (10)	0.0009 (8)	−0.0036 (7)	−0.0009 (8)
C3	0.0138 (10)	0.0181 (10)	0.0173 (10)	0.0009 (8)	−0.0036 (7)	0.0001 (8)
C4	0.0138 (10)	0.0235 (11)	0.0171 (10)	0.0018 (8)	−0.0053 (7)	0.0054 (8)
C5	0.0140 (10)	0.0200 (10)	0.0237 (11)	0.0045 (8)	−0.0051 (8)	0.0066 (8)
C6	0.0212 (11)	0.0361 (13)	0.0195 (11)	−0.0010 (10)	−0.0027 (8)	0.0017 (9)
C7	0.0218 (12)	0.0522 (16)	0.0193 (11)	−0.0009 (11)	−0.0017 (9)	0.0119 (10)
C8	0.0171 (11)	0.0420 (14)	0.0339 (13)	−0.0039 (10)	−0.0045 (9)	0.0221 (11)
C9	0.0172 (11)	0.0237 (11)	0.0356 (13)	−0.0026 (9)	−0.0070 (9)	0.0114 (9)
C10	0.0149 (10)	0.0193 (10)	0.0151 (10)	0.0015 (8)	−0.0009 (7)	−0.0019 (8)
C11	0.0347 (14)	0.0419 (14)	0.0162 (11)	−0.0165 (11)	0.0014 (9)	−0.0042 (10)
C12	0.0131 (9)	0.0162 (10)	0.0184 (10)	0.0035 (8)	−0.0027 (7)	0.0008 (8)
C13	0.0269 (12)	0.0347 (13)	0.0202 (11)	−0.0033 (11)	−0.0069 (9)	−0.0041 (9)

Geometric parameters (Å, º)

S1—C12	1.674 (2)	C4—C6	1.404 (3)
O1—C1	1.365 (2)	C5—C9	1.382 (3)
O1—C5	1.375 (3)	C6—C7	1.374 (3)
O2—C1	1.206 (2)	C6—H6	0.9500
N1—C10	1.282 (3)	C7—C8	1.392 (4)

N1—N2	1.366 (2)	C7—H7	0.9500
N2—C12	1.367 (3)	C8—C9	1.375 (3)
N2—H2	0.8800	C8—H8	0.9500
N3—C12	1.323 (3)	C9—H9	0.9500
N3—C13	1.446 (3)	C10—C11	1.494 (3)
N3—H3	0.8800	C11—H11A	0.9800
C1—C2	1.464 (3)	C11—H11B	0.9800
C2—C3	1.349 (3)	C11—H11C	0.9800
C2—C10	1.479 (3)	C13—H13A	0.9800
C3—C4	1.423 (3)	C13—H13B	0.9800
C3—H3A	0.9500	C13—H13C	0.9800
C4—C5	1.392 (3)		

C1—O1—C5	122.86 (16)	C6—C7—H7	120.1
C10—N1—N2	118.48 (16)	C8—C7—H7	120.1
N1—N2—C12	118.61 (16)	C9—C8—C7	121.8 (2)
N1—N2—H2	120.7	C9—C8—H8	119.1
C12—N2—H2	120.7	C7—C8—H8	119.1
C12—N3—C13	123.65 (18)	C8—C9—C5	117.6 (2)
C12—N3—H3	118.2	C8—C9—H9	121.2
C13—N3—H3	118.2	C5—C9—H9	121.2
O2—C1—O1	116.07 (18)	N1—C10—C2	114.68 (17)
O2—C1—C2	126.37 (19)	N1—C10—C11	123.86 (18)
O1—C1—C2	117.55 (17)	C2—C10—C11	121.29 (17)
C3—C2—C1	119.16 (18)	C10—C11—H11A	109.5
C3—C2—C10	121.28 (18)	C10—C11—H11B	109.5
C1—C2—C10	119.56 (17)	H11A—C11—H11B	109.5
C2—C3—C4	121.67 (18)	C10—C11—H11C	109.5
C2—C3—H3A	119.2	H11A—C11—H11C	109.5
C4—C3—H3A	119.2	H11B—C11—H11C	109.5
C5—C4—C6	117.92 (19)	N3—C12—N2	115.66 (17)
C5—C4—C3	118.43 (18)	N3—C12—S1	124.32 (15)
C6—C4—C3	123.51 (19)	N2—C12—S1	120.02 (15)
O1—C5—C9	117.38 (19)	N3—C13—H13A	109.5
O1—C5—C4	119.94 (18)	N3—C13—H13B	109.5
C9—C5—C4	122.7 (2)	H13A—C13—H13B	109.5
C7—C6—C4	120.3 (2)	N3—C13—H13C	109.5
C7—C6—H6	119.9	H13A—C13—H13C	109.5
C4—C6—H6	119.9	H13B—C13—H13C	109.5
C6—C7—C8	119.7 (2)		

C10—N1—N2—C12	−179.56 (18)	C5—C4—C6—C7	1.0 (3)
C5—O1—C1—O2	172.55 (18)	C3—C4—C6—C7	176.49 (19)
C5—O1—C1—C2	−6.3 (3)	C4—C6—C7—C8	−0.1 (3)
O2—C1—C2—C3	−171.9 (2)	C6—C7—C8—C9	−0.7 (3)
O1—C1—C2—C3	6.9 (3)	C7—C8—C9—C5	0.5 (3)
O2—C1—C2—C10	8.9 (3)	O1—C5—C9—C8	−179.46 (18)
O1—C1—C2—C10	−172.34 (17)	C4—C5—C9—C8	0.4 (3)

C1—C2—C3—C4	−2.7 (3)	N2—N1—C10—C2	−175.51 (16)
C10—C2—C3—C4	176.51 (17)	N2—N1—C10—C11	−0.1 (3)
C2—C3—C4—C5	−2.2 (3)	C3—C2—C10—N1	28.8 (3)
C2—C3—C4—C6	−177.73 (19)	C1—C2—C10—N1	−152.03 (18)
C1—O1—C5—C9	−178.67 (18)	C3—C2—C10—C11	−146.7 (2)
C1—O1—C5—C4	1.5 (3)	C1—C2—C10—C11	32.4 (3)
C6—C4—C5—O1	178.71 (18)	C13—N3—C12—N2	172.14 (19)
C3—C4—C5—O1	3.0 (3)	C13—N3—C12—S1	−8.2 (3)
C6—C4—C5—C9	−1.1 (3)	N1—N2—C12—N3	−5.4 (3)
C3—C4—C5—C9	−176.87 (18)	N1—N2—C12—S1	174.97 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	0.88	2.39	3.269 (3)	175
C11—H11*A*···O2^{i}	0.98	2.47	3.109 (3)	123
C7—H7···S1^{ii}	0.95	2.85	3.711 (3)	151
C11—H11*B*···S1^{iii}	0.98	2.87	3.728 (3)	146

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