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Crystal structure of (2*E*)-*N*-methyl-2-[(4-oxo-4*H*-chromen-3-yl)methylidene]-hydrazinecarbothioamide

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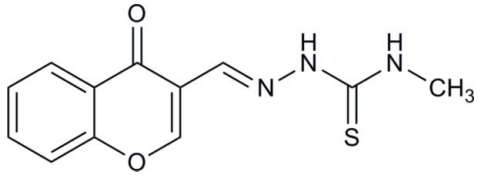
In the title compound, $C_{12}H_{11}N_3O_2S$, the dihedral angle between the 4*H*-chromen-4-one ring system and the –CH=N—NH—CS—NH– unit is 6.22 (1)°. In the crystal, inversion dimers linked by pairs of N—H···O hydrogen bonds generate $R_2^2(14)$ loops. The dimers are reinforced by a pair of C—H···O interactions, which generate $R_2^2(10)$ loops.

Keywords: crystal structure; hydrazinecarbothioamide; 4*H*-chromen-4-one; biological properties; hydrogen bonding.

CCDC reference: 1027156

1. Related literature

For the biological properties of related compounds, see: Khan *et al.* (2009); Tu *et al.* (2013); Kelly *et al.* (1996). For a related structure, see: Ishikawa & Watanabe (2014).



2. Experimental

2.1. Crystal data

$C_{12}H_{11}N_3O_2S$ M_r = 261.30

Monoclinic, $P2_1/n$
a = 6.3702 (7) Å
b = 20.647 (2) Å
c = 9.2717 (10) Å
β = 98.365 (3)°
V = 1206.5 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 293 K
0.30 × 0.25 × 0.20 mm

2.2. Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.924, T_{max} = 0.948
17429 measured reflections
3560 independent reflections
2257 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.131
S = 1.06
3560 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O2^{i}	0.86	2.11	2.897 (2)	152
C10—H10···O2^{i}	0.93	2.44	3.219 (2)	141

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7287).

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supporting information

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Crystal structure of (2*E*)-*N*-methyl-2-[(4-oxo-4*H*-chromen-3-yl)methylidene]hydrazinecarbothioamide

G. Vimala, J. Govindaraj, J. Haribabu, R. Karvembu and A. SubbiahPandi

S1. Comment

Thiosemicarbazones are of considerable interest because of their versatile chemistry and various biological activites such as antitumor, antibacterial, antiviral, antiamoebic and antimalarial (Kelly *et al.*, 1996). Schiff bases derived from 3-formylchromones have attracted much attention due to their biological functions such as enzyme inhibition (Khan *et al.*, 2009; Tu *et al.*, 2013).

The structure of the title compound (Figure 1) shows that the atoms of both 4*H*-chromen-4-one and the –CH=N—NH—CS—NH– segments are roughly planar and the largest deviations are -0.144 (2) and -0.114 (2) Å for O2 and C12 respectively. The dihedral angles between 4*H*-chromen-4-one and –CH=N—NH—CS—NH—C– unit and the benzene ring of 4*H*-chromen-4-one and –CH=N—NH—CS—NH—C– unit are 6.22 (1) and 7.12 (1)°, respectively.

In the crystal, inversion dimers linked by pairs of N—H···O hydrogen bonds generate $R_2^2(14)$ loops. The dimers are reinforced by a pair of C—H···O interactions, which generate $R_2^2(10)$ loops.

S2. Experimental

1.05 g (0.01 mol) of *N*-methylhydrazinecarbothioamide was dissolved in 20 ml of hot ethanol and to this 1.74 g of 4-oxo-4*H*-Chromene-3-carbaldehydein 10 ml of ethanol was added and continuously stirred for a period of 10 min with continuous stirring. The reaction mixture was refluxed for 2 h and allowed to cool whereby shining white was filtered and washed thoroughly with ethanol and then dried in vaccum. The compound was recrystallized from hot ethanol to yield colourless blocks in 92% yield.

S3. Refinement

All H atoms were fixed geometrically and allowed to ride on their parent C atoms, with C—H distances fixed in the range 0.93–0.97 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for all other H atoms.

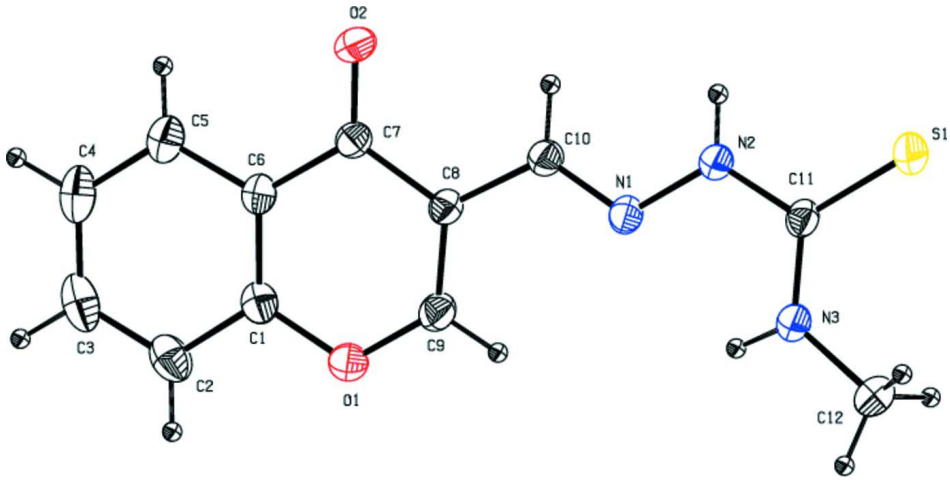

Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

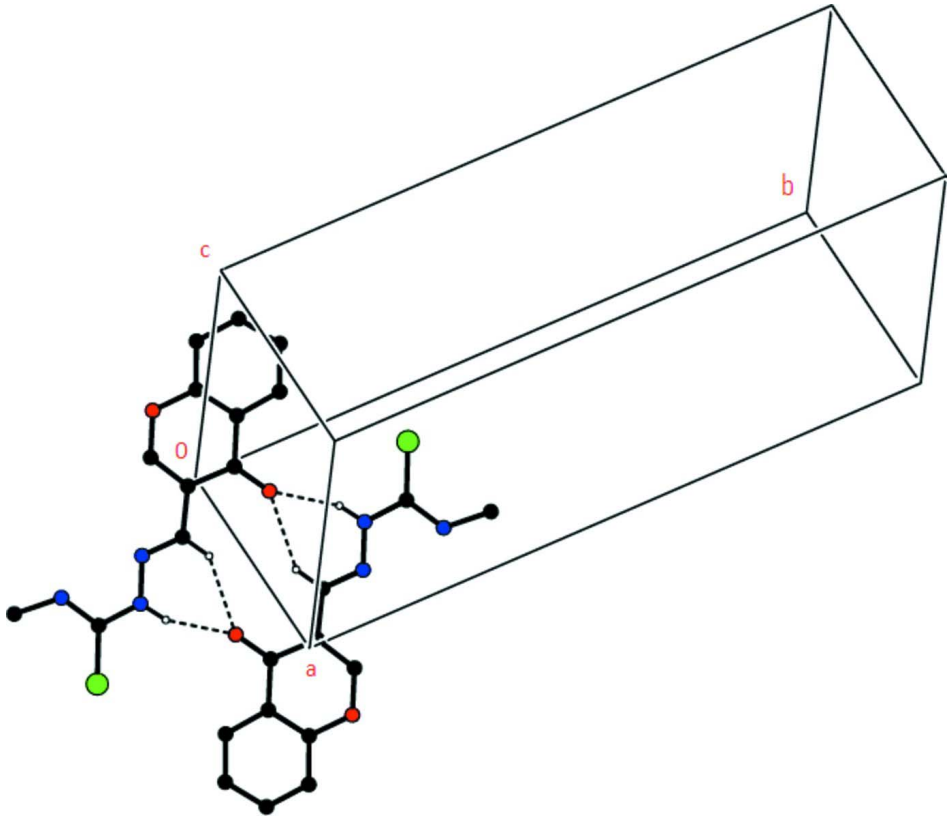

Figure 2

The packing of the title compound with hydrogen bonds represented by dashed lines. Hydrogen atoms not involved in these bonds are omitted for clarity.

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$\beta = 98.365$ (3)°
$V = 1206.5$ (2) Å^3
$Z = 4$
$F(000) = 544$
$D_x = 1.439$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\mu = 0.27$ mm^{-1}
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Block, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.924$, $T_{max} = 0.948$
17429 measured reflections
3560 independent reflections
2257 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 30.2°$, $\theta_{min} = 2.0°$
$h = -8 \rightarrow 8$
$k = -28 \rightarrow 28$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.131$
$S = 1.06$
3560 reflections
164 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.3687P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ 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	1.1216 (3)	−0.01086 (8)	−0.30947 (18)	0.0402 (4)
C2	1.2628 (3)	−0.03414 (11)	−0.3973 (2)	0.0536 (5)
H2	1.3795	−0.0097	−0.4138	0.064*
C3	1.2268 (4)	−0.09395 (12)	−0.4591 (2)	0.0615 (6)
H3	1.3198	−0.1102	−0.5187	0.074*

C4	1.0550 (4)	−0.13046 (11)	−0.4344 (2)	0.0590 (6)
H4	1.0321	−0.1708	−0.4784	0.071*
C5	0.9167 (3)	−0.10774 (9)	−0.3453 (2)	0.0485 (5)
H5	0.8020	−0.1329	−0.3279	0.058*
C6	0.9493 (3)	−0.04658 (8)	−0.28081 (17)	0.0359 (4)
C7	0.8095 (3)	−0.02066 (8)	−0.18335 (17)	0.0353 (4)
C8	0.8552 (3)	0.04523 (7)	−0.13502 (17)	0.0336 (3)
C9	1.0264 (3)	0.07560 (8)	−0.1711 (2)	0.0429 (4)
H9	1.0518	0.1177	−0.1376	0.051*
C10	0.7153 (3)	0.07618 (8)	−0.04415 (18)	0.0373 (4)
H10	0.5918	0.0552	−0.0274	0.045*
C11	0.6662 (3)	0.21399 (7)	0.16614 (18)	0.0367 (4)
C12	0.9249 (4)	0.30201 (10)	0.2112 (3)	0.0619 (6)
H12A	0.8427	0.3380	0.1689	0.093*
H12B	1.0703	0.3075	0.1976	0.093*
H12C	0.9158	0.2998	0.3136	0.093*
N1	0.7607 (2)	0.13156 (6)	0.01244 (15)	0.0367 (3)
N2	0.6206 (2)	0.15691 (6)	0.09629 (16)	0.0400 (3)
H2A	0.5048	0.1368	0.1046	0.048*
N3	0.8432 (3)	0.24283 (7)	0.14142 (18)	0.0456 (4)
H3A	0.9141	0.2252	0.0797	0.055*
O1	1.1633 (2)	0.04988 (6)	−0.25169 (15)	0.0482 (3)
O2	0.6644 (2)	−0.05230 (6)	−0.14399 (16)	0.0550 (4)
S1	0.49924 (9)	0.24309 (2)	0.27366 (6)	0.05253 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0460 (10)	0.0399 (9)	0.0355 (9)	0.0073 (7)	0.0089 (7)	0.0057 (7)
C2	0.0545 (12)	0.0624 (12)	0.0470 (11)	0.0127 (10)	0.0180 (9)	0.0078 (9)
C3	0.0724 (15)	0.0678 (14)	0.0469 (12)	0.0299 (12)	0.0167 (10)	0.0005 (10)
C4	0.0805 (16)	0.0484 (11)	0.0468 (11)	0.0189 (11)	0.0050 (11)	−0.0096 (9)
C5	0.0583 (12)	0.0403 (9)	0.0451 (10)	0.0052 (8)	0.0011 (9)	−0.0057 (8)
C6	0.0422 (9)	0.0336 (8)	0.0307 (8)	0.0050 (7)	0.0018 (7)	0.0015 (6)
C7	0.0365 (9)	0.0348 (8)	0.0339 (8)	−0.0016 (6)	0.0024 (7)	−0.0008 (6)
C8	0.0377 (9)	0.0302 (7)	0.0328 (8)	−0.0005 (6)	0.0052 (7)	0.0005 (6)
C9	0.0517 (11)	0.0329 (8)	0.0463 (10)	−0.0033 (7)	0.0147 (8)	0.0002 (7)
C10	0.0397 (9)	0.0353 (8)	0.0375 (9)	−0.0028 (7)	0.0080 (7)	−0.0028 (7)
C11	0.0430 (10)	0.0274 (7)	0.0401 (9)	0.0026 (6)	0.0072 (7)	0.0012 (6)
C12	0.0564 (13)	0.0406 (10)	0.0913 (17)	−0.0104 (9)	0.0190 (12)	−0.0151 (10)
N1	0.0445 (8)	0.0310 (7)	0.0357 (7)	0.0011 (6)	0.0097 (6)	−0.0006 (5)
N2	0.0427 (8)	0.0328 (7)	0.0469 (8)	−0.0036 (6)	0.0150 (7)	−0.0058 (6)
N3	0.0500 (9)	0.0330 (7)	0.0578 (10)	−0.0036 (6)	0.0213 (8)	−0.0072 (6)
O1	0.0510 (8)	0.0410 (7)	0.0572 (8)	−0.0043 (5)	0.0233 (6)	0.0007 (6)
O2	0.0539 (8)	0.0445 (7)	0.0712 (10)	−0.0181 (6)	0.0241 (7)	−0.0158 (6)
S1	0.0572 (3)	0.0399 (3)	0.0659 (4)	0.0015 (2)	0.0269 (3)	−0.0093 (2)

Geometric parameters (Å, º)

C1—O1	1.374 (2)	C8—C10	1.460 (2)
C1—C6	1.380 (2)	C9—O1	1.338 (2)
C1—C2	1.384 (3)	C9—H9	0.9300
C2—C3	1.367 (3)	C10—N1	1.274 (2)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.375 (3)	C11—N3	1.324 (2)
C3—H3	0.9300	C11—N2	1.356 (2)
C4—C5	1.375 (3)	C11—S1	1.6715 (17)
C4—H4	0.9300	C12—N3	1.444 (2)
C5—C6	1.400 (2)	C12—H12A	0.9600
C5—H5	0.9300	C12—H12B	0.9600
C6—C7	1.459 (2)	C12—H12C	0.9600
C7—O2	1.230 (2)	N1—N2	1.3695 (18)
C7—C8	1.449 (2)	N2—H2A	0.8600
C8—C9	1.342 (2)	N3—H3A	0.8600
O1—C1—C6	121.78 (15)	O1—C9—C8	124.97 (16)
O1—C1—C2	116.17 (17)	O1—C9—H9	117.5
C6—C1—C2	122.05 (17)	C8—C9—H9	117.5
C3—C2—C1	118.5 (2)	N1—C10—C8	120.64 (15)
C3—C2—H2	120.8	N1—C10—H10	119.7
C1—C2—H2	120.8	C8—C10—H10	119.7
C2—C3—C4	121.0 (2)	N3—C11—N2	115.89 (15)
C2—C3—H3	119.5	N3—C11—S1	124.97 (13)
C4—C3—H3	119.5	N2—C11—S1	119.14 (13)
C5—C4—C3	120.5 (2)	N3—C12—H12A	109.5
C5—C4—H4	119.7	N3—C12—H12B	109.5
C3—C4—H4	119.7	H12A—C12—H12B	109.5
C4—C5—C6	119.8 (2)	N3—C12—H12C	109.5
C4—C5—H5	120.1	H12A—C12—H12C	109.5
C6—C5—H5	120.1	H12B—C12—H12C	109.5
C1—C6—C5	118.20 (16)	C10—N1—N2	116.71 (14)
C1—C6—C7	119.82 (15)	C11—N2—N1	119.45 (14)
C5—C6—C7	121.97 (16)	C11—N2—H2A	120.3
O2—C7—C8	122.21 (15)	N1—N2—H2A	120.3
O2—C7—C6	122.79 (15)	C11—N3—C12	124.28 (16)
C8—C7—C6	115.00 (14)	C11—N3—H3A	117.9
C9—C8—C7	119.72 (15)	C12—N3—H3A	117.9
C9—C8—C10	121.73 (15)	C9—O1—C1	118.35 (14)
C7—C8—C10	118.52 (14)		
O1—C1—C2—C3	−179.09 (17)	C6—C7—C8—C9	−5.2 (2)
C6—C1—C2—C3	1.2 (3)	O2—C7—C8—C10	−4.0 (2)
C1—C2—C3—C4	−0.3 (3)	C6—C7—C8—C10	176.46 (14)
C2—C3—C4—C5	−0.8 (3)	C7—C8—C9—O1	0.6 (3)
C3—C4—C5—C6	0.9 (3)	C10—C8—C9—O1	178.80 (16)

O1—C1—C6—C5	179.29 (15)	C9—C8—C10—N1	−5.1 (3)
C2—C1—C6—C5	−1.0 (3)	C7—C8—C10—N1	173.16 (15)
O1—C1—C6—C7	−1.8 (2)	C8—C10—N1—N2	−179.90 (14)
C2—C1—C6—C7	177.85 (16)	N3—C11—N2—N1	3.0 (2)
C4—C5—C6—C1	−0.1 (3)	S1—C11—N2—N1	−177.53 (12)
C4—C5—C6—C7	−178.91 (17)	C10—N1—N2—C11	176.29 (15)
C1—C6—C7—O2	−173.71 (17)	N2—C11—N3—C12	−176.58 (18)
C5—C6—C7—O2	5.1 (3)	S1—C11—N3—C12	4.0 (3)
C1—C6—C7—C8	5.8 (2)	C8—C9—O1—C1	3.8 (3)
C5—C6—C7—C8	−175.36 (16)	C6—C1—O1—C9	−3.1 (2)
O2—C7—C8—C9	174.28 (17)	C2—C1—O1—C9	177.22 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O2^{i}	0.86	2.11	2.897 (2)	152
C10—H10···O2^{i}	0.93	2.44	3.219 (2)	141

Symmetry code: (i) −*x*+1, −*y*, −*z*.