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α-(2*H*-1-Benzopyran-2-ylidene)-α-(methylthio)acetonitrile, a Chromylidene Acetonitrile†

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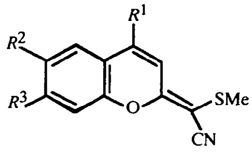
Abstract

The title compound, $C_{12}H_9NOS$, is the *E* derivative, the major product obtained from the reaction between salicylaldehyde and β-bromo-α-(methylthio)-crotononitrile. The molecular packing involves van der Waals contacts only, the shortest intermolecular distances being between the O and N atoms of one molecule, and the methyl group H atoms of the closest neighbouring molecules.

Comment

Coumarin and many of its derivatives have marked physiological effects and lasing properties (Kuo, 1994; Fabian, 1985). Only a few examples of their methylene derivatives (C═CXY instead of C═O) are known because the lactone ring has very low reactivity in direct condensations, such as Reformatsky (X = H, Y = CO_2Et; Pailer & Vostrowsky, 1971) or Knoevenagel reactions (X = Y = CN; Tkach *et al.*, 1992); other strategies have been developed from benzopyrylium salts (X = H, Y = Ph; Iwasaki & Akiba, 1987), 3-cyanocoumarins (X = H, Y = CN; Junek & Wilfinger, 1970) or salicylaldehydes (X = CHO, Y = CO_2Et; Werner *et al.*, 1994). Even when the compounds exist, the *Z*/*E* configuration has never been determined; in the last example of those cited above, the authors note an easy *Z*/*E* isomerization due to a low energy barrier (18 kcal). We have synthesized a new series of compounds, as shown in the scheme below, with R^1 = H, Ph or Me, R^2 = H or Me, and R^3 = H or OMe (Pochat & L'Haridon, 1998), where the methylene group displays a captodative effect (Stella *et al.*, 1980). All these new derivatives are obtained as *Z*/*E* mixtures.



(I) $R^1 = R^2 = R^3 = \mathrm{H}$

All the ^{1}H NMR spectra show two SMe peaks at δ = 2.30 and 2.40 p.p.m. However, the major isomer [(I), $R^1 = R^2 = R^3$ = H; δ SMe = 2.30 p.p.m.], derived from coumarin itself, was easily isolated through recrystallization from cyclohexane and its X-ray structure established. Molecule (I) (Fig. 1) exhibits the *E* configuration (SMe *trans* to the pyranyl O atom). The benzene and pyran rings are planar, with a maximum deviation of 0.013 Å for C2, whereas the plane around the C11 atom defined by C11, C2, C12 and S is slightly tilted in relation to the pyran plane by 4.9 (2)°. The methyl group and the N atom are located on the same side of this plane, with a distance of 1.683 (5) Å for C13 and a distance of 0.042 (5) Å for N, which thus lies very close to this plane. Bond lengths and angles in the benzene and pyran rings are close to the mean values observed for similar compounds (Jasinski & Woudenberg, 1994).

The shortest intermolecular contacts are O1···H133 ($1-x$, $-y$, $-z$) 2.86 (4), N···H131($x-1$, y, z) 2.87 (4)

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† Part of a synthetic study on benzopyrans and chromones (Pochat & L'Haridon, 1998).

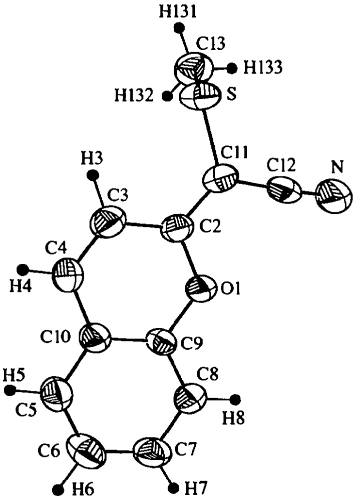

Fig. 1. *ORTEP*II (Johnson, 1976) drawing (50% probability ellipsoids) of the title compound with the atomic numbering scheme.

and N$\cdots$H132($1-x$, $-y$, $-z$) 2.90 (4) Å, with angles O1$\cdots$H133—C13 123.8 (4), N$\cdots$H131—C13 152.8 (4) and N$\cdots$H132—C13 156.4 (4)°. These values appear to be out of the ranges for usual hydrogen bonds so that the molecular packing involves only weak interactions.

Experimental

The title compound was obtained by reacting the sodium salt of salicylaldehyde with β-bromo-α-(methylthio)crotononitrile (*Z*/*E* mixture). Crystallization from cyclohexane gave yellow needles (m.p. 366–367 K).

Crystal data

$C_{12}H_9NOS$
$M_r = 215.28$
Monoclinic
$P2_1/c$
$a = 7.430\,(4)$ Å
$b = 18.453\,(2)$ Å
$c = 7.686\,(3)$ Å
$\beta = 96.32\,(2)°$
$V = 1047.5\,(7)$ Å^3
$Z = 4$
$D_x = 1.365$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 6–15°$
$\mu = 0.265$ mm^{-1}
$T = 293$ K
Needle
0.40 × 0.12 × 0.06 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2291 measured reflections
2135 independent reflections
1229 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.020$
$\theta_{\rm max} = 26.0°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 9$
3 standard reflections every 250 reflections intensity decay: 0.7%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.066$
$S = 1.15$
1229 reflections
137 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.07F_o^2)^2]$
$(\Delta/\sigma)_{\rm max} < 0.01$

$\Delta\rho_{\rm max} = 0.247$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.262$ e Å^{-3}
Extinction correction: Becker & Coppens (1975)
Extinction coefficient: $1.7\,(4) \times 10^{-7}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

S—C11	1.764 (4)	C2—C11	1.361 (5)
S—C13	1.792 (5)	C3—C4	1.334 (6)
O1—C2	1.366 (4)	C4—C10	1.432 (6)
O1—C9	1.379 (4)	C10—C5	1.394 (5)
N—C12	1.139 (5)	C10—C9	1.378 (5)
C2—C3	1.436 (5)	C11—C12	1.425 (5)
C11—S—C13	101.1 (2)	C4—C10—C5	123.6 (2)
C2—O1—C9	120.7 (3)	C4—C10—C9	117.9 (3)
O1—C2—C3	118.3 (3)	O1—C9—C10	121.6 (3)
O1—C2—C11	115.8 (2)	S—C11—C2	122.2 (3)
C3—C2—C11	125.8 (3)	S—C11—C12	116.7 (3)
C2—C3—C4	121.0 (3)	C2—C11—C12	121.1 (3)
C3—C4—C10	120.4 (3)	N—C12—C11	176.6 (4)

H atoms were fixed at ideal positions, each with $B_{\rm iso} = B_{\rm eq}$(bonded atom).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *BEGIN* in *SDP* (B. A. Frenz & Associates Inc., 1982). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982) in *SDP*. Program used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1258). Services for accessing these data are described at the back of the journal.

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1,5,8,12-Tetrathiaspiro[6.6]tridecane

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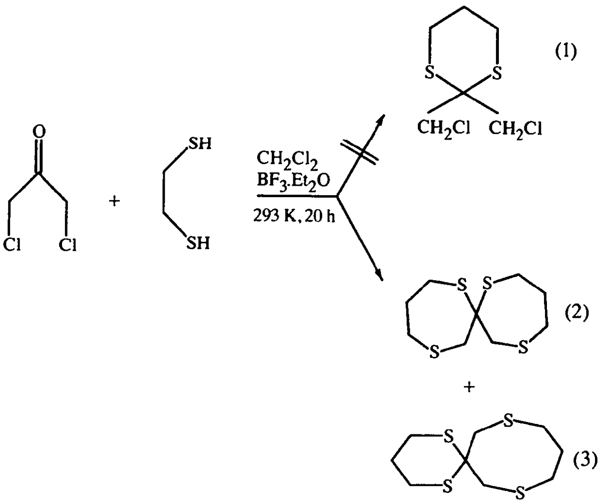
Abstract

The title compound, $C_9H_{16}S_4$, crystallizes in the space group $P\bar{1}$ with two molecules in the asymmetric unit. All seven-membered rings adopt a twist-chair (C_2 symmetry) conformation.

Comment

Our ongoing investigation of cyclopropene fatty acids as desaturase inhibitors in the biosynthesis of insect sex pheromones (Gosalbo *et al.*, 1994) led us to study alternative procedures to the previously reported preparations of these compounds (Baird *et al.*, 1992; Gensler *et al.*, 1970). We anticipated that cyclopropenone dithioacetal derivatives might be the appropriate precursor when submitted to reductive desulfuration. In this context, preparation of the dithioacetal (1) was required. However after the synthesis, unexpected formation of a mixture of 1,5,8,12-tetrathiaspiro[6.6]tridecane, (2), and 1,5,8,12-tetrathiaspiro[5.7]tridecane, (3), was found to have occurred.



Conformational analysis of seven-membered ring compounds is still a challenging problem because these compounds are flexible with many (conformational) possibilities. As shown in Fig. 1, the two crystallographically independent molecules of the title compound, (2), consist of two 1,4-dithiacycloheptane rings coupled together at the spiro-C atoms C7 or C7′. The molecules are similar and related by pseudo-symmetry operations. All four seven-membered rings adopt a twist-chair conformation with a pseudo-twofold axis running along C3 and the midpoint of C6—C7, and in the second ring, running along C7 and the midpoint of C10—C11. In the second molecule, the twofold axis runs along C7′ and the midpoints of bonds C3′—C4′ and C10′—C11′. The total puckering amplitude Q_T (Cremer & Pople, 1975) ranges from 1.062 (1) to 1.111 (1) Å. The conformational features agree with those reported previously for 1,4-dithiacycloheptane (Setzer *et al.*, 1981) and dioxepin (Ianelli *et al.*, 1989).

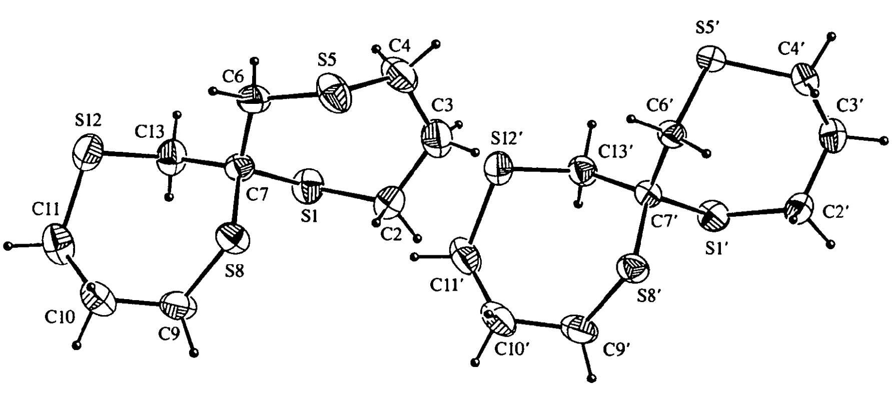


Fig. 1. The structure and labelling scheme for compound (2). Displacement ellipsoids are drawn at the 50% probability level.