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CHARACTERIZATION, AND CRYSTAL STRUCTURE OF THIOPHENYL-2-METHYLIDENE-2-AMINOPHENOL

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The Schiff base thiophenyl-2-methylidene-2-aminophenol (ImineOH) is obtained from a stoichiometric mixture of 2-thiophenecarboxaldehyde and 2-aminophenol in ethanol under reflux at 90°C. Its crystal structure is determined by single crystal X-ray diffraction. ImineOH packs in an orthorhombic unit cell in the *Pbca* space group with the unit cell parameters $a = 16.942(4)$ Å, $b = 13.4395(11)$ Å, and $c = 17.5857(12)$ Å, $V = 4004.1(10)$ Å^3, $Z = 16$. Strong hydrogen bonds are present in the ImineOH structure. Apart from the X-ray study, ImineOH was characterized by elemental analysis (CHN-S) and FT–IR (4000 cm^{-1} to 400 cm^{-1}), UV-Vis and ^{13}C, ^{1}H, and ^{15}N NMR spectroscopic measurements.

Keywords: Schiff base, thiophenyl-2-methylidene-2-aminophenol, 2-aminophenol, 2-thiophenecarboxaldehyde.

Schiff bases are compounds containing the azomethine group (RC=N–) formed by condensation of a primary amine with the carbonyl group of an aldehyde or a ketone. In this study, the Schiff base thiophenyl-2-methylidene-2-aminophenol, named ImineOH (molecular formula $C_{11}H_9NOS$), is presented. The ImineOH isomer, 2-[(4-hydroxyphenyl) iminomethyl]thiophene, was previously reported in the literature [1]. Since Schiff bases contain S, N, and/or O donor atoms, they have been extensively used as ligands in coordination chemistry [2]. They have shown promising applications in the biological field, for example, as potent anticoagulants [3]. Furthermore, a large number of Schiff bases or their metal derivatives have been investigated for their interesting properties [4]. Schiff base compounds remain an important and popular area of research due to their easy synthesis, versatility, and a number of applications, especially in biological systems [5, 6].

The aim of the present work is to report the molecular and crystal data of the organic compound: thiophenyl-2-methylidene-2-aminophenol.

Experimental methods. All NMR data were obtained in CDC13. Elemental analyses of carbon, hydrogen, nitrogen, and sulfur were performed using a CHNS–O EA 1110 Analyzer (CE Instruments). The infrared spectrum was recorded on a Perkin Elmer Spectrum 2000 FT–IR Spectrophotometer in the range 4000-400 cm^{-1}. The sample was prepared as a KBr pellet. The UV-Vis spectrum was recorded in DMSO solution using a Shimadzu UV-Vis spectrophotometer in the range 300–800 nm. The ^{1}H, ^{13}C and the [^{1}H–^{15}N] correlation nuclear magnetic resonance spectra (HMBC) were recorded on a Bruker Avance III 400 MHz (9.395 T) using a 5 mm probe at temperature of 298 K. The ^{1}H NMR spectrum was obtained at 400.1 MHz, while the ^{13}C–{^{1}H} spectrum was obtained at 100.6 MHz. For ^{13}C NMR: pulse 14.75 μs (90°); delay time 2 s. For ^{1}H–^{15}N NMR: ^{15}N pulse 27.50 μs (90°); delay time 1 s.

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TABLE 1. Crystal Data and Structure Refinement for ImineOH

Empirical formula	$C_{11}H_9NOS$
Formula weight	203.25
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions *a*, *b*, *c*, Å	16.942(4), 13.4395(11), 17.5857(12)
Volume, $Å^3$	4004.1(10)
Z	16
Density (calculated), mg/m^3	1.349
Absorption coefficient, mm^{-1}	0.286
F(000)	1696
Crystal size, mm	0.50×0.36×0.23
θ range for data collection, deg	2.25 to 25.97
Index ranges	$-20 \le h \le 0, -16 \le k \le 1, 0 \le l \le 21$
Reflections collected	4252
Independent reflections	3911 [*R*(int) = 0.0262]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3911/0/261
GOOF on F^2	1.021
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0552$, $wR_2 = 0.1412$
R indices (all data)	$R_1 = 0.1539$, $wR_2 = 0.1555$
Largest diff. peak and hole, $e \cdot Å^{-3}$	0.291 and –0.333

TABLE 2. Selected Bond Lengths (Å) and Angles (deg)

Bond lengths, Å		Bond angles, deg		Bond angles, deg	
N1–C1	1.281(4)	C1–N1–C11	118.1(3)	C1–C2–S1	123.6(3)
N1–C11	1.434(4)	C5–S1–C2	91.23(18)	C16–C11–N1	122.4(3)
O1–C12	1.353(4)	N1–C1–C2	125.8(3)	C12–C11–N1	117.8(3)
S1–C5	1.681(4)	C3–C2–C1	123.6(3)	O1–C12–C13	116.9(3)
S1–C2	1.716(3)	C3–C2–S1	112.8(2)	O1–C12–C11	123.9(3)

X-ray crystallography. A prismatic yellow crystal was selected for the crystallographic analysis; it was fixed at the end of a glass fiber. Experimental data were recorded on an Enraf-Nonius CAD-4 diffractometer at room temperature (graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å). Cell parameters were determined on the setting angles of 25 carefully centered reflections in the θ range from 5.21° to 19.19°. The intensities were measured using the ω/2θ scan technique. Collected reflections were corrected for Lorentz and polarization effects [7]. The structure was solved by direct methods with SIR97 [8] and refined by the full-matrix least squares procedure based on F^2 with the SHELXL97 software [9]. The hydrogen atoms attached to carbon atoms were placed at idealized positions, with C–H distances and U_{eq} values taken from the default settings of the refinement program and treated by the riding model. Hydrogen atoms of the alcohol groups were found from the Fourier difference map and refined as free atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Further crystallographic information is listed in Table 1 and a selection of bond lengths and angles are presented in Table 2.

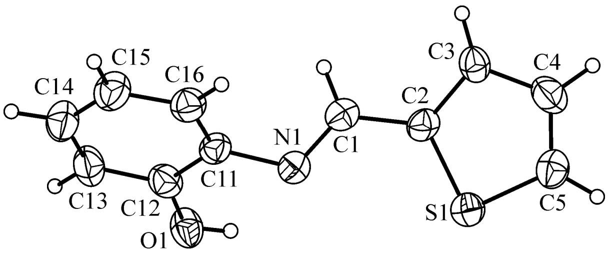

Fig. 1. ORTEP drawing of ImineOH with displacement ellipsoids plotted at a 40% probability level.

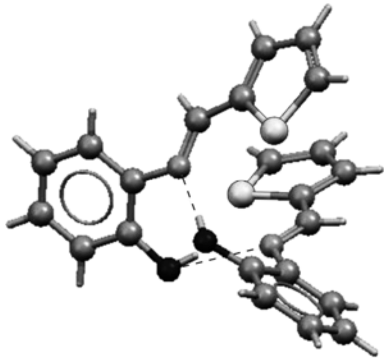

Fig. 2. Projection of two independent molecules presented in the unit cell. Intermolecular hydrogen interactions are indicated by dashed lines.

TABLE 3. Hydrogen Bond Distances (Å) and Angles (deg) in ImineOH

D–H…A	*d*(D–H)	*d*(H…A)	*d*(D…A)	∠(DHA)
O1–H1O…N2	0.81(4)	2.02(4)	2.830(4)	176(4)
O2–H2O…N1	0.81(4)	1.99(4)	2.770(4)	160(4)

Synthesis. The starting compounds (2-thiophenecarboxaldehyde and 2-aminophenol) were purchased from Sigma-Aldrich Laboratories. A mass of 2.332 g (21.4 mmol) of 2-aminophenol was dissolved in 30 ml of hot ethanol and 2.397 g (21.4 mmol) of 2-thiophenecarboxaldehyde were added slowly to the hot alcoholic 2-aminophenol solution. The solution was kept under reflux for 3 h at about 60°C. After the reaction time, anhydrous sodium sulfate was added to eliminate traces of water. The final alcoholic solution was concentrated until the formation of a viscous liquid. Then, microcrystalline powder was obtained by adding 30 ml of absolute methanol. Suitable crystals were obtained by slow evaporation of the filtrated methanolic solution.

Results and discussion. Crystal structure. The ORTEP view of ImineOH is shown in Fig. 1. Crystal and data collection of the X-ray structural analysis are shown in Table 1. There are two independent molecules of ImineOH in the asymmetric unit. The independent molecules have slight differrences in their conformation, which can be evidenced by different C11–N1–C1–C2 torsion angles of 175.4(3)° and 176.3(3)° and by the dihedral angles between the mean planes of phenyl and thiophenyl rings of 43.00(12)° and 44.97(14)°. The bond lengths and angles are very close to each other for the equivalent atoms of both molecules. Selected bond lengths and angles for one ImineOH are presented in Table 2. Hydrogen bonds are listed in Table 3.

The N1–C1 (1.281 Å) and N1–C11 (1.434 Å) bond lengths are slightly shorter than the C=N double and single bond distances due to electronic conjugation with the thiophenyl ring, which is almost coplanar with the C=N double bond. The mean plane of phenol is twisted about 40° in both molecules [10].

Two independent molecules are linked by strong intermolecular hydrogen bonds between the alcohol groups as donors and the nitrogen atom of the imine group as the acceptor. Geometric parameters for the hydrogen bonds of the title compound are listed in Table 3, while the hydrogen bonds between two ImineOH molecules are shown in Fig. 2.

Molecular structure. The molecular formula of ImineOH ($C_{11}H_9NOS$, MW 203.1 $gmol^{-1}$) was confirmed by the elemental analysis of C, H, N, and S. The experimental data on weight concentrations match with the calculated ones. Anal. calc. for $C_{11}H_9NOS$ (%): C 65.0; H 4.47; N 6.89; S 15.8%. Found (%): C 65.(0); H 4.3(5); N 6.7(5); S 15.5%. M.P.: 80.5-81.0°C.

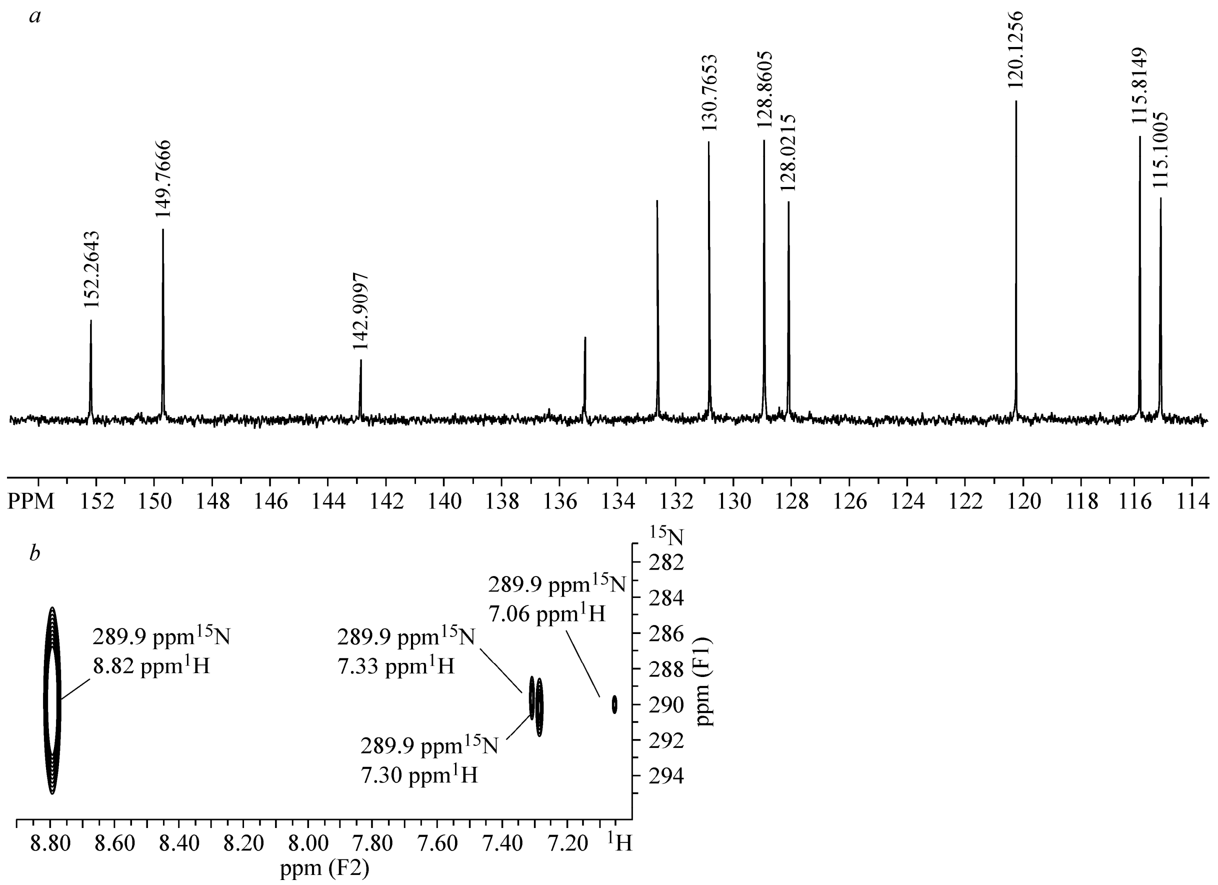

Fig. 3. ^{13}C NMR (*a*) and ^{1}H–^{15}N HMBC NMR (*b*) spectra of ImineOH.

The FT–IR analysis showed the presence of a strong and characteristic band of N=CR of the azomethilene group of imines at 1606 cm^{-1}. Other two main moieties present in the FT–IR spectrum of ImineOH are the phenol group and the thiophene skeleton. Usually, a broad and medium band for the –OH *ortho*-substitution of the phenyl group at 3466 cm^{-1} is assigned to the $\nu_{\text{O–H}}$ stretching frequency. Three bands are assigned to 2-monosubstituted thiophene at 1354 cm^{-1}, 1419 cm^{-1}, and 1379 cm^{-1} corresponding to the in-plane C=C stretching frequency ($\nu_{\text{C=C}}$) of the aromatic moiety [11].

The UV-Vis spectrum shows a band at 294 nm and a shoulder at 306 nm due to the localized *p*–*p** transition. Another band due the azomethine chromophore group is centered at 355 nm.

The ^{13}C NMR spectrum of ImineOH is shown in Fig. 3*a*. The major peaks in the ^{13}C NMR spectrum were observed at 152.3 ppm (C1, RC=N), 149.8 ppm (C12, C_{Ar}–OH), 142.9 ppm (C11, C_{Ar}–N), 135.1 ppm (C2, S–C–CN). Peaks due to other carbon atoms of the phenyl and thiophenyl groups are observed at 132.6 ppm, 130.8 ppm, 128.9 ppm, 128.0 ppm, 120.1 ppm, 115.8 ppm, and 116.1 ppm. In the ^{1}H NMR spectrum, a peak at δ = 8.82 ppm (s) is due to 1H, (H–C1). Another single peak due 1H, –OH is observed at δ = 9.99 ppm. The hydrogen atoms of the phenyl group are observed at δ = 7.27 ppm (d, H–C13), δ = 6.94 ppm (t, H–C14), δ = 7.23 ppm (t, H–C15), δ = 7.33 ppm (d, H–C16), and the hydrogen atoms of the thiophenyl group are observed δ = 7.30 ppm (d, H–C3) and δ = 7.06 ppm (m, H–C4 and H–C5) [12]. The assignment of the nitrogen resonance in the two-dimensional ^{1}H–^{15}N NMR spectrum was performed by the correlation between ^{15}N observed at 289.9 ppm, with protons at 8.82 ppm (H–C1, J2), at 7.33 ppm (H–C16, J3), and at 7.30 ppm (H–C3, J3). The interaction between ^{15}N and ^{1}H at 9.99 ppm (s, OH) was not observed. The ^{1}H–^{15}N and ^{13}C NMR spectra are shown in Fig. 3*b*.

As discussed above, the single crystal X-ray diffraction study shows that ImineOH has only *E* configuration around the C=N bond. No evidences of the *Z* configuration of ImineOH were obtained. The keto-amine tautomeric equilibrium can be present for Schiff bases such as ImineOH [13]. The conversion energies between the tautomers are very low and the structures can be present in the gas phase or in a cold solution [14].

Supplementary material. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center. Copies of the data (CCDC 812820) can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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