Refinement

Refinement on F^2
$R(F) = 0.063$
$wR(F^2) = 0.148$
$S = 0.960$
5797 reflections
343 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2]$
where $P = [\min(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.256$ e Å^{-3}
$\Delta\rho_{\min} = -0.287$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.215 (3)	O2—C18	1.213 (3)
N1—C9	1.465 (3)	N2—C26	1.459 (3)
N1—C10	1.460 (3)	N2—C27	1.462 (3)
N1—C12	1.413 (3)	N2—C29	1.413 (3)
C9—N1—C10	110.99 (17)	C26—N2—C27	111.29 (17)
C9—N1—C12	116.06 (18)	C26—N2—C29	117.62 (18)
C10—N1—C12	118.05 (19)	C27—N2—C29	117.95 (19)
C9—N1—C12—C13	50.7 (3)	C26—N2—C29—C30	5.5 (3)
C10—N1—C12—C17	2.3 (3)	C27—N2—C29—C34	−40.4 (3)

The unit-cell parameters were checked for the presence of higher lattice symmetry (Spek, 1988). Data were collected during 13 h of X-ray exposure time. Reflections were measured with a scan angle $\Delta\omega = (0.60 + 0.35\tan\theta)^\circ$; the horizontal and vertical apertures were 3.00 and 4.00 mm, respectively. The H atoms were included in the refinement on calculated positions, riding on their carrier atoms. The H atoms were refined with a fixed isotropic displacement parameter related to the equivalent isotropic displacement parameter of the carrier atom by a factor of 1.2. All non-H atoms were refined with anisotropic displacement parameters. The cited R value is calculated for 3078 reflections with $F > 4\sigma(F)$; wR is calculated for all observed reflections.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1991). Software used to prepare material for publication: *PLATON* (Spek, 1990*a*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1173). Services for accessing these data are described at the back of the journal.

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4-Ethyl-2-(2-hydroxynaphthylmethylidene)amino-5-methyl-3-thiophenecarbonitrile

Yalçın Elerman,[a] Ayhan Elmali,[a] Engin Kendi,[b] Süheyla Özbey[b] and Vedia Ertüzün[c]

[a]*Department of Physics Engineering, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey,* [b]*Department of Physics Engineering, Hacettepe University, 06532 Beytepe, Ankara, Turkey, and* [c]*Department of Chemistry, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey. E-mail: elerman@science.ankara.edu.tr*

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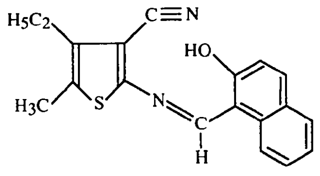
Abstract

The crystal structure of the title compound, $C_{19}H_{16}N_2OS$, has been determined. The core of the molecule (excluding the methyl group) is planar, with the largest deviation of 0.069 (2) Å for the O atom. An intramolecular O—H···N-type hydrogen bond occurs between the hydroxyl and amino groups [2.574 (3) Å].

Comment

Schiff bases have been extensively used as ligands in the field of coordination chemistry (Calligaris, Nardin & Randaccio, 1972). Schiff base compounds can be classified by their photochromic and thermochromic characteristics (Cohen, Schmidt & Flavian, 1964; Moustakali, Mavridis & Hadjoudis, 1978; Hadjoudis, Vitterakis, Moustakali & Mavridis, 1987). The intramolecular hydrogen bond between O and N atoms plays an important role in the formation of metal complexes and Schiff base compounds in the solid state by proton transfer from the hydroxyl O atom to the imine N atom (Moustakali *et al.*, 1978; Hadjoudis *et al.*, 1987; Xu, You, Sun, Wang & Liu, 1994). Proton transfer could also provide the basis of molecular switches. The charge transport occurs through overlapping intramolecular π orbitals with proton transfer (Xu *et al.*, 1994).

In the course of a systematic structural investigation of the Schiff bases, the structure of the title compound, (I), was determined (Elerman, Svoboda & Fuess, 1991; Elerman, Paulus, Svoboda & Fuess, 1992; Elerman, Elmali, Kabak, Aydin & Peder, 1994; Elerman, Elmali, Atakol & Svoboda, 1995; Elmali, Özbey, Kendi, Kabak & Elerman, 1995; Kevran, Elmali & Elerman, 1996). The molecular geometry is illustrated in Fig. 1.



(I)

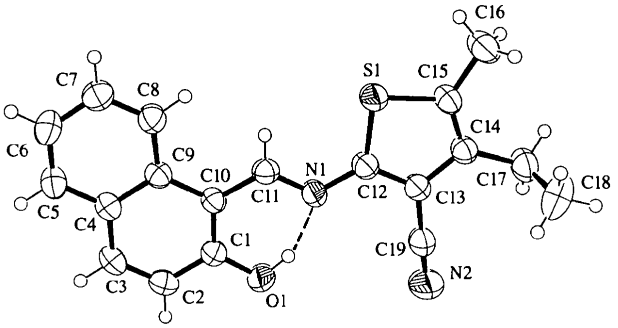


Fig. 1. The molecular structure of the title compound (*ORTEP*II; Johnson, 1976).

The N1=C11 bond distance of 1.293 (3) Å corresponds with typical values in related compounds [1.317 (6) (Elerman, Elmali, Atakol & Svoboda, 1995) and 1.323 (7) Å (Chinnakali, Sivakumar & Natarajan, 1990)]. The O1—C1 bond length of 1.356 (3) Å is in the range observed in similar structures (Inabe, Hoshino, Mitani & Maruyama, 1989; Bregman, Leiserowitz & Schmidt, 1964) and given in Table 2. A strong intramolecular hydrogen bond occurs between the O1 and N1 atoms, the H atom being essentially bonded to the O atom. The O1···N1, N1···H1 and O1—H1 bond distances are 2.574 (3), 1.76 (4) and 0.88 (4) Å, respectively, and the O1—H1···N1 angle is 153 (4)°. The sum of the van der Waals radii of O and N atoms (3.07 Å) is significantly longer than the intramolecular O···N hydrogen-bond length (Bondi, 1964). In the present study, the O1···N1 distance is comparable to that observed for thermochromic 2,2′-azinodimethyldiphenol [2.611 (6) Å; Xu *et al.*, 1994] and also for *N,N*′-disalicylidene-1,6-pyredeneamine [2.614 (5) Å; Inabe, Hoshino, Mitani & Maruyama, 1989]. The torsion angles N1—C11—C10—C1 [−0.4 (5)°], N1—C12—S1—C15 [−177.0 (3)°] and N1—C12—C13—C14 [176.4 (3)°] indicate that the molecule is practically planar.

Other geometrical details show small differences from similar structures (see Table 2). In Schiff base compounds, planarity of the molecule makes it possible for the proton to transfer through the hydrogen bond in the ground state with a small energy requirement (Bregman, Leiserowitz & Schmidt, 1964; Bregman, Leiserowitz & Osaki, 1964). From some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromic properties are planar, while those exhibiting photochromic properties are non-planar (Moustakali *et al.*, 1978). The core of the title molecule (excluding the methyl group) is planar. Thus, the title thermochromic Schiff base may be a candidate for construction of a novel type of conductive organic material in which the proton motion is essentially correlated to the electron conduction.

Experimental

The title compound was obtained from the condensation of 2-amino-4-ethyl-5-methyl-3-cyanothiophene and β-hydroxy-α-naphthylidene.

Crystal data

$C_{19}H_{16}N_2OS$
$M_r = 320.40$
Monoclinic
$P2_1/n$
$a = 8.362$ (2) Å
$b = 16.727$ (2) Å
$c = 11.554$ (2) Å
$\beta = 95.561$ (2)°
$V = 1608.4$ (6) Å^3
$Z = 4$
$D_x = 1.323$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 16 reflections
$\theta = 10$–$18°$
$\mu = 0.207$ mm^{-1}
$T = 293$ (2) K
Prismatic
0.64 × 0.56 × 0.32 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2268 measured reflections
2208 independent reflections
1682 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.048$
$\theta_{\rm max} = 26.3°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 0.01%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.118$
$S = 1.122$
2184 reflections
212 parameters
H atoms riding with fixed U's

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 1.0005P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.211$ e Å^{-3}
$\Delta\rho_{\min} = -0.182$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C12	1.731 (3)	C6—C7	1.387 (4)
S1—C15	1.736 (3)	C7—C8	1.370 (4)
O1—C1	1.356 (3)	C8—C9	1.407 (4)
N1—C11	1.293 (3)	C9—C10	1.452 (4)
N1—C12	1.379 (4)	C10—C11	1.432 (4)
N2—C19	1.138 (4)	C12—C13	1.376 (4)
C1—C10	1.391 (4)	C13—C14	1.423 (4)
C1—C2	1.406 (4)	C13—C19	1.435 (5)
C2—C3	1.359 (4)	C14—C15	1.357 (4)
C3—C4	1.412 (4)	C14—C17	1.517 (4)
C4—C9	1.413 (4)	C15—C16	1.491 (5)
C4—C5	1.414 (4)	C17—C18	1.492 (5)
C5—C6	1.363 (4)		
C12—S1—C15	92.20 (15)	C1—C10—C9	118.4 (2)
C11—N1—C12	122.2 (3)	C11—C10—C9	121.0 (2)
O1—C1—C10	122.2 (3)	N1—C11—C10	122.5 (3)
O1—C1—C2	116.2 (3)	C13—C12—N1	124.2 (3)
C10—C1—C2	121.6 (3)	C13—C12—S1	109.7 (2)
C3—C2—C1	119.9 (3)	N1—C12—S1	126.1 (2)
C2—C3—C4	121.5 (3)	C12—C13—C14	114.4 (3)
C3—C4—C9	119.6 (3)	C12—C13—C19	121.4 (3)
C3—C4—C5	120.8 (3)	C14—C13—C19	124.3 (3)
C9—C4—C5	119.6 (3)	C15—C14—C13	112.0 (3)
C6—C5—C4	121.0 (3)	C15—C14—C17	124.8 (3)
C5—C6—C7	119.4 (3)	C13—C14—C17	123.2 (3)
C8—C7—C6	121.2 (3)	C14—C15—C16	129.3 (3)
C7—C8—C9	121.1 (3)	C14—C15—S1	111.8 (2)
C8—C9—C4	117.7 (3)	C16—C15—S1	118.9 (2)
C8—C9—C10	123.4 (3)	C18—C17—C14	112.3 (3)
C4—C9—C10	118.9 (2)	N2—C19—C13	178.8 (4)
C1—C10—C11	120.5 (3)		

Table 2. *Bond lengths (Å) in some similar Schiff bases*

Reference	N···O	O—C	C═N	N—C
(i)	2.611 (6)	1.364 (8)	1.285 (7)	1.386 (9)
(ii*a*)	2.581 (6)	1.348 (6)	1.285 (6)	1.414 (6)
(ii*b*)	2.566 (6)	1.34 (1)	1.28 (1)	1.44 (1)
(ii*c*)	2.618 (9)	1.34 (2)	1.28 (2)	1.41 (2)
(iii)	2.615 (6)	1.357 (6)	1.285 (6)	1.420 (6)
(iv)	2.587 (5)	1.357 (3)	1.276 (4)	1.402 (4)
(v)	2.625 (7)	1.398 (1)	1.317 (6)	1.418 (8)
(vi)	2.575 (3)	1.357 (3)	1.294 (3)	1.379 (4)

References: (i) 2,2′-azinodimethyldiphenol ($C_{14}H_{12}N_2O_2$; Xu *et al.*, 1994); (ii*a*), (ii*b*), (ii*c*) *N*-(5-bromosalicylidene)-2-aminopyridine ($C_{12}H_9BrN_2O$; Moustakali *et al.*, 1978); (iii) bis-*N*,*N*′-*p*-chlorosalicylideneamine-1,2-diaminobenzene ($C_{20}H_{14}Cl_2N_2O_2$; Elerman *et al.*, 1994); (iv) *N*-benzylsalicylaldimine ($C_{14}H_{13}NO$; Elerman *et al.*, 1992); (v) *N*-(2-hydroxyphenyl)salicylaldimine ($C_{13}H_{11}NO$; Elerman *et al.*, 1995); (vi) 2-(β-hydroxy-α-naphthylidene)amino-4-ethyl-5-methyl-3-cyanothiophene ($C_{19}H_{16}N_2OS$; present work).

The title structure was solved by direct phase determination. The parameters of the complete structure could be refined by full-matrix anisotropic least squares. All phenyl rings were refined without any constraints. Values of distances and angles in the naphthyl moiety show no significant differences from those of an ideal benzene ring. All H-atom positions (except for the hydroxyl H atom) were calculated using a riding model and were considered with fixed isotropic U values in all refinements. The hydroxyl H atom was found in the difference Fourier map calculated near the end of the refinement process as a small positive electron density.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *MolEN* (Fair, 1990). Data reduction: *MolEN*. 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). Software used to prepare material for publication: *SHELXL*93.

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