3-Methyl-5-(4-oxo-4H-chromen-3-yl-methylene)-1,3-thiazolidine-2,4-dione

In the title compound, \( \text{C}_{14}\text{H}_{9}\text{NO}_{4}\text{S} \), 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 \( \text{C}—\text{H} \cdots \text{O} \) 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; Bozdag-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 \(^1\text{H} \) NMR, mass and IR spectroscopic techniques. The crystal structure of (I) was determined to elucidate its molecular conformation.

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-4H-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.
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-ethoxy carbonyl-1,4-benzodioxan-7-yl)-4H-1-benzopyran-4-one (ÖZbeyl 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-4H-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, 0.374 mmol) was added to this mixture and it was stirred at 313 K for 3 h. The reaction mixture was poured onto 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, 79.8%; m.p: 511–513 K). IR (em−1) (y pyrone CO): 1638; 1H NMR (DMSO-d6, 400 MHz, δ, p.p.m.): 3.06 (s, 3H, −CH3), 7.55 (dd, 1H, 6H), 6.79 (s, 1H, −CH), 7.73 (d, 1H, J = 8.40 Hz, 8H), 7.86 (dd, 1H, 7H), 8.11 (dd, 1H, J = 8.00 Hz, J = 1.60 Hz, 5H), 8.90 (s, 1H, 2H); ESM (ES (+), m/z): 288 (M + H). Analysis alculated for C16H9NO4S: C 58.53, H 3.16, N 4.88, S 11.06%; found: C 58.63, H 3.39, N 4.87, S 11.06%.

**Crystal data**

\[ C_{16}H_{9}NO_{4}S \]

\[ M_r = 287.28 \]

Monoclinic, \( P_2_1/c \)

\[ a = 5.9268 \] (3) Å

\[ b = 27.0630 \] (2) Å

\[ c = 7.6820 \] (4) Å

\[ \beta = 92.439 \] (4)°

\[ V = 1161.77 \] (9) Å³

\[ Z = 4 \]

**Data collection**

Stoe IPDS-II diffractometer

\( \omega \) scans

1800 reflections with \( I > 2 \sigma (I) \)

\( R_{int} = 0.047 \)

\( \theta_{max} = 26.0° \)

\( h = -6 \) to 6

\( k = -33 \) to 33

\( l = -9 \) to 9

**Refinement**

Refinement on \( F^2 \)

\[ R[F^2 > 2\sigma(F^2)] = 0.028 \]

\[ wR(F^2) = 0.0609 \]

\[ S = 0.96 \]

2261 reflections

197 parameters

H atoms treated by a mixture of independent and constrained refinement

\[ w = 1/\sigma_i^2(F_{o}^2) + (0.0455P)^2 \]

where \( P = (F_{o}^2 + 2F_{c}^2)/3 \)

\( \Delta F_{max} = 0.26 \) e Å⁻³

\( \Delta F_{min} = -0.26 \) e Å⁻³

**Table 1**

<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °).</th>
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<tbody>
<tr>
<td>S1—C11</td>
</tr>
<tr>
<td>C10—C11</td>
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<tr>
<td>S1—C13</td>
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<tr>
<td>C10—C9</td>
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<tr>
<td>O1—C7</td>
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<tr>
<td>C8—C9</td>
</tr>
<tr>
<td>O2—C8</td>
</tr>
<tr>
<td>O3—C12</td>
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<tr>
<td>C4—C13</td>
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</tbody>
</table>

**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) | 1.797 (18) | 2.087 (13) |
| C14—H14A···O4      | 0.970 (17) | 2.474 (18) | 1.866 (18) | 2.039 (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 \( U_{eq}(H) = 1.2U_{eq}(C) \). 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).

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**References**


