

Intermolecular contacts less than 3.6 Å in length are presented for both structures in Table 4; Figs. 4 and 5 display stereo packing diagrams. While both molecules are precluded by their constitution from showing typical hydrogen-bonding interactions it is interesting to note the proximity of O(17) to both C(4) and C(6) in (I) for molecules translated along the *b* axis. Indeed, the H(5)⋯O(17) and H(6)⋯O(17) distances of 2.28 (4) and 2.45 (3) Å, respectively, and C(4)—H(5)⋯O(17) and C(6)—H(6)⋯O(17) angles of 160 (2) and 144 (2)°, respectively, may indicate a preferred packing arrangement based on C—H⋯O hydrogen bonds. In the structure of (II) no such close contacts are evident. Instead, closest contacts are of the fluorine/fluorine and fluorine/carbon type.

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Acta Cryst. (1990). **C46**, 1691–1693

Structure of 2-[1-(2-Thienyl)ethylideneamino]phenol

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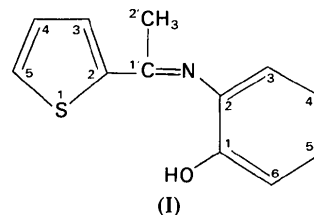
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(Received 22 May 1989; accepted 17 October 1989)

Abstract. C₁₂H₁₁NOS, *M_r* = 217.7, orthorhombic, *Pnca*, *a* = 15.582 (4), *b* = 16.162 (4), *c* = 8.729 (2) Å, *V* = 2198.3 Å³, *Z* = 8, *D_m* = 1.310 (1), *D_x* = 1.31 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.26 mm⁻¹, *F*(000) = 912, *T* = 292 K, *R* = 0.044 for 1367 observed reflexions. The thiophene and phenyl rings are planar and make a dihedral angle of 82.5 (3)°. The crystal structure is stabilized by an intermolecular H bond [2.835 (3) Å] from the phenolic OH to the imino N atom. A short intramolecular O—H⋯N contact of 2.866 (3) Å is also observed.

Introduction. Schiff bases are interesting ligands that give stable metal complexes. In continuing our studies of molybdenum(VI) complexes with Schiff-base ligands (Głowiak, Rucińska, Sobczak & Ziółkowski, 1987; Sobczak, Głowiak & Ziółkowski, 1990) we obtained a new crystalline monobasic

bidentate Schiff base from 2-thienyl ketone and *o*-aminophenol.



In this paper we report the synthesis and X-ray structure of 2-[1-(2-thienyl)ethylideneamino]phenol (I).

Experimental. A mixture of 0.1 mol 2-thienyl ketone, 0.1 mol *o*-aminophenol and 1 ml of formic acid as a catalyst in 150 ml of toluene was boiled using a Dean–Stark trap. After cooling, the title compound

Table 1. Positional parameters and equivalent isotropic temperature factors (\AA^2) with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i B_{ii}$$

	x	y	z	B_{eq}
S	0.3380 (1)	0.1451 (1)	0.1112 (1)	5.1 (1)
O	0.2331 (1)	-0.1063 (1)	0.4690 (2)	4.8 (2)
N	0.3517 (1)	-0.0134 (1)	0.2860 (3)	3.6 (2)
C(1)	0.3541 (2)	0.0472 (2)	0.0399 (3)	3.8 (2)
C(2)	0.3552 (2)	0.0487 (2)	-0.1184 (3)	4.8 (3)
C(3)	0.3434 (2)	0.1289 (2)	-0.1768 (4)	5.9 (3)
C(4)	0.3332 (2)	0.1863 (2)	-0.0669 (4)	5.6 (3)
C(5)	0.3683 (2)	-0.0226 (2)	0.1431 (3)	3.8 (2)
C(6)	0.4027 (2)	-0.1005 (2)	0.0710 (4)	5.6 (3)
C(7)	0.3787 (2)	-0.0737 (2)	0.3937 (3)	3.8 (2)
C(8)	0.4662 (2)	-0.0868 (2)	0.4219 (4)	5.5 (3)
C(9)	0.4940 (2)	-0.1381 (2)	0.5370 (5)	6.3 (3)
C(10)	0.4349 (2)	-0.1774 (2)	0.6277 (4)	5.6 (3)
C(11)	0.3486 (2)	-0.1667 (2)	0.6017 (4)	5.0 (3)
C(12)	0.3197 (2)	-0.1141 (2)	0.4871 (3)	3.9 (2)

Table 2. Bond lengths (\AA), valence angles ($^\circ$) and selected torsion angles ($^\circ$) with *e.s.d.*'s in parentheses

C(1)—C(2)	1.383 (4)	C(7)—C(8)	1.402 (4)
C(2)—C(3)	1.405 (5)	C(8)—C(9)	1.372 (5)
C(3)—C(4)	1.343 (5)	C(9)—C(10)	1.371 (5)
C(4)—S	1.692 (3)	C(10)—C(11)	1.374 (4)
S—C(1)	1.719 (3)	C(11)—C(12)	1.387 (4)
C(1)—C(5)	1.460 (4)	C(12)—C(7)	1.391 (4)
C(5)—C(6)	1.506 (4)	C(12)—O	1.364 (3)
C(5)—N	1.283 (4)		
N—C(7)	1.418 (3)		
C(1)—S—C(4)	92.1 (2)	N—C(7)—C(8)	120.6 (3)
S—C(1)—C(2)	110.3 (2)	N—C(7)—C(12)	121.0 (2)
C(1)—C(2)—C(3)	112.2 (3)	C(8)—C(7)—C(12)	117.9 (3)
C(2)—C(3)—C(4)	113.2 (3)	C(7)—C(8)—C(9)	121.8 (3)
S—C(4)—C(3)	112.3 (3)	C(8)—C(9)—C(10)	119.4 (3)
S—C(4)—C(1)	120.7 (2)	C(9)—C(10)—C(11)	120.2 (3)
C(2)—C(1)—C(5)	129.0 (3)	C(10)—C(11)—C(12)	120.9 (3)
C(1)—C(5)—N	118.7 (2)	C(11)—C(12)—C(7)	119.7 (3)
C(1)—C(5)—C(6)	116.2 (2)	O—C(12)—C(11)	117.5 (3)
C(6)—C(5)—N	125.1 (3)	O—C(12)—C(7)	122.8 (2)
C(5)—N—C(7)	120.4 (2)		
S—C(1)—C(5)—C(6)	-165.6 (3)	N—C(7)—C(12)—O	8.1 (4)
S—C(1)—C(5)—N	13.8 (3)	C(3)—C(2)—C(1)—C(5)	-176.6 (3)
C(1)—C(5)—N—C(7)	-168.7 (3)	C(2)—C(1)—C(5)—N	-169.6 (2)
C(6)—C(5)—N—C(7)	10.7 (3)	C(2)—C(1)—C(5)—C(6)	11.0 (3)
C(5)—N—C(7)—C(8)	66.1 (3)	C(4)—S—C(1)—C(5)	177.1 (2)
C(5)—N—C(7)—C(12)	-122.6 (3)		

crystallized from the reaction mixture as yellow prisms. These crystals were used for crystal structure determination without further purification. *M.p.*, uncorrected 404 K, was determined on a Boetius apparatus. Crystal of dimensions $0.50 \times 0.40 \times 0.40$ mm; D_m by flotation in aqueous ZnCl_2 ; orthorhombic, *Pnca* from Weissenberg photographs; Syntex P_2 , computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $19.0 \leq 2\theta(\text{Mo}) \leq 25.0^\circ$ measured on diffractometer; 1950 independent reflexions; $2\theta_{\text{max}} = 50.0^\circ$; variable θ - 2θ scans, scan rate 2.0 – $29.3^\circ \text{min}^{-1}$, depending on intensity; two

standards (183, 352) measured every 50 reflexions, variation in intensities $\pm 2\%$; correction for Lorentz and polarization factors, but not for absorption; 1367 with $I \geq 3\sigma(I)$ used for structure determination; index range h 0 to 18, k 0 to 19, l 0 to 10; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); direct methods SHELXS86 (Sheldrick, 1986); block-diagonal least squares [Syntex (1976) XTL/XTLE system]; minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$; difference synthesis revealed all H atoms; non-H atoms refined with anisotropic thermal parameters and H atoms with isotropic temperature factors, max. parameter shift in final LS cycle for non-H atoms 0.02σ , for H atoms 0.09σ , residual electron density in final difference map within -0.14 and $\pm 0.15 \text{ e \AA}^{-3}$, $R = 0.044$, $wR = 0.043$, $S = 3.41$.

Discussion. Final atomic parameters are given in Table 1.* The molecular structure and atom numbering are shown in Fig. 1. Interatomic distances, valence angles and selected torsion angles are in Table 2. The phenyl ring geometry in the present molecule is in agreement with the corresponding data for salicylic acid (Sundaralingam & Jensen, 1965) and *N*-salicylidene-2-aminopyridines (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978, 1980). The thiophene-ring distances and angles are comparable with those of thiophene itself (Harsbarger & Bauer, 1970).

The N—C(5) and N—C(7) bond distances of 1.283 (4) and 1.418 (3) \AA agree well with those found in similar structures (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978, 1980). Both the thiophene and the phenyl rings are planar; the maximum deviation from the least-squares plane through the thiophene ring, S and C(1)—C(4), is 0.002 (3) \AA , and the maximum deviation from the least-squares plane through the phenyl ring atoms, C(7)—C(12), is 0.010 (3) \AA .

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52737 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

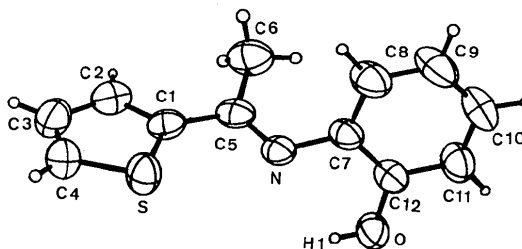


Fig. 1. Perspective view of the title molecule. Vibrational ellipsoids are at the 50% probability level (Johnson, 1976).

The phenolic O and H(1) atoms lie close to the phenyl plane [0·003 (2) and 0·002 (27) Å], with the imino N atom at a distance of -0·151 (2) Å from the plane. The molecule as a whole is non-planar, the dihedral angle between the two rings is 82·5 (3) Å.

Torsion angles defining the relationship of the ethylideneamino group to the two rings are in Table 2. The imino N atom is *cis* to the thiophene S atom; the methyl C(6) atom is *trans* to the S atom and *cis* to the phenyl ring about the C=N bond.

The crystal structure is stabilized by an intermolecular O—H···N interaction with O···N = 2·835 (3), H···N = 2·08 (3) Å and an O—H···N angle of 160 (3)° with N at $\frac{1}{2} - x, -y, z$. There is also an intramolecular interaction of the same type with geometry (in order given above) of 2·866 (3), 2·53 (3) Å, and 108 (3)°.

This work was supported by the Polish Academy of Sciences (Project CPBP 01.12).

Acta Cryst. (1990). **C46**, 1693–1697

Structures of 5-Dimethylamino-1-[*N*-(2,6-dimethylphenyl)benzimidoyl]tetrazole, $C_{18}H_{20}N_6$, and 7,9-Dimethyl-5-dimethylamino-2-phenyl-3*H*-1,3,4-benzotriazepine, $C_{18}H_{20}N_4$

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(Received 1 November 1989; accepted 11 December 1989)

Abstract. (IVa), $C_{18}H_{20}N_6$, $M_r = 320\cdot40$, monoclinic, $P2_1/c$, $a = 9\cdot785$ (1), $b = 7\cdot701$ (1), $c = 23\cdot847$ (3) Å, $\beta = 100\cdot31$ (1)°, $V = 1768\cdot0$ (4) Å³, $Z = 4$, $D_x = 1\cdot203$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 6\cdot14$ cm⁻¹, $F(000) = 680$, $T = 291$ K, final $R = 0\cdot060$ for 3091 independent reflections. The geometry of the five-membered ring resembles that of other tetrazoles. Thus the ring is planar and the N2—N3 linkage, 1·278 (4) Å, is predominantly double bond in character. (VIIb), $C_{18}H_{20}N_4$, $M_r = 292\cdot38$, monoclinic, $P2_1/c$, $a = 11\cdot592$ (1), $b = 14\cdot781$ (2), $c = 9\cdot497$ (1) Å, $\beta = 98\cdot32$ (1)°, $V = 1610\cdot1$ (3) Å³, $Z = 4$, $D_x = 1\cdot206$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 5\cdot88$ cm⁻¹, $F(000) = 624$, $T = 291$ K, final $R = 0\cdot056$ for 2703 significant independent reflections. The seven-membered ring is severely puckered and the endocyclic bond lengths indicate double bonds

between N1—C2, 1·274 (3) Å, and N4—C5, 1·286 (2) Å. In the crystal the H atom at N3 is hydrogen bonded to N1 in a symmetry-related molecule; the N···N separation is 3·096 (3) Å.

Introduction. We recently reported general syntheses of 1- and 2-benzimidoyltetrazoles and the conversion of some of these compounds into novel 3*H*-1,3,4-benzotriazepines (Boyd, Cobb, Lindley, Mitchell & Nicolaou, 1987). Here we describe the X-ray structures of a tetrazole and a benzotriazepine.

Treatment of a mixture of *N*-benzoyl-2,6-dimethylaniline and dimethylcyanamide with phosphorus oxychloride, followed by perchloric acid, gave the salt (Ia) (Boyd, Khurshid, Nicolaou & Smith, 1988), which afforded the azido perchlorate (IIa) with sodium azide. The action of sodium

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