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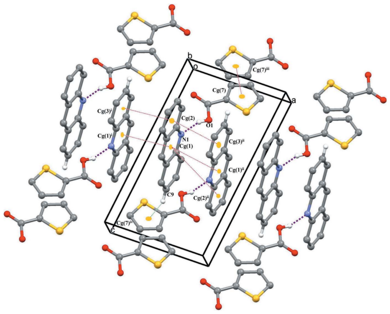


Supramolecular interactions in a 1:1 co-crystal of acridine and 3-chlorothiophene-2-carboxylic acid

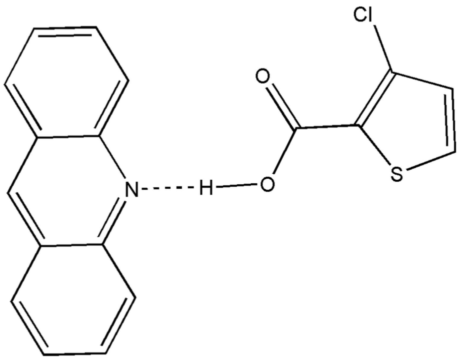
Olakkandiyil Prajina,[a] Packianathan Thomas Muthiah[a]* and Franc Perdih[b]

[a]School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India, and [b]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Vecna pot 113, PO Box 537, SI-1000 Ljubljana, Slovenia. *Correspondence e-mail: tommtrichy@yahoo.co.in

In the title co-crystal, $C_5H_3ClO_2S\cdot C_{13}H_9N$, the components interact with each other *via* an O—H···N hydrogen bond. Acridine–acridine stacking, thiophene–thiophene stacking and acridine–thiophene C—H···π interactions also occur in the crystal.

1. Chemical context

Co-crystals are solids in which two or more molecules crystallize together and interact through non-covalent interactions (Odiase *et al.*, 2015). The study of non-covalent interactions in co-crystals not only adds to our knowledge but also has an undeniable relevance in the context of their pharmaceutical and biological interest (Chakraborty *et al.*, 2014; Desiraju, 1989). The main interactions concerned are various hydrogen bonding, π–π and C—H···π interactions (Aakeröy *et al.*, 2010). The acridine molecule is a component present in anti-helminthic agents which are used in animals (Durchheimer *et al.*, 1980). Acridine derivatives also show *in vitro* activity against protozoa (Ngadi *et al.*, 1993). The acridine group is a well known intercalator interacting with nucleobase pairs (Raju *et al.*, 2016; Nafisi *et al.*, 2007; Sazhnikov *et al.*, 2013). Acridine dyes are also widely used (Solovyeva *et al.*, 2014, Yasarawan *et al.*, 2011). Halogenated thiophene carboxylic acid derivatives are the building blocks of many commercially available insecticides (Hull *et al.*, 2007). We extended our study on supramolecular architectures in acridine molecules with the investigation of the title co-crystal with 3-chlorothiophene-2-carboxylic acid (3TPC).



2. Structural commentary

The compound (**1**) is a 1:1 co-crystal of 3TPC and acridine. The internal angle at N1 [C6—N1—C18 = 119.30 (15)°] and

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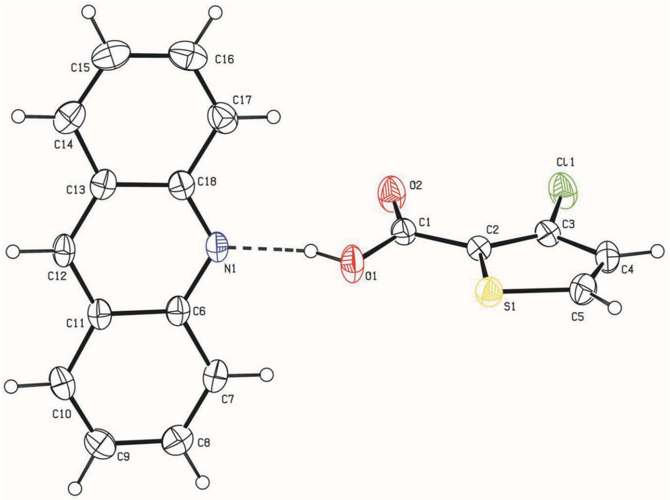

Figure 1
The asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line represents the O—H···N hydrogen bond.

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*7 is the centroid of the thiophene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.83	2.615 (2)	159
C9—H9···*Cg*7^{i}	0.93	2.94	3.773 (2)	150

Symmetry code: (i) $-x+1, -y+1, -z+1$.

bond lengths [C18—N1 = 1.346 (2) and C6—N1 = 1.354 (2) Å] agree with those reported for neutral acridine structures (Aghabozorg *et al.*, 2011; Binder *et al.*, 1982; Goeta *et al.*, 2002). The two external bond angles at the carbon atom of the carboxyl group are 124.13 (17) and 110.75 (15)°. The high discrepancy between these two angles is typical of an unionized carboxyl group. The C═O distance of 1.316 (2) Å and C—OH distance of 1.199 (2) Å are also typical of the carboxyl group. These values also agree with the carboxylic acids reported in the literature (Kowalska *et al.*, 2015; Sienkiewicz-Gromiuk *et al.*, 2016). The dihedral angle between the carboxylic acid group and the thiophene ring is 9.01 (13)°. The bond distances and angles involving the thiophene ring agree with those in structures reported earlier (Zhang *et al.*, 2014).

3. Supramolecular features

The 3TPC and acridine moieties are linked by an O—H···N hydrogen-bonding interaction between (O1—H1) of the carboxyl group and the acridine nitrogen atom (N1) (Table 1 and Fig. 1). This O—H···N hydrogen bond is reminiscent of

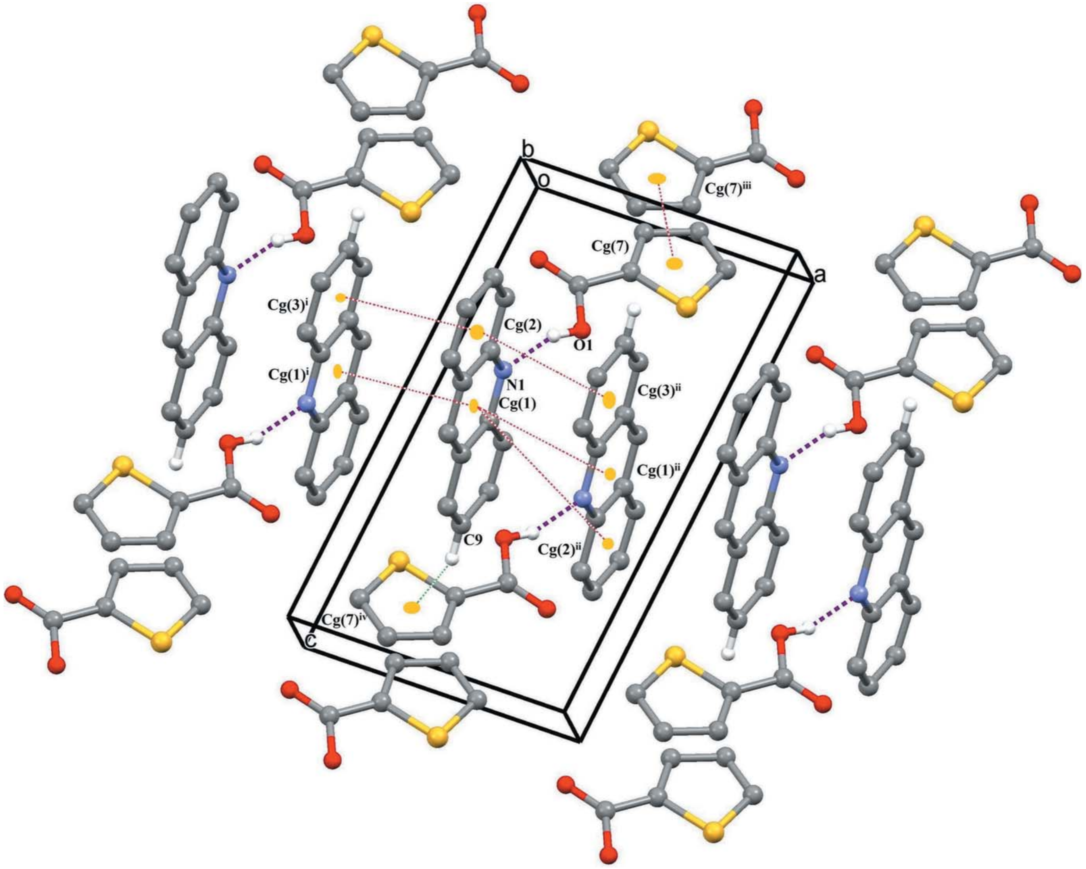

Figure 2
A view of the O—H···N hydrogen bonds (purple dashed lines), π–π stacking (acridine–acridine and thiophene–thiophene; red dashed lines) and C—H···π interactions between the acridine C—H group and the π-system of thiophene (green dashed lines).

the frequently used supramolecular synthon in crystal engineering involving a carboxylic acid and a pyridine molecule (Seaton, 2014; Lemmerer & Bernstein, 2010; Thomas *et al.*, 2010). A similar type of supramolecular synthon is observed in a series of nine co-crystals involving acridine and benzoic acids (Kowalska *et al.*, 2015). This supramolecular synthon is also present in the co-crystal of 5-chlorothiophene-2-carboxylic acid and acridine reported from our laboratory (Jennifer & Muthiah, 2014). This co-crystal and the title co-crystal differ only in the position of chlorine in the thiophene ring. The hydrogen-bonded units are linked *via* π–π stacking interactions between the aromatic systems of acridine molecules [$Cg1\cdots Cg1^{\rm i}$ = 3.6419 (9), $Cg1\cdots Cg1^{\rm ii}$ = 3.7526 (9), $Cg1\cdots Cg2^{\rm ii}$ = 3.7293 (12), $Cg2\cdots Cg3^{\rm i}$ = 3.6748 (12) and $Cg2\cdots Cg3^{\rm ii}$ = 3.7298 (12) Å where *Cg*1 is the centroid of the N1/C6/C11/C12/C13/C18 ring, *Cg*2 is the centroid of the C6–C11 ring and *Cg*3 is the centroid of the C13–C18 ring; symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $1-x, 2-y, 1-z$] and between the thiophene rings [$Cg7\cdots Cg7^{\rm iii}$ = 3.7611 (12) Å where *Cg*7 is the centroid of the thiophene ring; symmetry code: (iii) $1-x, 1-y, -z$]. The crystal structure also features C—H$\cdots\pi$ interactions, forming a three-dimensional supramolecular architecture (Table 1 and Fig. 2).

4. Database survey

The crystal structures of a number of acridine co-crystals, acridinium salts and their metal complexes have been investigated in a variety of crystalline environments such as diphenic acid–acridine (1:1) (Shaameri *et al.*, 2001*a*), 4,4′-bis(hydroxyazobenzene)–acridine (Chakraborty *et al.*, 2014), orcinol–acridine (1:2) and orcinol–acridine (1:1) co-crystal hydrate (Mukherjee *et al.*, 2011), acridinium isophthalate (Shaameri *et al.*, 2001*b*) and acridinium 6-carboxypyridine-2-carboxylate monohydrate (Derikvand *et al.*, 2011). A variety of metal complexes of acridine have also been reported (Ha, 2010, 2012; Sloufova & Slouf, 2000, 2001).

5. Synthesis and crystallization

To 10 ml of a hot methanol solution of 3TPC (40.6 mg, 25 mmol) were added 10 ml of a hot methanolic solution of acridine (44.8 mg, 25 mmol). The resulting solution was warmed over a water bath for half an hour and then kept at room temperature for crystallization. After a week yellow plate-like crystals of (**1**) were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were readily located in difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions, with C—H = 0.93 and O—H = 0.82 Å, and with $U_{\rm iso}$(H) = $kU_{\rm eq}$(C, O), where k = 1.5 for hydroxy and 1.2 for all other H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_3ClO_2S\cdot C_{13}H_9N$
M_r	341.80
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	7.3371 (4), 8.3286 (5), 13.3819 (8)
α, β, γ (°)	107.577 (5), 97.706 (5), 93.953 (5)
V (Å^3)	767.32 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.39
Crystal size (mm)	0.60 × 0.30 × 0.10
Data collection	
Diffractometer	Agilent SuperNova Dual Source diffractometer with an Atlas detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{\rm min}$, $T_{\rm max}$	0.813, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7182, 3516, 2722
$R_{\rm int}$	0.022
(sin $\theta/\lambda)_{\rm max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.109, 1.02
No. of reflections	3516
No. of parameters	209
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.21, −0.23

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Acknowledgements

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Olakkandiyil Prajina, Packianathan Thomas Muthiah and Franc Perdih

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Acridine–3-chlorothiophene-2-carboxylic acid (1/1)

Crystal data

$C_5H_3ClO_2S\cdot C_{13}H_9N$
$M_r = 341.80$
Triclinic, $P\overline{1}$
$a = 7.3371$ (4) Å
$b = 8.3286$ (5) Å
$c = 13.3819$ (8) Å
$\alpha = 107.577$ (5)°
$\beta = 97.706$ (5)°
$\gamma = 93.953$ (5)°
$V = 767.32$ (8) Å^3
$Z = 2$
$F(000) = 352$
$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2635 reflections
$\theta = 3.9$–29.2°
$\mu = 0.39$ mm^{-1}
$T = 293$ K
Plate, yellow
0.60 × 0.30 × 0.10 mm

Data collection

Agilent SuperNova Dual Source diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Detector resolution: 10.4933 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{min} = 0.813$, $T_{max} = 1.000$
7182 measured reflections
3516 independent reflections
2722 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.8°$
$h = -9 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.109$
$S = 1.02$
3516 reflections
209 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.133P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Cl1	0.21228 (7)	0.16757 (7)	−0.02749 (4)	0.05748 (17)
S1	0.69521 (6)	0.48402 (6)	0.14957 (4)	0.04516 (15)
O1	0.42177 (19)	0.63242 (19)	0.26579 (11)	0.0581 (4)
H1	0.3486	0.6911	0.2968	0.087*
O2	0.16569 (18)	0.49072 (19)	0.15614 (11)	0.0569 (4)
N1	0.26273 (19)	0.85354 (18)	0.39993 (11)	0.0390 (3)
C1	0.3309 (2)	0.5158 (2)	0.18026 (14)	0.0392 (4)
C2	0.4606 (2)	0.4179 (2)	0.11735 (13)	0.0366 (4)
C3	0.4277 (2)	0.2754 (2)	0.03048 (14)	0.0403 (4)
C4	0.5886 (3)	0.2201 (3)	−0.00919 (16)	0.0499 (5)
H4	0.5890	0.1248	−0.0675	0.060*
C5	0.7426 (3)	0.3226 (3)	0.04802 (16)	0.0512 (5)
H5	0.8614	0.3061	0.0331	0.061*
C6	0.2995 (2)	0.8560 (2)	0.50232 (14)	0.0367 (4)
C7	0.3599 (2)	0.7110 (2)	0.52526 (16)	0.0451 (4)
H7	0.3756	0.6162	0.4701	0.054*
C8	0.3948 (3)	0.7096 (3)	0.62689 (17)	0.0508 (5)
H8	0.4331	0.6131	0.6407	0.061*
C9	0.3742 (3)	0.8518 (3)	0.71176 (16)	0.0505 (5)
H9	0.3994	0.8485	0.7811	0.061*
C10	0.3179 (3)	0.9933 (3)	0.69378 (15)	0.0470 (5)
H10	0.3050	1.0864	0.7508	0.056*
C11	0.2784 (2)	1.0008 (2)	0.58805 (14)	0.0374 (4)
C12	0.2206 (2)	1.1415 (2)	0.56483 (14)	0.0406 (4)
H12	0.2070	1.2375	0.6197	0.049*
C13	0.1826 (2)	1.1413 (2)	0.45997 (15)	0.0397 (4)
C14	0.1250 (3)	1.2834 (3)	0.43165 (18)	0.0521 (5)
H14	0.1088	1.3814	0.4843	0.063*
C15	0.0936 (3)	1.2765 (3)	0.3283 (2)	0.0606 (6)
H15	0.0577	1.3706	0.3104	0.073*
C16	0.1148 (3)	1.1285 (3)	0.24777 (19)	0.0631 (6)
H16	0.0921	1.1263	0.1773	0.076*
C17	0.1677 (3)	0.9888 (3)	0.27050 (16)	0.0528 (5)
H17	0.1788	0.8915	0.2159	0.063*
C18	0.2061 (2)	0.9916 (2)	0.37835 (14)	0.0398 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0514 (3)	0.0565 (3)	0.0477 (3)	−0.0036 (2)	0.0025 (2)	−0.0040 (2)
S1	0.0407 (3)	0.0458 (3)	0.0437 (3)	0.00472 (19)	0.00429 (19)	0.0075 (2)
O1	0.0474 (8)	0.0552 (9)	0.0509 (8)	0.0084 (7)	0.0069 (6)	−0.0141 (7)
O2	0.0397 (8)	0.0638 (10)	0.0539 (9)	0.0063 (6)	0.0081 (6)	−0.0012 (7)
N1	0.0361 (8)	0.0383 (8)	0.0363 (8)	0.0043 (6)	0.0094 (6)	0.0008 (7)
C1	0.0435 (10)	0.0365 (10)	0.0355 (9)	0.0045 (7)	0.0057 (7)	0.0085 (8)
C2	0.0401 (9)	0.0374 (10)	0.0318 (9)	0.0077 (7)	0.0050 (7)	0.0096 (8)
C3	0.0442 (10)	0.0398 (10)	0.0339 (9)	0.0052 (7)	0.0035 (7)	0.0082 (8)
C4	0.0549 (12)	0.0478 (12)	0.0415 (10)	0.0136 (9)	0.0119 (9)	0.0027 (9)
C5	0.0465 (11)	0.0576 (13)	0.0505 (12)	0.0165 (9)	0.0154 (9)	0.0132 (10)
C6	0.0282 (8)	0.0371 (10)	0.0405 (10)	0.0006 (6)	0.0098 (7)	0.0049 (8)
C7	0.0423 (10)	0.0379 (10)	0.0516 (11)	0.0065 (8)	0.0148 (8)	0.0057 (9)
C8	0.0464 (11)	0.0514 (12)	0.0594 (13)	0.0073 (9)	0.0118 (9)	0.0227 (11)
C9	0.0502 (11)	0.0574 (13)	0.0436 (11)	−0.0018 (9)	0.0069 (8)	0.0175 (10)
C10	0.0491 (11)	0.0457 (11)	0.0376 (10)	−0.0037 (8)	0.0092 (8)	0.0015 (9)
C11	0.0303 (8)	0.0360 (9)	0.0386 (9)	−0.0029 (7)	0.0078 (7)	0.0016 (8)
C12	0.0339 (9)	0.0341 (10)	0.0432 (10)	−0.0011 (7)	0.0092 (7)	−0.0038 (8)
C13	0.0273 (8)	0.0377 (10)	0.0497 (11)	−0.0001 (7)	0.0074 (7)	0.0074 (8)
C14	0.0380 (10)	0.0440 (12)	0.0718 (14)	0.0030 (8)	0.0063 (9)	0.0158 (11)
C15	0.0440 (11)	0.0639 (15)	0.0809 (17)	0.0051 (10)	0.0024 (11)	0.0366 (14)
C16	0.0498 (12)	0.0863 (18)	0.0580 (14)	0.0021 (11)	0.0013 (10)	0.0343 (14)
C17	0.0444 (11)	0.0654 (14)	0.0438 (11)	0.0043 (9)	0.0050 (8)	0.0116 (10)
C18	0.0278 (8)	0.0465 (11)	0.0405 (10)	0.0012 (7)	0.0059 (7)	0.0075 (8)

Geometric parameters (Å, º)

Cl1—C3	1.7207 (18)	C8—H8	0.9300
S1—C5	1.692 (2)	C9—C10	1.352 (3)
S1—C2	1.7261 (17)	C9—H9	0.9300
O1—C1	1.316 (2)	C10—C11	1.427 (3)
O1—H1	0.8200	C10—H10	0.9300
O2—C1	1.199 (2)	C11—C12	1.379 (2)
N1—C18	1.346 (2)	C12—C13	1.393 (2)
N1—C6	1.354 (2)	C12—H12	0.9300
C1—C2	1.478 (3)	C13—C14	1.421 (3)
C2—C3	1.368 (3)	C13—C18	1.426 (3)
C3—C4	1.408 (3)	C14—C15	1.355 (3)
C4—C5	1.353 (3)	C14—H14	0.9300
C4—H4	0.9300	C15—C16	1.404 (3)
C5—H5	0.9300	C15—H15	0.9300
C6—C7	1.418 (2)	C16—C17	1.357 (3)
C6—C11	1.426 (2)	C16—H16	0.9300
C7—C8	1.354 (3)	C17—C18	1.426 (3)
C7—H7	0.9300	C17—H17	0.9300
C8—C9	1.405 (3)		

C5—S1—C2	92.22 (9)	C8—C9—H9	119.6
C1—O1—H1	109.5	C9—C10—C11	120.52 (19)
C18—N1—C6	119.31 (15)	C9—C10—H10	119.7
O2—C1—O1	125.12 (18)	C11—C10—H10	119.7
O2—C1—C2	124.13 (17)	C12—C11—C6	118.43 (16)
O1—C1—C2	110.75 (15)	C12—C11—C10	123.13 (17)
C3—C2—C1	130.54 (16)	C6—C11—C10	118.44 (17)
C3—C2—S1	109.54 (14)	C11—C12—C13	120.66 (17)
C1—C2—S1	119.91 (13)	C11—C12—H12	119.7
C2—C3—C4	113.99 (17)	C13—C12—H12	119.7
C2—C3—Cl1	124.70 (15)	C12—C13—C14	122.99 (18)
C4—C3—Cl1	121.31 (15)	C12—C13—C18	117.77 (16)
C5—C4—C3	111.64 (19)	C14—C13—C18	119.23 (17)
C5—C4—H4	124.2	C15—C14—C13	120.2 (2)
C3—C4—H4	124.2	C15—C14—H14	119.9
C4—C5—S1	112.61 (15)	C13—C14—H14	119.9
C4—C5—H5	123.7	C14—C15—C16	120.6 (2)
S1—C5—H5	123.7	C14—C15—H15	119.7
N1—C6—C7	119.41 (16)	C16—C15—H15	119.7
N1—C6—C11	121.65 (16)	C17—C16—C15	121.5 (2)
C7—C6—C11	118.94 (16)	C17—C16—H16	119.2
C8—C7—C6	120.47 (19)	C15—C16—H16	119.2
C8—C7—H7	119.8	C16—C17—C18	119.8 (2)
C6—C7—H7	119.8	C16—C17—H17	120.1
C7—C8—C9	120.91 (19)	C18—C17—H17	120.1
C7—C8—H8	119.5	N1—C18—C17	119.21 (18)
C9—C8—H8	119.5	N1—C18—C13	122.18 (16)
C10—C9—C8	120.73 (18)	C17—C18—C13	118.61 (17)
C10—C9—H9	119.6		

O2—C1—C2—C3	−7.7 (3)	C7—C6—C11—C12	179.62 (14)
O1—C1—C2—C3	171.99 (17)	N1—C6—C11—C10	179.36 (15)
O2—C1—C2—S1	170.91 (14)	C7—C6—C11—C10	−0.4 (2)
O1—C1—C2—S1	−9.4 (2)	C9—C10—C11—C12	179.99 (16)
C5—S1—C2—C3	0.03 (13)	C9—C10—C11—C6	0.0 (3)
C5—S1—C2—C1	−178.87 (14)	C6—C11—C12—C13	0.5 (2)
C1—C2—C3—C4	178.94 (16)	C10—C11—C12—C13	−179.48 (15)
S1—C2—C3—C4	0.2 (2)	C11—C12—C13—C14	−179.16 (15)
C1—C2—C3—Cl1	−1.6 (3)	C11—C12—C13—C18	−0.2 (2)
S1—C2—C3—Cl1	179.68 (10)	C12—C13—C14—C15	178.67 (17)
C2—C3—C4—C5	−0.4 (2)	C18—C13—C14—C15	−0.2 (3)
Cl1—C3—C4—C5	−179.89 (13)	C13—C14—C15—C16	0.9 (3)
C3—C4—C5—S1	0.4 (2)	C14—C15—C16—C17	−0.3 (3)
C2—S1—C5—C4	−0.25 (16)	C15—C16—C17—C18	−1.1 (3)
C18—N1—C6—C7	−179.75 (14)	C6—N1—C18—C17	179.93 (15)
C18—N1—C6—C11	0.5 (2)	C6—N1—C18—C13	−0.2 (2)
N1—C6—C7—C8	−179.02 (16)	C16—C17—C18—N1	−178.39 (17)

C11—C6—C7—C8	0.7 (2)	C16—C17—C18—C13	1.8 (3)
C6—C7—C8—C9	−0.7 (3)	C12—C13—C18—N1	0.1 (2)
C7—C8—C9—C10	0.3 (3)	C14—C13—C18—N1	179.06 (14)
C8—C9—C10—C11	0.0 (3)	C12—C13—C18—C17	179.95 (15)
N1—C6—C11—C12	−0.6 (2)	C14—C13—C18—C17	−1.1 (2)

Hydrogen-bond geometry (Å, º)

*Cg*7 is the centroid of the thiophene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.83	2.615 (2)	159
C9—H9···*Cg*7$^{\rm i}$	0.93	2.94	3.773 (2)	150

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.