

Methyl *trans*-6-oxo-11-thiophen-2-yl-11,12-dihydro-6*H*-dibenzo[*c,h*]chromene-12-carboxylateMilen G. Bogdanov^{a*} and Iliya S. Todorov^b^aFaculty of Chemistry, University of Sofia, 1, James Bouchier blv., 1164 Sofia, Bulgaria, and^bDepartment of Chemistry and Biochemistry, University of Notre Dame, 257 Nieuwland Science Hall, Notre Dame, IN 46556, USA

Correspondence e-mail:

mbogdanov@chem.uni-sofia.bg

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$

Disorder in main residue

R factor = 0.084

wR factor = 0.254

Data-to-parameter ratio = 12.5

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

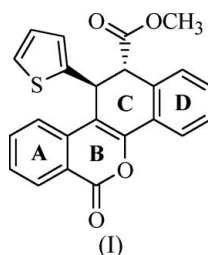
In the title compound, $\text{C}_{23}\text{H}_{16}\text{O}_4\text{S}$, the dibenzo[*c,h*]chromene ring system is almost planar. The *trans*-substituted thiophenyl and methoxycarbonyl groups are in an antiperiplanar conformation. The molecules are linked into dimers through weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds [$\text{H}\cdots\text{O} = 2.53 \text{ \AA}$]. The molecule has a thienyl-ring flip disorder.

Received 26 May 2006

Accepted 5 July 2006

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 *et al.*, 1977; Kozekov *et al.*, 2002; Stoyanova *et al.*, 2003) focused our attention on some isochroman-1-one derivatives (Bogdanov & Palamareva, 2004; Bogdanov *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 (Beugelmann *et al.*, 1985; Duval & Mavou, 1990); these constitute an important class of isoquinoline alkaloids.



The structure of (I) was determined by spectroscopic analysis (^1H , ^{13}C NMR, IR and MS) and microanalysis (Bogdanov & Palamareva, 2004) and was confirmed by single-crystal X-ray diffraction analysis. Rings A and B (see Fig. 1) are coplanar. Ring C is in a distorted twist conformation. The angle between rings A and B and ring D is $14.9(8)^\circ$. Thus, the dibenzo[*c,h*]chromene ring system A, B, C and D can be considered to be almost planar. The small deviation from the mean plane of this ring system can be attributed to the distorted twist conformation of ring C. In addition, the X-ray analysis confirms the *trans*-configuration of (I) and its conformation with an antiperiplanar position of the methoxycarbonyl and thiophenyl substituents.

Recently, we have shown (Bogdanov *et al.*, 2004) that the vicinal coupling constant in a given conformational flexible isochromanone depends on the polarity of the solvent used for

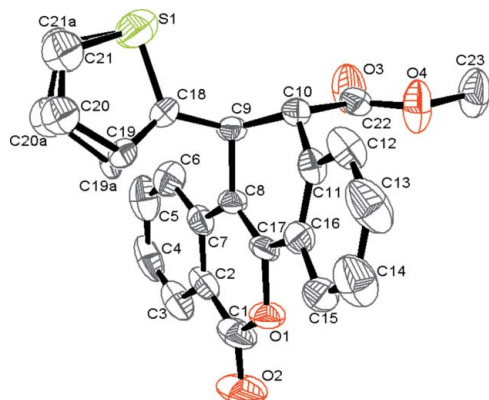


Figure 1

ORTEP plot and numbering of (I). Displacement ellipsoids are drawn at the 40% probability level and, for the sake of clarity, the H atoms have been omitted. Both disordered components are shown.

measuring the NMR spectra. According to the Karplus (1963) equation, the lower value of $^3J_{9,10} = 1.3$ Hz in the ^1H NMR spectra (both in CDCl_3 and in $\text{DMSO}-d_6$) of (I) is in agreement with a synclinal position and torsion angle of about 80° between the vicinal protons H9 and H10. In (I), the H9–C9–C10–H10 torsion angle is 78.0° . 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 π – π interactions.

Experimental

The synthesis of (I) was described by Bogdanov & Palamareva (2004). Single crystals were obtained by slow evaporation of a chloroform–ethyl acetate (3:1) solution at room temperature. The ^1H 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 (δ) are expressed in parts per million (p.p.m.) from tetramethylsilane as an internal standard. ^1H NMR (250 MHz, deuteriochloroform) $\delta = 3.61$ (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 , Th–H), 7.01 (1H, $dd, J = 1.5, 4.8$ Hz, 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). ^1H NMR (250 MHz, $\text{DMSO}-d_6$) $\delta = 3.53$ (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

$\text{C}_{23}\text{H}_{16}\text{O}_4\text{S}$	$Z = 8$
$M_r = 388.42$	$D_x = 1.390$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 10.6396$ (10) Å	$\mu = 0.20$ mm^{-1}
$b = 15.3834$ (10) Å	$T = 293$ (2) K
$c = 22.6827$ (10) Å	Irregular block, colorless
$\beta = 91.405$ (10)°	$0.22 \times 0.2 \times 0.15$ mm
$V = 3711.4$ (5) Å ³	

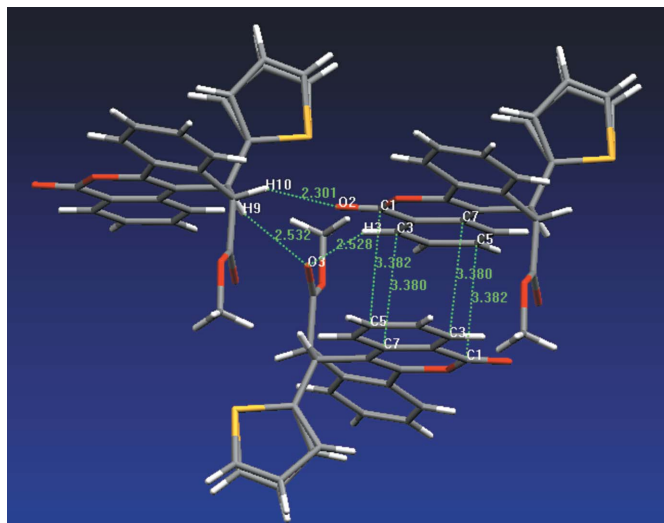


Figure 2

The crystal packing of (I), showing the intermolecular hydrogen bonds (dashed lines) and the π – π interactions in a dimeric unit. Distances are in Å.

Data collection

Enraf–Nonius CAD-4 diffractometer	4035 independent reflections
ω – 2θ scans	2063 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scans (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.057$
$T_{\text{min}} = 0.835$, $T_{\text{max}} = 0.970$	$\theta_{\text{max}} = 27.0^\circ$
4131 measured reflections	3 standard reflections every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1153P)^2 + 1.7754P]$
$R[F^2 > 2\sigma(F^2)] = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.254$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.36$ e Å ^{–3}
3247 reflections	$\Delta\rho_{\text{min}} = -0.46$ e Å ^{–3}
260 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

S1–C21	1.770 (19)	O3–C22	1.181 (7)
O1–C1	1.372 (8)	O2–C1	1.195 (7)
O4–C22	1.306 (7)	C8–C17	1.336 (7)
C1–O1–C17	121.7 (5)	C18–C9–C8	110.2 (4)
C22–O4–C23	117.1 (5)	C11–C10–C22	112.1 (5)
C7–C8–C9–C18	80.4 (6)	C18–C9–C10–C22	–156.8 (5)
C8–C9–C10–C11	–46.8 (6)	C11–C16–C17–C8	–14.8 (8)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10–H10 \cdots O2 ⁱ	0.98	2.30	3.185 (8)	150
C9–H9 \cdots O3 ⁱⁱ	0.98	2.53	3.473 (7)	161
C3–H3 \cdots O3 ⁱⁱⁱ	0.93	2.53	3.277 (9)	138

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

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, $U_{\text{iso}}(\text{H})$ values were taken to be $1.5U_{\text{eq}}(\text{C})$; for all other H atoms, $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C})$. 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. $\theta_{\text{max}} = 25^\circ$.)

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*.

The authors thank Professor Dr. Karl Törnroos for discussion of the subject and Mr. Yavor Mitrev for recording NMR spectra.

References

- Beugelman, R., Chastanet, J., Ginsburg, H., Quintero-Cortes, L. & Roussi, G. (1985). *J. Org. Chem.* **50**, 4933–4938.
- Bogdanov, M. G. & Palamareva, M. D. (2004). *Tetrahedron*, **60**, 2525–2530.
- Bogdanov, M. G., Todorov, I. S., Manolova, P. G., Cheshmedzhieva, D. V. & Palamareva, M. D. (2004). *Tetrahedron Lett.* **45**, 8383–8386.
- Bogdanov, M., Kandinska, M., Yliev, B. & Palamareva, M. (2005). *Pharmacia*, **52**, 7–11.
- Duval, O. & Mavou, L. (1990). *Tetrahedron*, **46**, 1253–1262.
- Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
- Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
- Haimova, M., Stanoeva, E., Ivanova, S., Palamareva, M. & Spassov, S. (1977). *Commun. Dept. Chem. Bulg. Acad. Sci.* **10**, 489–509.
- Karplus, M. (1963). *J. Am. Chem. Soc.* **85**, 2870–2871.
- Kozekov, I. D., Koleva, R. I. & Palamareva, M. D. (2002). *J. Heterocycl. Chem.* **39**, 229–235.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1994). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoyanova, M. P., Kozekov, I. D. & Palamareva, M. D. (2003). *J. Heterocycl. Chem.* **40**, 795–803.