

STRUCTURE OF ORGANIC
COMPOUNDSCrystal Structure, Spectroscopic and DFT Computational Studies
of *N*-(4-Fluorophenyl)-1-(5-Nitrothiophen-2-yl)methanimineHasan Tanak^{a,*}, Şadiye Karataş^a, Seher Meral^b, and Ayşen Alaman Ağar^c^a Department of Physics, Faculty of Arts and Sciences, Amasya University, Amasya, 05100 Turkey^b Boyabat Vocational School, Sinop University, Sinop, Turkey^c Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey

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Abstract—A novel Schiff base compound was synthesized and characterized by IR spectroscopy and X-ray diffraction method. The compound crystallizes in monoclinic space group $P2_1/c$ with $Z = 4$ in the unit cell. The ring systems are perfectly planar but the whole molecule is not planar. The dihedral angle between the thiophene and phenyl rings is $38.7(3)^\circ$. In the crystal, intermolecular $C-H\cdots O$ interactions link the molecules into a $C(7)$ chain along the $[20\bar{1}]$ direction. The crystal packing is also stabilized by $N-O\cdots\pi$ interaction. The molecular structure and vibrational frequencies of the title compound were calculated using the DFT/B3LYP method with the 6-311++G(d,p) basis set. The calculated results show that the optimized geometry can well reproduce the crystal structure, and the theoretical vibrational frequencies show good agreement with experimental results.

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INTRODUCTION

Schiff base are the compound containing azomethine group ($-HC=N-$). Organic compounds containing the azomethine group in their structure is called imines [1]. Schiff base are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances [2–5]. Also, they are reported to show a variety of biological activities including antibacterial, antifungal, anticancer and herbicidal activities [6, 7]. On the industrial scale, they have a wide range of applications, such as in dyes and pigments [8].

In recent years, thiophene containing compounds have been reported to possess broad spectrum of biological properties including anti-inflammatory, antidepressant, analgesic, antimicrobial, and anticonvulsant activities [9–11]. Also, nitrothiophene compounds are reported to exhibit a variety of biological activities such as antibacterial and antifungal [12–14]. In order to search new heterocyclic compounds with biological activities, our group has designed and synthesised a novel series of derivatives of nitrothiophene containing Schiff base. During this study, we have obtained the crystal structure of the title compound.

In this study, we present results of a detailed investigation of synthesis and structural characterization of *N*-(4-Fluorophenyl)-1-(5-nitrothiophen-2-yl)methanimine using the single crystal X-ray diffraction, FT-IR, and density functional theory (DFT) calculations.

The optimized geometric parameters and vibrational frequencies have been calculated using the DFT/B3LYP method with the 6-311++G(d,p) basis set.

EXPERIMENTAL
AND COMPUTATIONAL METHODS

Synthesis

N-(4-Fluorophenyl)-1-(5-nitrothiophen-2-yl)methanimine was prepared by refluxing a mixture of a solution containing 5-nitrothiophene-2-carboxyaldehyde (17.4 mg, 0.111 mmol) in ethanol (20 mL) and a solution containing 4-fluoroaniline (12.3 mg, 0.111 mmol) in ethanol (20 mL). The reaction mixture was stirred for 5 h under reflux. Single crystals of the title compound for X-ray analysis were obtained by slow evaporation of an ethanol solution (yield 60%; m.p. 396–398 K).

Characterization

Using a Schmadzu FTIR-8900 spectrophotometer with KBr pellets, the IR spectrum of the compound was recorded in the range 4000–400 cm^{-1} .

Computational Methods

The theoretical calculations were performed using the DFT/B3LYP method with the 6-311++G(d,p)

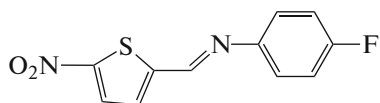


Fig. 1. Chemical diagram of *N*-(4-fluorophenyl)-1-(5-nitrothiophen-2-yl)methanimine.

basis set by Gaussian 09 [15] program package. The output files were visualized by means of GaussView 5.0 program [16]. The optimized geometry was used in the harmonic vibrational frequency calculations.

Crystal Data and Structure Determination

All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) on a BRUKER APEX II diffractometer. Reflections were collected in the rotation mode and cell parameters were determined by using Bruker SAINT software [17]. Absorption correction was achieved by the integration method via Bruker SAINT software [17]. The structure was solved by direct methods using SHELXS 97 [18]. The non-hydrogen atoms of the crystal structure were obtained by refining the Fourier differences and least squares of F^2 with anisotropically. All H atoms were placed in calculated positions and treated using a riding model (C–H = 0.93 Å, fixing the bond lengths). The figures have prepared by using the program ORTEP-3 for windows [19]. The crystallographic data and refinement parameters for the structural analyses are as follows: $C_{11}H_7FN_2O_2S$, $M_r = 250.25$, prism and orange, size $0.08 \times 0.10 \times 0.15$ mm, space group $P2_1/c$, monoclinic, $a = 3.8647$ (6)° Å, $b = 21.446$ (4) Å, $c = 13.606$ (3) Å, $\beta = 92.039$ (6)°, $V = 1127.0$ (4) Å³, $Z = 4$, $D_x = 1.475$ Mg m⁻³, $\mu = 0.29$ mm⁻¹, $3^\circ \leq \theta \leq 24.2^\circ$ measured reflections = 9421, reflections with $I > 2\sigma(I)$: 1510, $R_{int} = 0.073$, $GOF = 1.14$, R_1 ($I > 2\sigma(I)$) = 0.091, wR_2 ($I > 2\sigma(I)$) = 0.239, Number of refined parameters = 155, $-4 \leq h \leq 4$, $-26 \leq k \leq 26$, $-16 \leq l \leq 17$, $T_{min}/T_{max} = 0.6383/0.7457$, $\Delta\rho_{max}/\Delta\rho_{min} = 0.97/-0.31$ e/Å³.

CCDC-1918255 contains the supplementary crystallographic data for the compound reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure of the title compound is determined by X-ray diffraction method and the atomic numbering scheme is given in Fig. 2a. Compound crystallizes in the monoclinic space group $P2_1/c$

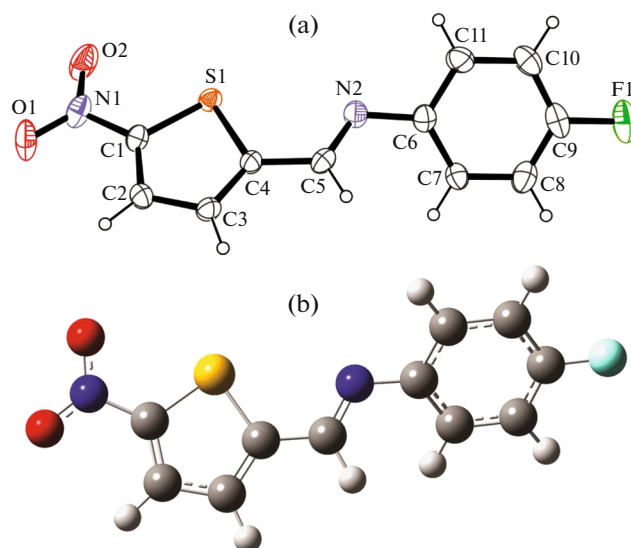


Fig. 2. (a) ORTEP-3 diagram of the title compound. (b) The theoretical geometric structure of the title compound.

with one molecule in the asymmetric unit. The C1–C4/S1 and C6–C11 rings are perfectly planar but the whole molecule is not planar. The dihedral angle between the C1–C4/S1 thiophene and C6–C11 phenyl rings is $38.7(3)^\circ$. The imine C5=N2 bond length is $1.261(6)$ Å, it is slightly shorter than standard 1.28 Å value of C=N double bond and consistent with the related structures [20, 21]. The C1–S1 and C4–S1 bond lengths of the thiophene ring are $1.714(5)$ and $1.720(5)$ Å, respectively, are slightly different than the accepted value for an Csp^2 –S single bond (1.76 Å) [21]. Selected bond lengths, bond angles and torsion angles are given in Table 1. They are within normal ranges and are comparable with those in related structures [22–24].

In the crystal structure, molecules are linked together by intermolecular C–H $\cdots$ O hydrogen bonds. The C5–H5 $\cdots$ O1 (symmetry code: $-1 + x, 1/2 - y, 1/2 + z$) hydrogen bond links the molecules into a C(7) [25] chain along the $[20\bar{1}]$ direction (Fig. 3). There is also a N–O $\cdots$ π interaction, namely N1–O2 $\cdots$ Cg1 (Cg1 is thiophene ring). The details of the hydrogen bonds are summarized in Table 2. A packing diagram of the title compound is shown in Fig. 4.

Optimized Geometry

The optimization calculation of the title compound were carried out using the DFT/B3LYP method with the 6-311++G(d,p) basis set. Calculated geometric parameters are listed in Table 1 along with the experimental data. The optimized geometric structure is presented Fig. 2b. When the X-ray structure of the title compound is compared with its optimized counterpart, conformational discrepancies are observed

between them. The orientation of the thiophene and phenyl rings is defined by torsion angles C4–C5–N2–C6 (-176.0 (4°)) and C5–N2–C6–C7 (36.2 (7°)). These torsion angles have been calculated at -177.57° and 32.518° for B3LYP. The C5=N2 bond length of imine is $1.261(6)$ Å in X-ray structure, whereas the corresponding value in optimized geometry is 1.278 Å. The dihedral angle between the thiophene and phenyl rings is $38.7(3)^\circ$ for X-ray, whereas the dihedral angle has been calculated as 33.72° for B3LYP.

A logical method for globally comparing the molecular structures obtained from the calculations is by superimposing the molecular skeleton on that obtained from X-ray experiment, giving an root mean square error (RMSE) of 0.144 Å for B3LYP (Fig. 5). Although the differences between theoretical and experimental geometric parameters observed, optimized geometric parameters represent a good approximation for the title compound.

Vibrational Spectra

Harmonic vibrational frequencies of the title compound were calculated using the DFT/B3LYP method with the 6-311++G(d,p) basis set. The calculated frequencies were scaled with 0.96 for B3LYP. The calculated and experimental vibration frequencies are tabulated in Table 3.

The symmetric and asymmetric C–H stretching modes were observed at 3115 – 3164 and 3092 cm^{-1} experimentally, and calculated at 3078 – 3109 and 3056 cm^{-1} for B3LYP level, respectively. The characteristic region of the Schiff base derivative spectrum is 1550 – 1650 cm^{-1} , which is attributed to imine C=N stretching vibration [20]. In this study, the experimental C=N stretching mode was observed as a sharp band at 1642 cm^{-1} and calculated at 1602 cm^{-1} theoretically. The bands observed at 1096 , 1233 , and 1332 cm^{-1} ,

Table 1. Selected molecular structure parameters

Parameters	Experimental	DFT
Bond lengths, Å		
S1–C1	1.714(5)	1.735
S1–C4	1.720(5)	1.742
N2–C5	1.261(6)	1.278
N2–C6	1.408(7)	1.402
C1–N1	1.429(7)	1.441
N1–O2	1.220(6)	1.229
N1–O1	1.229(6)	1.226
F1–C9	1.371(7)	1.353
Bond angles, deg		
C1–S1–C4	88.8(2)	89.39
C5–N2–C6	119.0(5)	121.28
N2–C5–C4	122.4(5)	121.62
O2–N1–O1	124.1(5)	125.31
O2–N1–C1	117.9(5)	117.15
O1–N1–C1	118.1(5)	117.52
C8–C9–F1	118.3(6)	118.80
Torsion angles, deg		
C5–N2–C6–C7	36.2(7)	32.518
C6–N2–C5–C4	$-176.0(4)$	-177.57
C3–C4–C5–N2	$-178.1(5)$	-179.00
C2–C1–N1–O2	$-177.1(5)$	179.64
C2–C1–N1–O1	$1.7(8)$	-0.360
C5–N2–C6–C11	$-146.4(5)$	-149.98

which can be attributed to the C–N stretching vibrations, were calculated at 1093 , 1161 , and 1300 cm^{-1} for B3LYP, respectively. The strong FT-IR bands at 1496 and

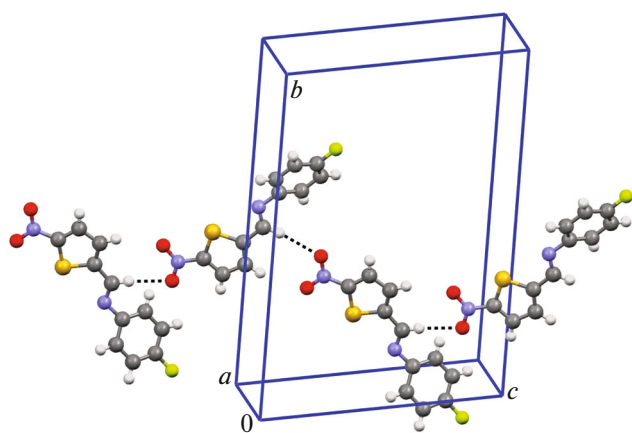


Fig. 3. A view of the intermolecular interactions in the title compound. The intramolecular interactions are shown as dashed lines.

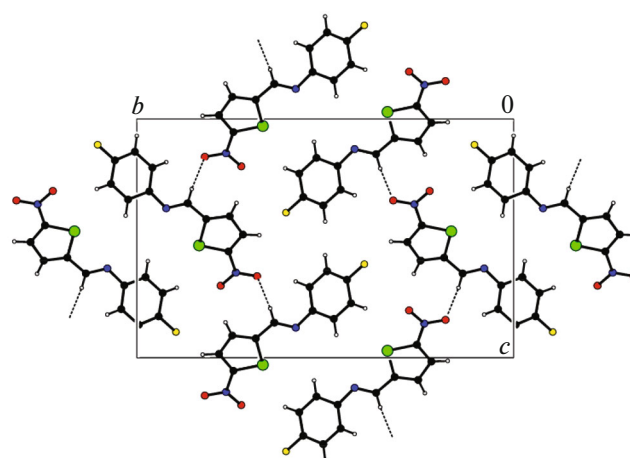


Fig. 4. Packing diagram of *N*-(4-fluorophenyl)-1-(5-nitrothiophen-2-yl)methanimine.

Table 2. Hydrogen-bond geometry (Å, deg)

D—H...A	D—H	H...A	D...A	D—H...A
C5—H5...O1 ⁽ⁱ⁾	0.93	2.58	3.484(7)	163
N1—O2...Cg1 ⁽ⁱⁱ⁾	1.220 (6)	3.765(5)	3.620(5)	73.8(3)

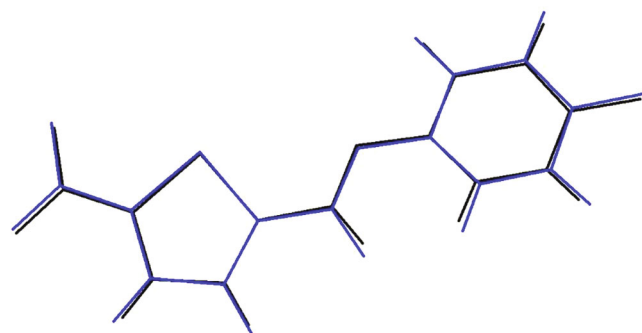
Symmetry codes: (i) $-1 + x, 1/2 - y, 1/2 + z$; (ii) $1 + x, y, z$.

Table 3. Experimental and calculated vibrational frequencies (cm^{-1}) of the title compound

Assignments ^a	Experimental	DFT
ν (C—H) s	3164	3109
ν (C—H) s	3115	3078
ν (C—H) as	3092	3056
ν (C=N) + ν (C=C)	1642	1602
ν (NO ₂) as	1496	1514
ν (C—N) + ν (NO ₂) s	1332	1300
ν (C—F) + ν (C—N) + γ (C—H)	1233	1209
τ (CCCH) + ν (C—N) + ν (C—C)	1186	1161
α (C—H)	1150	1123
ν (C—N)	1096	1093
ν (S—C) + τ (CCCH)	733	771

^a ν : stretching, α : scissoring, γ : rocking, τ : torsion, s: symmetric, as: asymmetric.

1332 cm^{-1} were assigned to asymmetric and symmetric stretching modes of NO₂ group, respectively. The experimental C—F and C—S stretching bands were observed at 1233 and 733 cm^{-1} , and were calculated at 1209 and 771 cm^{-1} , respectively. The above conclusions are in good agreement with the similar Schiff base compounds [26, 27]. The other vibrational frequencies can be seen in Table 3.

**Fig. 5.** Atom-by-atom superimposition of the calculated structures (blue) on the X-ray structures (black) for the title compound.

CONCLUSIONS

A novel Schiff base compound *N*-(4-fluorophenyl)-1-(5-nitrothiophen-2-yl)methanimine has been synthesized and characterized by FT-IR and X-ray diffraction methods. The X-ray structure is found to be very slightly different from its optimized counterpart, and the crystal structure is stabilized by C—H...O and N—O... π intermolecular interactions. In spite of the differences observed in the geometric parameters, the general agreement is good and the calculations support the solid-state structure. The vibrational frequencies are precisely assigned to its molecular structure with the aid of the theoretical calculations at B3LYP/6-311++G(*d,p*) level, in which the experimental and theoretical results support each other.

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