

1-(Thiophen-3-yl)ethanone

Ewa Rozycka-Sokolowska,* Andrzej Borowski† and
Bernard MarciniakInstitute of Chemistry, Environmental Protection and Biotechnology, Jan Dlugosz
University, Armii Krajowej 13/15, 42-200 Czestochowa, Poland
Correspondence e-mail: e.sokolowska@ajd.czest.pl

Received 25 March 2011

Accepted 21 April 2011

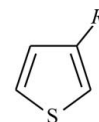
Online 19 May 2011

The structure of the title compound, C_6H_6OS , exhibits a flip-type disorder of the thiophene ring [occupancy ratio = 0.848 (3):0.152 (3)], which is typical for many thiophene derivatives. The puckered thiophene ring is essentially coplanar with the plane formed by the non-H atoms of the acetyl substituent, similar to its simple analogues, *i.e.* 3-acetyl-2-carboxythiophene, 4-acetyl-3-carboxythiophene and 3,5-diacetyl-2-ethylamino-4-methylthiophene. In the crystal structure, molecules are connected by $C-H \cdots \pi$ hydrogen bonds, forming a sheet parallel to the (001) plane. Moreover, an inspection of the crystal lattice reveals that there are short $S \cdots O$ contacts connecting the molecules of adjacent sheets. Comparison of the title crystal structure with its simple 3-methoxythiophene analogue shows a close similarity in the herringbone arrangement of molecules and in the presence of $C-H \cdots \pi$ interactions and $S \cdots O$ contacts.

Comment

Thiophene and its derivatives belong to the five-membered heterocycle family which is of considerable importance in chemistry (Roux *et al.*, 2003). These compounds play an important role in the synthesis of fine chemicals, such as pharmaceuticals, agrochemicals and dyestuffs (Russell & Press, 1996). Moreover, thiophene derivatives find applications as functional materials in liquid crystals, molecular wires, organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), organic solar cells, *etc.* (Liang *et al.*, 2007, and references 3*a*–3*j* therein). Electron-withdrawing substituents (COMe and CHO) at the C2 or C3 atoms of the thiophene ring facilitate $S-C5$ and $S-C2$ bond cleavage in the stoichiometric reactions of these thiophene derivatives with the ruthenium complex $[Ru(\eta^4\text{-cyclooctadiene})(\eta^6\text{-cyclooctatriene})]$ to form thiaruthenacycles (Giner Planas *et al.*, 1999). In the presence of the ruthenium bis(dihydrogen) complex $[RuH_2(\eta^2\text{-}H_2)_2[P(C_6H_{11})_3]_2]$, the $S-C5$ bond in 2-acetylthio-

phene splits, followed by hydrogenation of two $C=C$ double bonds and formation of a new $C=C$ double bond (Borowski *et al.*, 2003). A similar reaction of this complex with 3-acetylthiophene leads to a complex where the metal binds *via* a σ bond to C2 and coordinates to the O atom of the acetyl group forming a five-membered ring incorporating also the $C2-C3$ bond of the thienyl ring. A search of the Cambridge Structural Database (CSD, Version 5.23 of November 2010; Allen, 2002) for thiophenes containing an acetyl group as a substituent at position 3 reveals only three reports of multisubstituted thiophenes, *i.e.* 3-acetyl-2-carboxythiophene (CSD refcode CACTHP; Griffe *et al.*, 1972), 4-acetyl-3-carboxythiophene (refcode ACETTP; Griffe *et al.*, 1972) and 3,5-diacetyl-2-ethylamino-4-methylthiophene (refcode MIQRAG; Liang *et al.*, 2007). We present here the structure of 3-acetylthiophene, (I), and compare it with those of two simple 3-substituted thiophenes, *i.e.* 3-methoxythiophene, (II) (refcode GUFJEW; Blake *et al.*, 1999), and 3-thiophenecarboxylic acid, (III) [refcodes THIPAC (Hudson & Robertson, 1964) and THIPAC01 (Roux *et al.*, 2003)].

(I) $R = \text{COMe}$ (II) $R = \text{OMe}$ (III) $R = \text{COOH}$

The molecule of (I) contains a thiophene ring and one acetyl group attached to it on the C3 atom (Fig. 1). Similar to previous observations made for structures containing a thiophene skeleton [*e.g.* (*E*)-3'-[2-(anthracen-9-yl)ethenyl]-2,2':5',2''-terthiophene, (*E*)-3'-[2-(1-pyrenyl)ethenyl]-2,2':5',2''-terthiophene and (*E,E*)-2,5-dimethoxy-1,4-bis[2-(2,2':5',2''-terthiophen-3'-yl)ethenyl]benzene (refcodes HIBTUI, HIBVAQ and HIBVEU, respectively; Wagner & Officer, 2005), 2,5-bis(2-cyano-2-thienylvinyl)thiophene (refcode SESVES; Wagner *et al.*, 2006), 1,4-diphenyl-2,3-dithien-3-ylcyclopentadien-1-one (refcode HUYZIK; Linehan *et al.*, 2003)], the five-membered ring exhibits a flip disorder over two sites with occupancies of 0.848 (3) and 0.152 (3). In the following discussion, only the

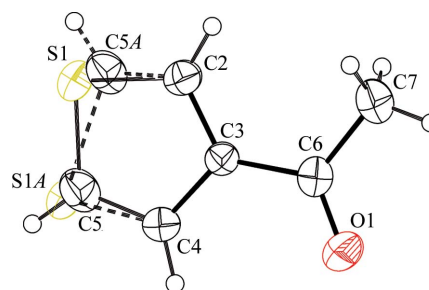


Figure 1

A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The disorder on atoms S1, C5 and C5A is represented by dashed lines, with the suffix *A* denoting non-H atoms of the minor component.

† Also at Centre of Polymer and Carbon Materials, Polish Academy of Sciences, ul. Sowinskiego 5, 44-121 Gliwice, Poland.

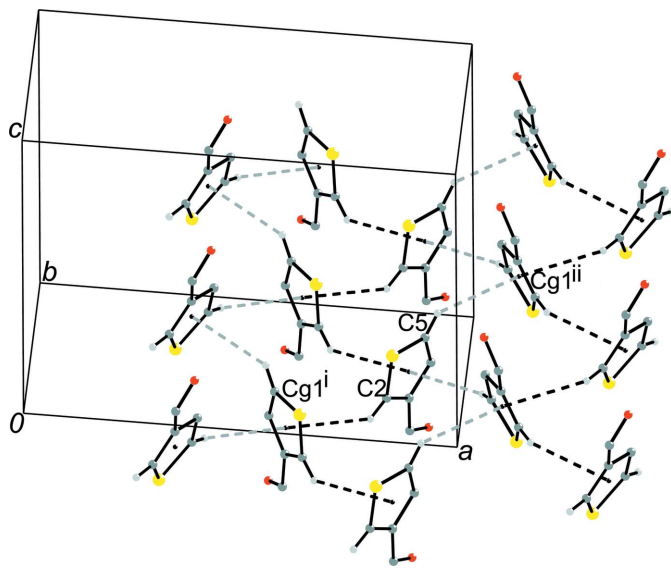


Figure 2 Part of the crystal structure of (I), showing the two symmetry-independent intermolecular C—H \cdots π hydrogen bonds (black and grey dashed lines), which together produce a sheet parallel to the (001) plane. All H atoms not involved in these interactions and methyl C atoms have been omitted for clarity. Cg1 is the centroid of the thiophene ring and is denoted by small spheres. [Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$]

geometric parameters of the major component are presented.

The bond lengths within the thiophene ring [C2—C3 = 1.373 (3) Å, C4—C5 = 1.371 (9) Å, C3—C4 = 1.411 (3) Å, S1—C2 = 1.691 (3) Å and S1—C5 = 1.686 (11) Å] are in agreement with those given by Allen *et al.* (1987) for thiophene [1.362 (25), 1.424 (15) and 1.712 (13) Å for $Csp^2=Csp^2$, Csp^2-Csp^2 and Csp^2-S , respectively]. The five-membered ring is planar, with the largest out-of-plane deviation being 0.007 (10) Å for atom C5. The deviations of the acetyl atoms O1, C6 and C7 from this plane are only -0.071 (2), 0.006 (2) and 0.110 (3) Å, respectively. Thus, the dihedral angle between this plane and the plane formed by the non-H atoms of the acetyl substituent is only 4.2 (1)°. This angle, near to zero, is in close agreement with those observed for ACETTP, CACTHP and MIQRAG [0.000, 0.00 (7) and 4.5 (2)°, respectively]. It is noteworthy that this coplanar orientation of the thiophene ring and the atoms of the substituents attached to it at the 3-position was also observed for simple thiophenes possessing at this position oxygen-containing substituents different from the acetyl group, *i.e.* for compounds (II) and (III) [2.8 (2) and 4.4 (THIPAC), and 3.9 (1)° (THIPAC01), respectively].

In the crystal structure of (I), there are two symmetry-independent nonconventional weak C—H \cdots π hydrogen bonds (Desiraju & Steiner, 1999) (Table 1), which connect each molecule with four others. Atom C2 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H2, to the thiophene ring (centroid Cg1) of the molecule at $(-x + \frac{3}{2}, y - \frac{1}{2}, z)$ (Fig. 2), thus forming a chain running parallel to the shortest crystallographic axis, *i.e.* the b axis. A chain parallel to

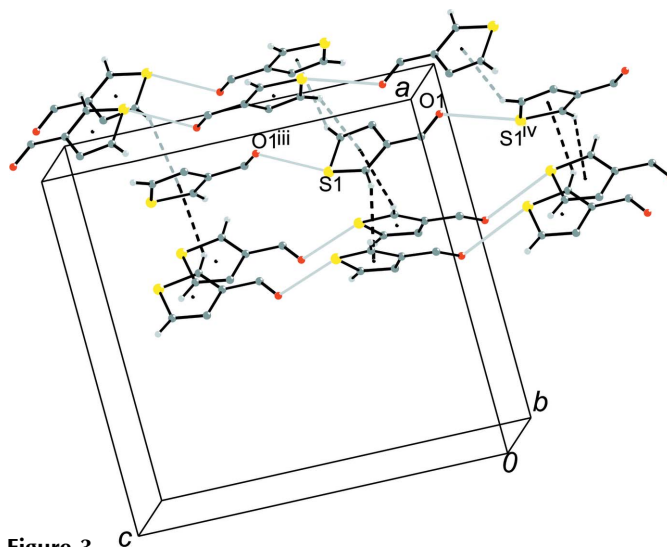


Figure 3 Part of the crystal structure of (I), showing the intermolecular S \cdots O contacts (grey solid lines) linking the molecules of adjacent (001) sheets formed by the C—H \cdots π hydrogen bonds (black and grey dashed lines). All H atoms not involved in these interactions and methyl C atoms have been omitted for clarity. Cg1 is the centroid of the thiophene ring and is denoted by small spheres. [Symmetry codes: (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

the same direction is also formed by the C5—H5 \cdots Cg1ⁱⁱ hydrogen bond [symmetry code: (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$] (Fig. 2). These interactions together produce a sheet parallel to the (001) plane (Fig. 2). Two such sheets pass through each unit cell, and the non-H atoms belonging to them lie in domains $(-0.03 + z/2) < c < (0.53 + z/2)$ (z is zero or an integer) (Fig. 3). There are no direction-specific interactions between adjacent sheets, only the intermolecular S \cdots O contacts of 3.213 (2) Å. As shown in Fig. 3, atoms S1 and O1 belonging to the molecule at (x, y, z) are connected with atoms O1 at $(x, -y + \frac{1}{2}, z + \frac{1}{2})$ and S1 at $(x, -y + \frac{1}{2}, z - \frac{1}{2})$, respectively, thus generating a chain parallel to the c axis. The presence of intermolecular S \cdots O contacts of a similar distance between S and O atoms is a common characteristic of the crystal lattices of (I) and its simple analogue possessing a methoxy group as a substituent at position 3, *i.e.* (II) crystallizing with $Z' = 1$ in the space group $P2_12_12_1$, while the distances between these atoms in (III) (space group $C2/c$, $Z' = 1$) are ca 0.4 Å larger (S \cdots O = 3.591 and 3.654 Å for THIPAC and THIPAC01, respectively). In contrast to (I) and (II), the crystal structure of (III) is stabilized mainly by O—H \cdots O and C—H \cdots O hydrogen bonds and weak C—H \cdots S contacts (Roux *et al.*, 2003). It is also worth noting that in the crystal packing in (I) and (II), there is an additional common feature, namely the herringbone arrangement of molecules and the presence of C—H \cdots π interactions.

Experimental

3-Acetylthiophene of 98% purity was purchased from Aldrich. Crystals of the title compound suitable for X-ray studies were grown from a solution in acetone by slow evaporation of the solvent at a constant temperature of 293 K.

Crystal data

C_6H_6OS	$V = 1214.7 (4) \text{ \AA}^3$
$M_r = 126.17$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 14.592 (3) \text{ \AA}$	$\mu = 0.42 \text{ mm}^{-1}$
$b = 5.5108 (11) \text{ \AA}$	$T = 290 \text{ K}$
$c = 15.106 (3) \text{ \AA}$	$0.42 \times 0.28 \times 0.15 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	6176 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	1106 independent reflections
$T_{\min} = 0.966$, $T_{\max} = 1.000$	683 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	82 parameters
$wR(F^2) = 0.083$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$
1106 reflections	$\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

Cg1 is the centroid of the thiophene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots Cg1^i$	0.93	2.94	3.660 (3)	136
$C5-H5\cdots Cg1^{ii}$	0.93	2.99	3.755 (10)	141

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$.

The disorder on the S1 and C5 atoms was resolved by finding alternative positions from the difference Fourier map, and was subsequently refined over two positions with an occupancy of 0.848 (3) for the major component. The anisotropic displacement parameters of the S and C atoms of the minor components were constrained to be the same as those of the major components. All H atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H distances of 0.93 (aromatic) or 0.96 \AA (methyl) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3405). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Blake, A. J., Clark, B. A. J., Gierens, H., Gould, R. O., Hunter, G. A., McNab, H., Morrow, M. & Somerville, C. C. (1999). *Acta Cryst.* **B55**, 963–974.
- Borowski, A. F., Sabo-Etienne, S., Donnadiou, B. & Chaudret, B. (2003). *Organometallics*, **22**, 4803–4809.
- Brandenburg, K. (2006). *DIAMOND*. Version 3.1e. Crystal Impact GbR, Bonn, Germany.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.
- Giner Planas, J., Hirano, M. & Komiya, S. (1999). *Chem. Commun.* pp. 1793–1794.
- Griffe, M., Durant, F. & Pieret, A. F. (1972). *Bull. Soc. Chim. Belg.* **81**, 319–332.
- Hudson, P. & Robertson, J. H. (1964). *Acta Cryst.* **17**, 1497–1505.
- Liang, F., Li, D., Zhang, L., Gao, J. & Qun, L. (2007). *Org. Lett.* **9**, 4845–4848.
- Linehan, J., Crundwell, G., Herron, S. R. & Kantardjieff, K. A. (2003). *Acta Cryst.* **E59**, o466–o468.
- Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.37. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Roux, M. V., Temprado, M., Jimenez, P., Davalos, J. Z., Foces-Foces, C., Garcia, M. V. & Redondo, M. I. (2003). *Thermochim. Acta*, **404**, 235–244.
- Russell, R. K. & Press, J. B. (1996). *Comprehensive Heterocyclic Chemistry II*, Vol. 2, edited by A. R. Katritzky, C. W. Rees, E. W. F. Scriven & A. Padwa, pp. 679–729. New York: Pergamon.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Wagner, P. & Officer, D. L. (2005). *Synth. Met.* **154**, 325–328.
- Wagner, P., Officer, D. L. & Kubicki, M. (2006). *Acta Cryst.* **E62**, o5931–o5932.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.