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Acta Cryst. (1998). C**54**, 529–531

2-Salicylideneamino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile

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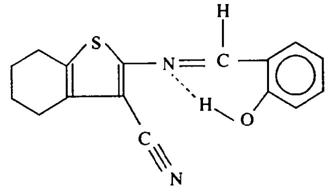
Abstract

Molecules of the title compound, $C_{16}H_{14}N_2OS$, are nearly planar. Each molecule contains an intramolecular O···N hydrogen bond [2.626 (2) Å].

Comment

Schiff bases have been used widely as ligands in the formation of transition metal complexes. Many such complexes have been structurally characterized, but only a relatively small number of free Schiff bases have been similarly characterized (Calligaris & Randaccio, 1987). N-Substituted salicylaldimines have been found to display thermochromism and photochromism in the solid state by proton transfer from the hydroxy O atom to the imine N atom, which may be reversible (Moustakali *et al.*, 1978; Hadjoudis *et al.*, 1987; Xu *et al.*, 1994). The charge transport occurs through overlapping intermolecular π orbitals with proton transfer; the proton transfer may also be a basis for the development of molecular switches (Xu *et al.*, 1994). Interest in photochromic compounds has been increasing ever since the potential applications of photochromic materials were realised in various areas, such as the control and measurement of radiation intensity, optical computers and display systems (Dürr, 1989; Dürr & Bouas-Laurent, 1990).

Our structural investigation of the Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997; Elmali *et al.*, 1995; Kevran *et al.*, 1996; Elmali & Elerman, 1997) have led us to examine the title compound, (I). The molecular geometry is illustrated in Fig. 1.



(I)

On the basis of some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar (Moustakali *et al.*, 1978), and that planarity of the molecule facilitates proton transfer through the hydrogen bond in the ground state (Bregman, Leiserowitz & Schmidt, 1964; Bregman, Leiserowitz & Osaki, 1964). In agreement with the above conclusions, the present molecule (excluding C13 and C14) is planar [with the largest deviation from planarity being 0.346 (2) Å for atom C13] and thermochromic (Kabak, 1998). There is a strong intramolecular hydrogen bond O1···N1 [2.626 (2) Å] in which the H atom is bonded to the O atom (the H1O atom was located from a difference Fourier map at the end of the refinement process as a small positive electron density). The sum of the van der Waals radii of O and N (3.07 Å; Bondi, 1964) is significantly longer than the O···N hydrogen-bond length, which is similar to the corresponding bond lengths in *N*-(2-hydroxyphenyl)salicylaldimine [2.625 (7) Å; Elerman *et al.*, 1995], 2,2′-azinodimethyldiphenol [2.611 (6) Å; Xu *et al.*, 1994] and bis-*N*,*N*′-*p*-chlorosalicylideneamine-1,2-diaminobenzene [2.615 (6) Å; Elerman *et al.*, 1994]. The O1—H1O and H1O···N1 distances are 0.88 (3) and 1.83 (3) Å, respectively. The O1—H1O···N1 angle is 150 (2)°. The unit cell and hydrogen-bonding scheme are shown in Fig. 2. Apart from the intramolecular hydrogen bond, there is also an intermolecular C—H···N contact, C7···N2$(\frac{1}{2}-x, \frac{1}{2}+y, z)$ 3.401 (3) Å. Such C—H···N contacts are thought to represent significant polar attractions (Berkovitch-Yellin & Leiserowitz, 1984) contributing to the overall packing.

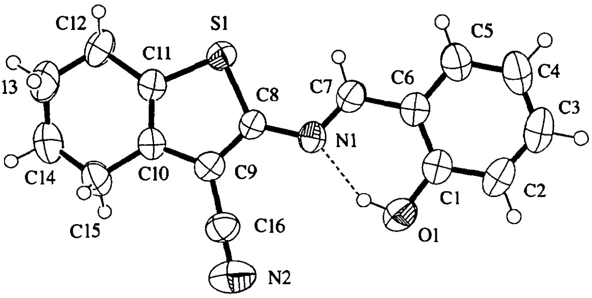


Fig. 1. The molecular structure of the title compound with the atomic labelling scheme and displacement ellipsoids at the 50% probability level. H atoms have arbitrarily small radii. The intramolecular hydrogen bond is shown as a dashed line.

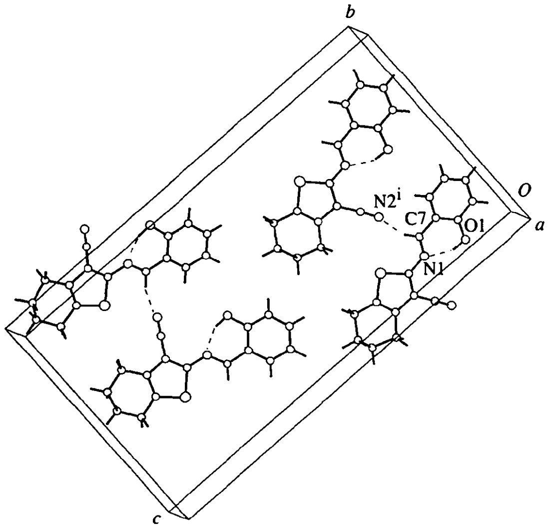


Fig. 2. Unit-cell contents with the hydrogen-bonding scheme indicated by dashed lines [symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2} + y$, z].

Experimental

The title compound was obtained from the reaction of 2-amino-4,5-tetramethylene-3-cyanothiophene (0.01 mol) in 50 ml of hot ethanol with a solution of salicylaldehyde (0.01 mol) in 40 ml of hot ethanol. The precipitate was recrystallized for 5–6 d from 2 g of Schiff base in 25 ml of acetonitrile solution.

Crystal data

$C_{16}H_{14}N_2OS$
$M_r = 282.35$
Orthorhombic
Pbca
$a = 7.424\,(4)$ Å
$b = 14.303\,(3)$ Å
$c = 26.510\,(2)$ Å
$V = 2815.0\,(16)$ Å^3
$Z = 8$
$D_x = 1.332$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.75–17.54°$
$\mu = 0.226$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.40 × 0.20 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2156 measured reflections
1809 independent reflections
1353 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.036$
$\theta_{\rm max} = 25.63°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 120 min
intensity decay: 5.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.083$
1809 reflections
184 parameters
H atoms: riding with fixed $U_{\rm iso}$ values

$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.1935P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.131$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.508$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C8	1.7265 (14)	N1—C7	1.281 (2)
S1—C11	1.729 (2)	N1—C8	1.386 (2)
O1—C1	1.360 (2)	N2—C16	1.132 (2)
C8—S1—C11	91.77 (8)	C9—C8—S1	110.38 (10)
C7—N1—C8	121.18 (13)	N1—C8—S1	126.70 (11)
O1—C1—C2	118.0 (2)	C10—C11—S1	112.59 (12)
O1—C1—C6	121.70 (15)	C12—C11—S1	122.74 (13)
N1—C7—C6	121.6 (2)	N2—C16—C9	177.8 (2)
C9—C8—N1	122.92 (13)		

All H-atom positions, except that of the hydroxy H atom, were calculated using a riding model and included with fixed isotropic displacement parameters in all refinements. The hydroxy H atom was found in the final difference Fourier map as a small positive electron density and refined.

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1510). Services for accessing these data are described at the back of the journal.

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

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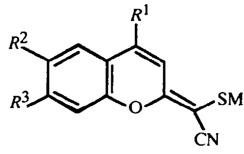
Abstract

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═C*XY* 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).