Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Methyl-5-(4-oxo-4*H*-chromen-3-ylmethylene)-1,3-thiazolidine-2,4-dione

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.069
Data-to-parameter ratio = 11.5

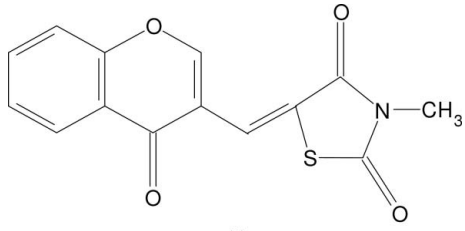
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 2 March 2006
Accepted 8 March 2006

In the title compound, $C_{14}H_9NO_4S$, the benzopyran and thiazolidine ring systems are each planar. The thiazolidine ring makes a dihedral angle of 3.84 (4)° with the benzopyran ring system. The molecular structure is stabilized by intramolecular C—H···O interactions.

Comment

Thiazolidinediones (TZDs) are a new class of insulin-sensitizing agents that reduce plasma glucose and glucose production, and also increase glucose clearance in patients with Type 2 diabetes, thus reducing insulin resistance (Stumvoll & Häring, 2002). The chromone structure is found within the chemical structure of the flavonoids, a group of naturally occurring substances that are of current interest due to their biological activities (Inaba *et al.*, 2000; Ma *et al.*, 2000; Budzisz *et al.*, 2002; Bozdağ-Dündar *et al.*, 2003, 2005). The title compound, (I), is a thiazolidinedione agent, as represented by rosiglitazone and pioglitazone. It also has some structural features of a chromone core framework. Initially, the chemical structure of (I) was investigated by elemental analysis, and ^{1}H NMR, mass and IR spectroscopic techniques. The crystal structure of (I) was determined to elucidate its molecular conformation.



(I)

The benzopyran ring system is planar (Fig. 1) and all the bond lengths and angles in the ring have normal values (Table 1). The thiazolidine ring is essentially planar, with a maximum deviation of 0.037 (2) Å, and makes a dihedral angle of 3.84 (4)° with the benzopyran ring system. The angle O2—C1—C6 is widened to [121.43 (13)°] and C6—C7—C9 is narrowed to [114.45 (12)°]. These angles are 121.4 (2) and 114.9 (2)°, respectively, in 3-(4-chlorobenzyl)-5-(4-oxo-4*H*-chromen-3-ylmethylene)-1,3-thiazolidine-2,4-dione, (II) (Özgen *et al.*, 2005), and 121.2 (2) and 115.6 (2)°, respectively, in morin (Cody & Luft, 1994). The methyl group attached to N1 is slightly twisted, with torsion angles of 175.8 (1) and −177.9 (1)° for C14—N1—C12—C11 and C14—N1—C13—S1, respectively.

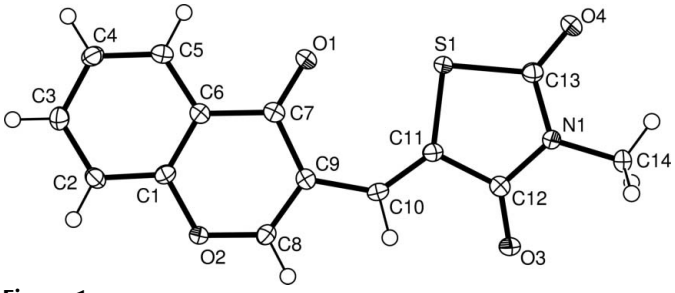


Figure 1
ORTEP-3 (Farrugia, 1997) view of (I), showing displacement ellipsoids drawn at the 50% probability level.

The structure is stabilized by intramolecular C—H ··· O hydrogen bonds (Table 2). Similar interactions were found in (II) (Özgen *et al.*, 2005) and in 2-(2)-ethoxycarbonyl-1,4-benzodioxan-7-yl)-4*H*-1-benzopyran-4-one (Özbey *et al.*, 1997).

Experimental

The chemical reagents used in the synthesis were purchased from E. Merck (Darmstadt, Germany) and Aldrich (Milwaukee, MI, USA). 2,4-Thiazolidinedione was prepared according to the literature procedure of DeLima *et al.* (1992). A mixture of chromone-3-carbaldehyde (0.3 g, 1.72 mmol) and 2,4-thiazolidinedione (0.202 g, 1.72 mmol) was heated at 413–423 K in the presence of glacial acetic acid (1 ml) and sodium acetate (0.234 g, 1.72 mmol) for 1 h. The crude product was crystallized from dimethylformamide (DMF). Then 5-(4-oxo-4*H*-chromen-3-ylmethylene)thiazolidine-2,4-dione (0.1 g, 0.37 mmol) and anhydrous sodium carbonate (0.039 g, 0.37 mmol) were dissolved in 3 ml DMF. Methyl iodide (0.023 ml, 0.74 mmol) was added to this mixture and it was stirred at 313 K for 3 h. The reaction mixture was poured on to ice. The residue was filtered. The filtrate was purified by column chromatography, using silica gel 60 (230–400 mesh ASTM) as the adsorbent and petroleum ether–chloroform (1:1) as the eluent (yield: 0.083 g, 78.9%; m.p: 511–513 K). IR (cm^{-1}) (γ pyrone CO): 1638; ^{1}H NMR (DMSO-d_6, 400 MHz, δ, p.p.m): 3.06 (*s*, 3H, $-CH_3$), 7.55 (*ddd*, 1H, 6H), 7.69 (*s*, 1H, ═CH), 7.73 (*d*, 1H, $J_{8,7}$ = 8.40 Hz, 8H), 7.86 (*ddd*, 1H, 7H), 8.11 (*dd*, 1H, $J_{5,6}$ = 8.00 Hz, $J_{5,7}$ = 1.60 Hz, 5H), 8.90 (*s*, 1H, 2H); ESMS [ES (+), *m*/*z*]: 288 (*M* + H). Analysis alculated for $C_{14}H_9NO_4S$: C 58.53, H 3.16, N 4.88, S 11.16%; found: C 58.63, H 3.39, N 4.87, S11.06%.

Crystal data

$C_{14}H_9NO_4S$
M_r = 287.28
Monoclinic, $P2_1/c$
a = 5.5926 (3) Å
b = 27.0630 (2) Å
c = 7.6829 (4) Å
β = 92.439 (4)°
V = 1161.77 (9) Å^3
Z = 4
D_x = 1.642 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14348 reflections
θ = 1.5–26.0°
μ = 0.29 mm^{-1}
T = 295 (2) K
Prism, colourless
0.3 × 0.2 × 0.1 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.918, T_{max} = 0.971
15165 measured reflections
2261 independent reflections
1802 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 26.0°
$h = -6 \rightarrow 6$
$k = -33 \rightarrow 33$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.069
S = 0.96
2261 reflections
197 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C11	1.7528 (15)	C10—C11	1.345 (2)
S1—C13	1.7754 (15)	C10—C9	1.453 (2)
O1—C7	1.2289 (18)	C9—C8	1.355 (2)
O2—C8	1.3367 (18)	O3—C12	1.2122 (18)
O2—C1	1.3784 (17)	N1—C14	1.4559 (19)
O4—C13	1.2102 (18)		
C11—S1—C13	91.81 (7)	C12—N1—C13	116.54 (12)
C11—C10—C9	134.22 (14)	N1—C13—S1	110.62 (10)
C11—C10—C9—C7	−2.3 (3)	C13—N1—C12—C11	−5.94 (18)
C5—C6—C1—O2	179.84 (13)	C9—C10—C11—C12	179.47 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O3	0.936 (17)	2.393 (19)	2.836 (2)	108.7 (13)
C14—H14*A*···O4	0.970 (17)	2.474 (18)	2.866 (2)	103.9 (13)

The positions of the H atoms bounded to C atoms in aromatic ring were calculated (C—H = 0.93 Å) and included in the structure-factor calculations using a riding model, with U_{iso}(H) = 1.2U_{eq}(C). The H atom on C10 and methyl H atoms were located in difference maps and their coordinates were refined freely.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDSII diffractometer (purchased under grant F.279 of the University Research Fund).

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