Data collection

Siemens AED diffractometer
θ–2θ scans
Absorption correction: none
3916 measured reflections
2025 independent reflections
1317 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0675$
$\theta_{\rm max} = 70.49°$
$h = -1 \rightarrow 16$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 9$
1 standard reflection monitored every 50 reflections
intensity variation: within statistical fluctuation

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0830$
$wR(F^2) = 0.2314$
$S = 1.114$
1988 reflections
189 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1742P)^2 + 0.2112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.011$
$\Delta\rho_{\rm max} = 0.278$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.215$ e Å^{-3}
Extinction correction: $F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
Extinction coefficient: 0.010 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. All reflections were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by anisotropic full-matrix least squares. All the H atoms were found in the final $\Delta\rho$ map and refined isotropically with free displacement parameters in spite of the fact that the intensity data were of poor quality as the crystals were affected by twinning.

The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma).

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *PARSTCIF* (Nardelli, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(6aα,6bβ,12bβ,12cα)-6a,6b,12b,12c-Tetrahydrocyclobuta[1,2-*c*:4,3-*c*′]-di[1]benzothiopyran-6,7-dione†

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Abstract

Irradiation (350 nm) of 1-thiocoumarin in solution affords the title compound in 55% yield. This compound crystallizes in the chiral space group $P6_5$ with two

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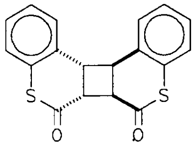
† Dedicated to Professor Dr.Dr. h.c. Hansjörg Sinn on the occasion of his 65th birthday.

molecules in the asymmetric unit. The absolute structure of the title compound was determined through the Flack parameter, $x = 0.00(2)$ [Flack (1983). *Acta Cryst.* **A39**, 876–881]. The experimental data are compared to those of the corresponding coumarin dimer. The cyclobutane ring of the title compound shows a puckered conformation. The fused six-membered thiopyran rings adopt conformations between half-chair (H conformation) and twist-boat (S conformation). The total puckering amplitudes, Q, in the six-membered rings are small, indicating that these rings are rather flat.

Comment

Irradiation (350 nm) of 1-thiocoumarin (10^{-2} M in CH_2Cl_2) and subsequent chromatographic purification (SiO_2/CH_2Cl_2) affords the *anti* head-to-head dimer (I) [$R_f = 0.50$, 55%, m.p. 512–513 K, from pentan (Karbe & Margaretha, 1991)]. The X-ray analysis was undertaken in order to characterize its structure and stereochemistry. The results allow us to compare the photochemical behaviour of thiocoumarin with coumarin in solution.



(I)

Fig. 1 shows the molecular structure and the atomic numbering scheme of the title compound. Only one molecule of the title compound is drawn because the conformation of both molecules of the asymmetric unit are almost identical. The positions of all the H atoms were refined with distance restraints for the C—H distances (Sheldrick, 1993). All other distances and angles are generally as expected.

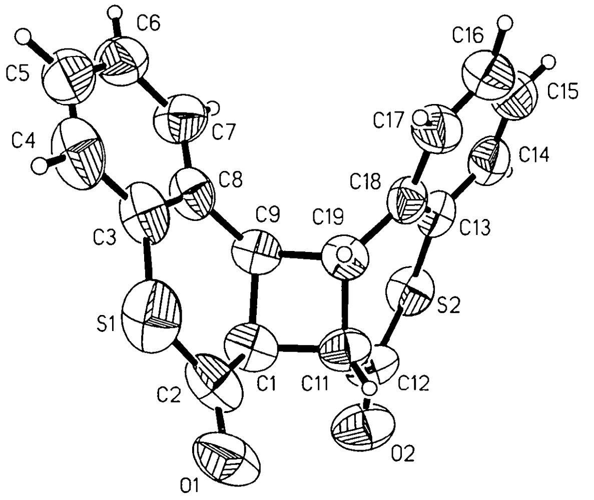


Fig. 1. *SHELXTL-Plus* drawing (Sheldrick, 1992) and atomic numbering scheme of the title compound.

The cyclobutane ring in the title compound shows a puckered conformation. A comparison of the puckering parameters (Cremer & Pople, 1975) of (I) [$Q = 0.314(5)$ Å] and the corresponding *anti* head-to-head coumarin dimer [$Q = -0.314$ Å (Saigo, Yonezawa, Sekimoto, Hasegawa, Ueno & Nakanishi, 1985)] shows that they are almost identical, but have opposite signs.

Experimental

Crystal data

$C_{18}H_{12}O_2S_2$
$M_r = 324.40$
Hexagonal
$P6_5$
$a = 9.936$ (1) Å
$c = 52.27$ (1) Å
$V = 4469$ (1) Å^3
$Z = 12$
$D_x = 1.446$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 42.6$–$48.2°$
$\mu = 3.269$ mm^{-1}
$T = 293$ (1) K
Transparent block
0.60 × 0.30 × 0.30 mm
Pale yellow
Crystal source: recrystallized from n-pentane

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: none
8937 measured reflections
6275 independent reflections
5463 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.1757$
$\theta_{\rm max} = 76.5°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = -65 \rightarrow 65$
3 standard reflections
frequency: 120 min
intensity variation: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0663$
$wR(F^2) = 0.1817$
$S = 0.996$
6272 reflections
422 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1273P)^2 + 1.6383P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max/mean} = -3.108/0.032$
$\Delta\rho_{\rm max} = 0.373$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.317$ e Å^{-3}

Extinction correction: $F_c^* = kF_c[1 + (0.001x \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $x = 0.0000(2)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	1.1579 (2)	−0.1056 (2)	0.70268 (4)	0.0888 (5)
S2	0.7351 (1)	0.1658 (2)	0.66093 (3)	0.0692 (3)
O1	0.8662 (6)	−0.2775 (5)	0.7078 (1)	0.092 (1)
O2	0.5992 (5)	−0.0665 (5)	0.6915 (1)	0.094 (1)

C1	0.9244 (6)	−0.0205 (6)	0.6988 (1)	0.066 (1)
C2	0.9654 (9)	−0.1443 (7)	0.7040 (1)	0.077 (2)
C3	1.2764 (7)	0.0961 (6)	0.6975 (1)	0.066 (1)
C4	1.4353 (8)	0.1562 (9)	0.7023 (1)	0.085 (2)
C5	1.5351 (7)	0.3153 (9)	0.6996 (1)	0.082 (2)
C6	1.4827 (7)	0.4126 (8)	0.6916 (1)	0.080 (2)
C7	1.3254 (6)	0.3505 (7)	0.6872 (1)	0.074 (1)
C8	1.2216 (6)	0.1938 (6)	0.6907 (1)	0.059 (1)
C9	1.0511 (5)	0.1290 (5)	0.6854 (1)	0.057 (1)
C11	0.8241 (6)	−0.0559 (5)	0.6745 (1)	0.061 (1)
C12	0.7077 (6)	−0.0032 (6)	0.6772 (1)	0.069 (1)
C13	0.8745 (5)	0.2037 (5)	0.6371 (1)	0.054 (1)
C14	0.8797 (6)	0.2983 (6)	0.6164 (1)	0.066 (1)
C15	0.9835 (7)	0.3324 (7)	0.5974 (1)	0.079 (2)
C16	1.0866 (7)	0.2773 (8)	0.5979 (1)	0.079 (2)
C17	1.0774 (6)	0.1809 (7)	0.6171 (1)	0.068 (1)
C18	0.9766 (5)	0.1450 (5)	0.6376 (1)	0.053 (1)
C19	0.9756 (5)	0.0486 (5)	0.6595 (1)	0.054 (1)
S51	1.0390 (2)	−0.5520 (2)	0.72434 (3)	0.0755 (4)
S52	0.6399 (2)	−0.5912 (2)	0.82387 (3)	0.0796 (4)
O51	0.8047 (6)	−0.8159 (5)	0.7347 (1)	0.098 (2)
O52	0.6427 (5)	−0.8351 (4)	0.8102 (1)	0.080 (1)
C51	0.8778 (5)	−0.6551 (5)	0.7716 (1)	0.057 (1)
C52	0.8925 (6)	−0.6930 (6)	0.7446 (1)	0.071 (1)
C53	1.1611 (5)	−0.3943 (5)	0.7446 (1)	0.060 (1)
C54	1.3087 (6)	−0.2939 (6)	0.7354 (1)	0.073 (1)
C55	1.4112 (6)	−0.1659 (7)	0.7490 (2)	0.082 (2)
C56	1.3662 (6)	−0.1393 (6)	0.7728 (1)	0.079 (2)
C57	1.2185 (5)	−0.2405 (5)	0.7825 (1)	0.066 (1)
C58	1.1136 (5)	−0.3682 (5)	0.7679 (1)	0.053 (1)
C59	0.9581 (5)	−0.4784 (4)	0.7785 (1)	0.052 (1)
C61	0.7208 (5)	−0.6593 (5)	0.7753 (1)	0.055 (1)
C62	0.6666 (5)	−0.7109 (5)	0.8030 (1)	0.059 (1)
C63	0.6755 (5)	−0.4245 (5)	0.8063 (1)	0.056 (1)
C64	0.6219 (6)	−0.3335 (6)	0.8180 (1)	0.066 (1)
C65	0.6464 (6)	−0.1987 (6)	0.8063 (1)	0.066 (1)
C66	0.7232 (7)	−0.1546 (6)	0.7827 (1)	0.072 (1)
C67	0.7747 (6)	−0.2490 (6)	0.7715 (1)	0.062 (1)
C68	0.7511 (4)	−0.3832 (5)	0.7833 (1)	0.051 (1)
C69	0.8050 (5)	−0.4825 (5)	0.7703 (1)	0.051 (1)

Table 2. *Selected geometric parameters* (Å, °)

S1—C2	1.754 (7)	S51—C52	1.778 (6)
S1—C3	1.765 (6)	S52—C62	1.730 (5)
S2—C13	1.758 (5)	S52—C63	1.768 (5)
S2—C12	1.777 (6)	O51—C52	1.206 (7)
O1—C2	1.207 (8)	O52—C62	1.195 (6)
O2—C12	1.201 (7)	C51—C52	1.488 (8)
C1—C2	1.501 (7)	C51—C61	1.551 (6)
C1—C11	1.543 (8)	C51—C59	1.565 (6)
C1—C9	1.552 (7)	C53—C58	1.378 (7)
C3—C8	1.377 (6)	C58—C59	1.484 (6)
C8—C9	1.506 (7)	C59—C69	1.562 (5)
C9—C19	1.561 (7)	C61—C69	1.545 (6)
C11—C12	1.495 (7)	C61—C62	1.539 (7)
C11—C19	1.547 (6)	C63—C68	1.366 (7)
C13—C18	1.400 (6)	C68—C69	1.501 (5)
S51—C53	1.774 (6)		
C2—S1—C3	106.9 (3)	C53—S51—C52	105.7 (3)
C13—S2—C12	105.9 (2)	C62—S52—C63	106.8 (2)
C2—C1—C11	111.7 (4)	C52—C51—C61	109.7 (4)
C2—C1—C9	116.3 (4)	C52—C51—C59	116.3 (4)
C11—C1—C9	88.3 (4)	C61—C51—C59	86.8 (3)
O1—C2—C1	121.4 (6)	O51—C52—C51	123.4 (6)
O1—C2—S1	116.7 (5)	O51—C52—S51	115.8 (5)
C1—C2—S1	121.8 (5)	C51—C52—S51	120.7 (4)
C8—C3—C4	120.2 (6)	C54—C53—C58	120.7 (5)
C8—C3—S1	124.4 (4)	C54—C53—S51	116.1 (5)
C4—C3—S1	115.2 (4)	C58—C53—S51	123.2 (4)
C3—C8—C7	119.5 (5)	C53—C58—C57	118.9 (4)
C3—C8—C9	120.2 (5)	C53—C58—C59	121.3 (4)
C7—C8—C9	120.2 (4)	C57—C58—C59	119.7 (5)
C8—C9—C1	121.9 (4)	C58—C59—C69	123.9 (4)
C8—C9—C19	121.8 (4)	C58—C59—C51	120.1 (4)
C1—C9—C19	87.0 (4)	C69—C59—C51	87.9 (3)
C12—C11—C1	111.5 (4)	C69—C61—C62	116.1 (4)
C12—C11—C19	118.4 (4)	C69—C61—C51	89.0 (3)
C1—C11—C19	87.8 (4)	C62—C61—C51	107.9 (4)
O2—C12—C11	121.7 (5)	O52—C62—C61	119.8 (4)
O2—C12—S2	117.8 (4)	O52—C62—S52	119.4 (4)
C11—C12—S2	120.4 (4)	C61—C62—S52	120.8 (3)
C18—C13—C14	119.8 (5)	C68—C63—C64	121.4 (5)
C18—C13—S2	123.6 (4)	C68—C63—S52	124.1 (3)
C14—C13—S2	116.5 (4)	C64—C63—S52	114.6 (4)
C17—C18—C13	117.3 (5)	C63—C68—C67	119.1 (4)
C17—C18—C19	122.1 (4)	C63—C68—C69	121.7 (4)
C13—C18—C19	120.6 (4)	C67—C68—C69	119.1 (4)
C18—C19—C11	120.8 (4)	C68—C69—C61	120.1 (4)
C18—C19—C9	119.4 (4)	C68—C69—C59	121.3 (4)
C11—C19—C9	87.8 (4)	C61—C69—C59	87.1 (3)

Friedel opposites have been collected for the range: $h = -10 \rightarrow -6$, $k = -10 \rightarrow 0$ and $l = -65 \rightarrow 65$. These Friedel pairs are regarded as symmetry independent and were not merged.

Since the title compound crystallizes in a polar space group, polar axis restraints were applied by the method of Flack & Schwarzenbach (1988).

Data collection and cell refinement: Enraf–Nonius CAD-4 diffractometer software. Data reduction: *CADSHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*88 (Keller, 1988). Software used to prepare material for publication: *CIF2TEX* (Kopf, 1992*a*); *FCF2FOC* (Kopf, 1992*b*). Program used to calculate special details of molecular geometry: *PLATON*92 (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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