Methyl trans-6-oxo-11-thiophen-2-yl-11,12-dihydro-6H-dibenzo[\textit{c,h}]chromene-12-carboxylate

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Methyl \textit{trans}-6-oxo-11-thiophen-2-yl-11,12-dihydro-6\textit{H}-dibenzo[c,h]chromene-12-carboxylate

In the title compound, C_{23}H_{16}O_{4}S, the dibenzo[c,h]chromene ring system is almost planar. The \textit{trans}-substituted thiophenyl and methoxycarbonyl groups are in an antiperiplanar conformation. The molecules are linked into dimers through weak intermolecular C—H\cdots{\text{O}} hydrogen bonds [H\cdots{\text{O}} = 2.53 \text{\AA{}}]. The molecule has a thienyl-ring flip disorder.

Comment

The systematic studies on the synthesis of new heterocyclic compounds with expected pharmacological activities on the basis of homophthalic anhydride carried out in our laboratory (Haimova \textit{et al.}, 1977; Kozekov \textit{et al.}, 2002; Stoyanova \textit{et al.}, 2003) focused our attention on some isochroman-1-one derivatives (Bogdanov & Palamareva, 2004; Bogdanov \textit{et al.}, 2005). Thus, we have isolated (Bogdanov & Palamareva 2004) the title compound (I) as a by-product of a reaction between homophthalic anhydride and thiophene-2-carbaldehyde in pyridine. In this paper, we report the X-ray crystallographic study of (I). Compounds containing the dibenzo[c,h]chromene ring system are interesting from a synthetic point of view because of their one-step conversion into benzo[c]phenanthridones (Beugelman \textit{et al.}, 1985; Duval & Mavou, 1990); these constitute an important class of isoquinoline alkaloids.
measuring the NMR spectra. According to the Karplus (1963) equation, the lower value of $J_{9,10} = 1.3$ Hz in the $^1$H NMR spectra (both in CDCl$_3$ and in DMSO-$d_6$) of (I) is in agreement with a synclinal position and torsion angle of about $80^\circ$ between the vicinal protons H9 and H10. In (I), the H9—C9—C10—H10 torsion angle is $78.0^\circ$. This shows that (I) is a conformationally rigid compound and that the observed conformation stays intact in the crystal structure and in solution alike, independent of the polarity of the solvent. The ring system A, B, C and D is approximately parallel to the (101) plane of the monoclinic cell. The molecules pack into two separate layers. These layers interconnect via hydrogen bonds (see Fig. 2 and Table 2) and $\pi-\pi$ interactions.

### Experimental

The synthesis of (I) was described by Bogdanov & Palamareva (2004). Single crystals were obtained by slow evaporation of a chloroform–ethanol acetate (3:1) solution at room temperature. The $^1$H NMR spectra of (I) were obtained on a Bruker DRX-250 spectrometer at 250.13 MHz in different solvents (see text) at 293 K. Chemical shifts ($\delta$) are expressed in parts per million (p.p.m.) from tetramethylsilane as an internal standard. $^1$H NMR (250 MHz, deuterochloroform) $\delta = 3.61$ (3H, s, OCH$_3$), 4.12 (1H, d, $J = 1.3$ Hz, H-10), 5.33 (1H, d, $J = 1.3$ Hz, H-9), 6.73–6.79 (2H, m, Ph—H), 7.01 (1H, dd, $J = 1.5, 4.8$ Hz, H-6, Th—H), 7.29–7.53 (4H, m, Ph—H), 7.65–7.75 (2H, m, Ph—H), 7.99 (1H, dd, $J = 1.3, 7.6$ Hz, Ph—H), 8.36 (1H, dm, $J = 7.6$ Hz, Ph—H). $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta = 3.55$ (3H, s, OCH$_3$), 4.37 (1H, d, $J = 1.3$ Hz, H-10), 5.46 (1H, d, $J = 1.3$ Hz, H-9), 6.81 (1H, dd, $J = 3.5$ & 5 Hz, Th—H), 7.00 (1H, d, $J = 3.3$ Hz, Th—H), 7.20 (1H, dd, $J = 1.3$ & 5 Hz, Th—H), 7.38–7.52 (3H, m, Ph—H), 7.59–7.66 (1H, m, Ph—H), 7.80 (1H, d, $J = 7.6$ Hz, Ph—H), 7.88–7.90 (2H, m, Ph—H), 8.25 (1H, d, $J = 7.8$ Hz, Ph—H).

### Crystal data

- $C_{23}H_{16}O_4S$
- Z = 8
- $D = 1.390$ Mg m$^{-3}$
- Mo Kα radiation
- $\mu = 0.20$ mm$^{-1}$
- $T = 293$ (2) K
- Irregular block, colorless
- $0.22 	imes 0.2 	imes 0.15$ mm

### Data collection

Data collection

- Enraf–Nonius CAD-4 diffractometer
- $\omega$–$2\theta$ scans

Absorption correction: ψ scans

(North et al., 1968)

- $\theta_{	ext{min}} = 0.835$, $\theta_{	ext{max}} = 0.970$
- 4131 measured reflections
- $R_{	ext{int}} = 0.057$

### Table 1

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<thead>
<tr>
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<tbody>
<tr>
<td>O1–C1</td>
<td>1.372 (6)</td>
<td>C2–O2</td>
<td>1.366 (7)</td>
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<tr>
<td>O4–C22</td>
<td>1.306 (7)</td>
<td>C8–C17</td>
<td>1.298 (7)</td>
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### Table 2

Hydrogen-bond geometry (Å, °).

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<tr>
<th>D–H···A</th>
<th>D–H</th>
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<th>D···A</th>
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<tr>
<td>C10–H10–O2</td>
<td>0.98</td>
<td>2.30</td>
<td>3.185 (8)</td>
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<tr>
<td>C9–H9–O3</td>
<td>0.98</td>
<td>2.53</td>
<td>3.473 (7)</td>
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<td>C3–H3–O3</td>
<td>0.93</td>
<td>2.53</td>
<td>3.277 (9)</td>
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</tr>
</tbody>
</table>

Symmetry codes: (i) $x, y, z$; (ii) $-x, -y, -z$; (iii) $x+\frac{1}{2}, y-\frac{1}{2}, z$.
All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å. For methoxy H atoms, $U_{iso}(H)$ values were taken to be $1.5U_{eq}(C)$; for all other H atoms, $U_{iso}(H)$ values were set at $1.2U_{eq}(C)$. There was some residual electronic density around the thiophene ring. Apparently, the ring occupies two distinct positions in the crystal structure. The occupancy factors of the carbon atoms at the two positions refined to values close to 0.5 and were fixed at this value. The structure was refined against F2 with 3247 independent reflections (i.e. $\theta_{max} = 25^\circ$).

Data collection: CAD-4 Software (Enraf–Nonius, 1977); cell refinement: CAD-4 Software; data reduction: SDP (Enraf–Nonius, 1985); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1994); software used to prepare material for publication: SHELXTL.

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References