Crystal Structure of (4-Fluorophenyl)(2-(methylthio)thiophen-3-yl)methanone

S. NAGARAJU,* M. A. SRIDHAR,*† N. R. SREENATHA,** C. S. PRADEEPA KUMARA,*** and M. P. SADASHIVA***

*Department of Studies in Physics, Manasagangotri, University of Mysore, Mysuru, Karnataka, India

**Department of Physics, Government Engineering College, Hassan, Karnataka, India

***Department of Studies in Chemistry, Manasagangotri, University of Mysore, Mysuru, Karnataka, India

This paper reports on a newly synthesized compound (4-fluorophenyl)(2-(methylthio)thiophen-3-yl)methanone which is crystallized into a monoclinic system with the space group of $P2_1$; the cell parameters are $a = 5.4232(4)\text{Å}$, $b = 14.1405(6)$, $c = 7.5318(4)\text{Å}$, $\beta = 94.198(5)^\circ$ and $Z = 2$. The structure is solved by a direct method and refined by full-matrix least squares on F^2 reduced to $R_1 = 0.0337$, $wR_2 = 0.0806$. Also, the crystal structure, molecules are stabilized by short C-H...O and C-H...F contacts.

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Thiophene is a five-membered, sulfur-containing hetero aromatic ring. Its nucleus has been one of the most important potential entities in the rapidly growing chemical world of heterocyclic compounds during the last few decades due to diverse applications in material science and pharmaceuticals. Substituted thiophenes have exhibited a wide spectrum of biological activities, ranging from antibacterial, antifungal, antioxidant, antiviral, antianxiety, antiprotozoal, insecticidal, antiproliferative and herbicide.¹⁻³ Moreover, polymeric thiophenes are also broadly utilized as thin-film transistors, organic field-effect transistors, organic light-emitting transistors (OLET), chemical sensors, and solar cells.⁴⁻⁷ In view of the above mentioned importance, the synthesis and crystal structure of the title compound (4-fluorophenyl)(2-(methylthio)thiophen-3-yl)methanone is reported here.

The compound 1-(4-fluorophenyl)-3-((2,2-diethoxyethyl)-thio)-3-(methylthio)prop-2-en-1-one was taken into a round-bottomed flask and mixed with 5 mL of dry ethanol, followed by orthophosphoric acid (5 mL). The reaction mixture was heated for a period of 80 min at 80°C . The progress of the reaction was monitored by TLC (EtOAc:pet.ether, 2:8), and the reaction mixture was concentrated in a rotary evaporator. Further, the concentrated reaction mixture was poured into ice-cold water and extracted with ethyl acetate and dried (Na_2SO_4); the solvent was distilled out in a rotary evaporator. The residue

obtained was purified by passing through silica gel and then eluted with 5% ethyl acetate and petroleum ether to yield the product (4-fluorophenyl)(2-(methylthio)thiophen-3-yl)methanone and recrystallized by ethanol. A schematic diagram of the synthesis of the title compound is shown in Fig. 1.

A yellow block-shaped crystal of the title compound, $\text{C}_{12}\text{H}_9\text{FOS}_2$ with dimensions of $0.25 \times 0.23 \times 0.21\text{ mm}^3$, was chosen for an X-ray diffraction study using a Bruker X8 Proteum diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 1.54178\text{ Å}$) at 296 K. Data collection, integration, and scaling of the reflections were performed using the APEX2 program.⁸

Fig. 1 Chemical diagram of the title compound.

† To whom correspondence should be addressed.
E-mail: mas@physics.uni-mysore.ac.in

Table 1 Crystal data and structure refinement details for the title compound

Empirical formula: $\text{C}_{12}\text{H}_9\text{FOS}_2$	
Formula weight = 252.33	
Temperature = 293 K	
Wavelength = 0.71073 Å	
Crystal system: monoclinic	Space group: $P2_1$
Unit cell dimensions	
$a = 5.4232(4)\text{Å}$,	Volume = $576.04(5)\text{Å}^3$
$b = 14.1405(6)\text{Å}$,	$Z = 2$
$c = 7.5318(4)\text{Å}$,	
$\beta = 94.198(5)^\circ$	
Calculated density = 1.455 g/cm^3	
Absorption coefficient = 0.448 mm^{-1}	$F(0\ 0\ 0) = 260$
Crystal size = $0.300 \times 0.280 \times 0.260\text{ mm}$	
θ range for data collection = 3.07 to 25.03°	
Limiting indices:	
$-6 \leq h \leq 5$	
$-16 \leq k \leq 16$	
$-8 \leq l \leq 8$	
Reflections collected/unique: $[R_{\text{int}}] = 5639/2018$ [$R_{\text{int}} = 0.0259$]	
Refinement method: Full-matrix least-squares on F^2	
Data/restraints/parameters = 2018/1/146	
R value/ wR_2 : $R_1 = 0.0337$, $wR_2 = 0.0806$	
Goodness-of-fit on $F^2 = 1.044$	
Largest diff. peak and hole = 0.125 and -0.117 eÅ^{-3}	
CCDC number: 1542125

Fig. 2 ORTEP of the title compound showing the atomic numbering system. Displacement ellipsoids are drawn with 50% probability.

Fig. 3 Crystal packing of the molecules viewed down the *a* axis. The dotted lines indicate the hydrogen bonds.

The structure was solved by direct methods using SHELXS.⁹ It was refined by a full-matrix least squares method with anisotropic temperature factors for non-hydrogen atoms using SHELXL-97.⁹ The hydrogen atoms were placed at chemically acceptable positions and were allowed to ride on their parent atoms. The details of the crystal data and structure refinement are given in Table 1. Figure 2 represents an ORTEP¹⁰ diagram of the molecule with thermal ellipsoids drawn at 50% probability. Analytical results of compound (4-fluorophenyl)(2-(methylthio)-thiophen-3-yl)methanone: Solid. m.p. 95 – 98 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.798 – 7.763 (3H, m), 7.238 (*J* = 10 Hz, d, 1H), 7.144 – 7.102 (2H, m), 2.597 (MeS, 3H, s). ¹³C NMR (100 MHz, CDCl₃): 188.39 (C=O), 18.944 (MeS), 166.13, 163.62, 153.54, 135.35, 134.10, 131.47, 131.47, 130.25, 121.87, 115.43, 18.94. HRMS (ESI): calcd. for C₁₂H₉FOS₂ [M+H]⁺ 253.0112 found 253.0155.

The bond lengths and bond angles of the thiophene ring agrees with those of previously reported compounds.¹¹ The crystal structure exhibits short inter-molecular hydrogen bonding C2–H2···O1 with bond symmetry codes *x*, *y*, –1+*z* and C10–H10···F1 with symmetry codes 3–*x*, –1/2+*y*, –1–*z* whose

bond lengths are 3.268(3) Å, 3.179(4) Å and bond angles are 166°, 126°, respectively. The crystal structure exhibits a one-dimensional polymeric chain, as shown in Fig. 3. The dihedral angle between the planes of the thiophene ring and the fluorophenyl ring is defined by C8–C9–C10–S1–C11 and F1–C1–C2–C3–C4–C5–C6 is 43.01(2)°. The methyl group substituted at the C12 position is in the *-syn-periplanar* conformation, defined by the dihedral value of –1.7(2)° for the atoms C12–S2–C11–S1. The thiophene ring is almost planar, though the sulfur atom in the thiophene ring deviates from the Cremer and Pople plane by 0.0147(13) Å.

The title compound was synthesized and characterized by ¹H NMR, ¹³C NMR, and finally confirmed by the three-dimensional molecular structure using a single crystal X-ray diffraction method. The thiophene ring is not planar with the fluoro phenyl ring. The crystal structure exhibits short intermolecular C–H···O and C–H···F contacts.

Supporting Information

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as a supplementary publication (number 1542125). This material is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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