Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2*H*-Thiochromene-2-thione

Parthapratim Munshi and T. N. Guru Row*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Correspondence e-mail: ssctng@sscu.iisc.ernet.in

Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.077
Data-to-parameter ratio = 11.4

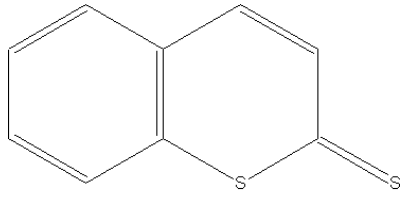
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 15 October 2004
Accepted 25 October 2004
Online 30 October 2004

The crystal structure of the title compound (systematic name: 2*H*-1-benzothiopyran-2-thione), $C_9H_6S_2$, also known as dithiocoumarin, has been determined. The molecule is essentially planar and the structure is stabilized *via* S···S and C—H···π interactions.

Comment

Coumarins have been extensively studied as they have applications in several areas of synthetic chemistry, medicinal chemistry and photochemistry. One of the most important of these applications is the formation of [2+2]-cycloaddition products on irradiation (Vishnumurthy *et al.*, 2001). Substituted coumarin derivatives find application in the dye industry (Hooper *et al.*, 1982; Morris & Russell, 1971) and with regard to laser dyes (Khalfan *et al.*, 1987; Nemkovich *et al.*, 1997), based on the fact that these compounds show state-dependent variation in the static dipole moment. Coumarin and its sulfur derivatives possess well defined dipole moments and exhibit second harmonic generation (SHG) effects, since they mostly crystallize in non-centrosymmetric space groups (Munshi & Guru Row, 2001, 2002*a*,*b*, 2003). Coumarins also exhibit a wide variety of pharmacological activities, such as antiviral (Domagala *et al.*, 1996) and antimicrobial activity (Eid *et al.*, 1994), and constitute the well known antibiotic Novobiocin (Reynolds, 1993). Coumarin dyes such as coumarin 138 (Jasinski & Woudenberg, 1995), coumarin 152 (Jasinski & Paight, 1994), coumarin 153 (Yip *et al.*, 1996) and coumarin 314 (Honda *et al.*, 1996) exhibit polymorphism. Coumarin derivatives such as 4-styrylcoumarin (Narasimha Moorthy & Venkatesan, 1994), its 3-fluoro derivative (Vishnumurthy *et al.*, 2002) and 3-acetylcoumarin (Munshi *et al.*, 2004) also display polymorphism (Bernstein *et al.*, 1999).



(I)

We report here the structure of the title compound, (I), which is also known as dithiocoumarin. The single-crystal X-ray analysis at 90 K confirms that (I) crystallizes in the centrosymmetric space group $P\overline{1}$. The molecular structure of dithiocoumarin along with the atom labeling is shown in Fig. 1. The molecule is essentially planar; the dihedral angle between the plane of the two six-membered rings (C1–C3/C8/

C9/S2 and C4–C9) is 0.60 (6)° and the S2/C1/S1 plane deviates by about 2.5° from these two rings. The packing diagram (Fig. 2) shows that the molecules are stacked along the *a* axis, with intermolecular separations of *ca* 3.43 and 3.48 Å between adjacent layers. There is a short S2···S2($-x$, $1-y$, $1-z$) contact (Guru Row & Parthasarthy, 1981) of 3.427 (1) Å. In addition, the molecules are stabilized by a weak C—H···π interaction (Table 2) of 2.930 (17) Å, belonging to region 3 as categorized by Umezawa *et al.* (1999).

Experimental

The title compound, (I), was synthesized in four steps. The product, 2*H*-thiochromen-2-one, obtained from *o*-nitrobenzaldehyde *via* a three-step reaction (Meth-cohn & Tarnowski, 1978), was treated with an equimolar amount of methoxyphenylthionophosphine sulfide (Lawesson's Reagent) (Scheibye *et al.*, 1979) in dry toluene at 383 K to obtain (I) (yield 99%). Crystals of (I) were grown by slow evaporation at 283 K from dioxane–hexane (1:3) (m.p. 373 K).

Crystal data

$C_9H_6S_2$
M_r = 178.28
Triclinic, $P\overline{1}$
a = 7.4427 (13) Å
b = 7.5697 (13) Å
c = 8.2490 (14) Å
α = 83.270 (2)°
β = 67.445 (2)°
γ = 65.599 (2)°
V = 390.39 (12) Å^3
Z = 2
D_x = 1.516 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3853 reflections
θ = 2.7–25.4°
μ = 0.60 mm^{-1}
T = 90.0 (2) K
Plate, dark red
0.40 × 0.26 × 0.06 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.805, T_{max} = 0.967
3853 measured reflections
1417 independent reflections
1348 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 25.4°
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.077
S = 1.07
1417 reflections
124 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1946P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.6626 (16)	C1—C2	1.437 (2)
S2—C1	1.7298 (17)	C2—C3	1.331 (2)
S2—C8	1.7440 (16)	C3—C9	1.447 (2)
C1—S2—C8	106.14 (8)	C2—C3—C9	125.00 (15)
C2—C1—S2	119.14 (12)	C9—C8—S2	122.12 (12)
C3—C2—C1	126.17 (15)		

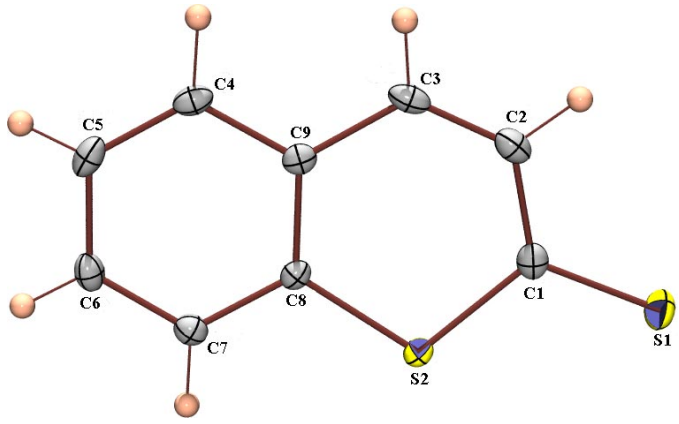


Figure 1
The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level.

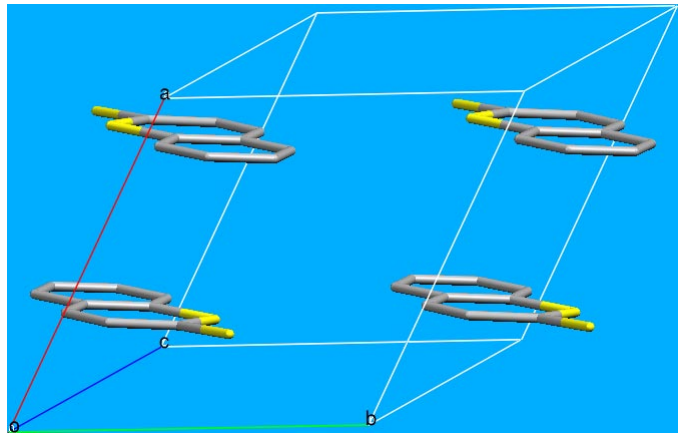


Figure 2
Packing diagram of (I). H atoms have been omitted.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···C2^{i}	0.94 (2)	2.93 (2)	3.479 (2)	119 (2)

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

All the H atoms were located in difference Fourier maps and refined isotropically. The C—H bond lengths are 0.87 (2)–0.97 (2) Å.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997), *POV-Ray for Windows* (The POV-Ray Team, 2004), *WinGX* (Version 1.64.05; Farrugia, 1999) and *MERCURY for Linux* (Taylor & Macrae, 2001; Bruno *et al.*, 2002); software used to prepare material for publication: *PLATON* (Spek, 2003).

PM thanks the CSIR, India, for a senior research fellowship. We thank DST–IRHPA, India, for the CCD facility at IISc, Bangalore.

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