Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis, characterization, crystal structure and supramolecularity of ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate and a new polymorph of ethyl (*E*)-2-cyano-3-(thiophen-2-yl)acrylate

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Received 3 August 2019
Accepted 14 August 2019

Edited by B. Therrien, University of Neuchâtel, Switzerland

Keywords: crystal structure; thiophene-based cyanoacrylates; polymorph; crystal supramolecularity.

CCDC references: 1947083; 1947082

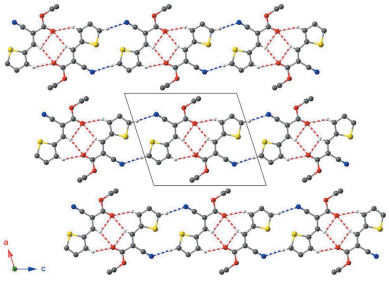
Supporting information: this article has supporting information at journals.iucr.org/e

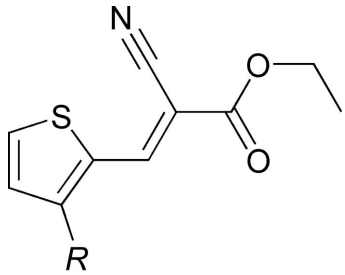
The synthesis, crystal structure and structural motif of two thiophene-based cyanoacrylate derivatives, namely, ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate (**1**), $C_{11}H_{11}NO_2S$, and ethyl (*E*)-2-cyano-3-(thiophen-2-yl)acrylate (**2**), $C_{10}H_9NO_2S$, are reported. Derivative **1** crystallized with two independent molecules in the asymmetric unit, and derivative **2** represents a new monoclinic (*C*2/*m*) polymorph. The molecular conformations of **1** and the two polymorphs of **2** are very similar, as all non-H atoms are planar except for the methyl of the ethyl groups. The intermolecular interactions and crystal packing of **1** and **2** are described and compared with that of the reported monoclinic (*C*2/*m*) polymorph of derivative **2** [Castro Agudelo *et al.* (2017). *Acta Cryst.* E**73**, 1287–1289].

1. Chemical context

Cyanoacrylate derivatives are of industrial interest being subunits used to build many adhesives and polymeric materials (Faggi *et al.*, 2019). They are also considered important intermediate precursors for the synthesis of different heterocyclic derivatives, see for example Qian *et al.* (2018), and as nitrile-activated species in bioreduction reactions (Brenna *et al.*, 2013, 2015; Kong *et al.*, 2016) among others. In addition, they show important practical properties, such as in organic dye-sensitized solar cells (DSSCs) (He *et al.*, 2017; Zhou *et al.*, 2015). Within these voltaic cells, cyanoacrylic acid is one of the most commonly employed acceptors. Thiophene and its derivatives, known to exhibit high charge mobility, serve as π-bridges (donor-π–acceptor structure) to provide conjugation and enhance light absorbance (Liu *et al.*, 2012).

An understanding of the structure of thiophene-based acrylate subunits is necessary to benefit from their properties in photovoltaic cells. In a continuation of our work on the X-ray structural characterization of thiophene-containing derivatives (Ibrahim *et al.*, 2019; Al-Refai *et al.*, 2014, 2016), we report here the synthesis, characterization and crystal structures of two thiophene-based acrylate derivatives, namely, ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate (**1**) and ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate (**2**). Derivative **2** is a polymorph of a reported structure (Castro Agudelo *et al.*, 2017), but with no disorder of the ethoxy group. The crystal supramolecularity of both compounds is also discussed.





1 R = CH_3
2 R = H

2. Structural commentary

The molecular structures of the title compounds are depicted in Fig. 1. The asymmetric unit contains two independent molecules, *A* and *B*, in **1** and one molecule in **2**. In these molecules, the bond distances and angles fall within similar ranges to those reported for similar compounds (Castro Agudelo *et al.*, 2017; Xu *et al.*, 2016). In both compounds, all non-hydrogen atoms, except for the methyl groups, lie nearly in the same planes. The differences in torsion angles [C1—C2—C3—C4 = −177.78 (14) and C1—O2—C12—C13 = 83.60 (15)° (molecule *A*), C14—C15—C16—C17 = 179.71 (15)° and C14—O15—C26—C27 = −88.66 (2)° (molecule *B*) in **1** and C1—C2—C3—C4 = −178.77 (11) and C1—O2—C11—C12 = −83.41 (13)° in **2**] indicate an out-of-plane deviation of the methyl group. The planarity of the molecules allows intramolecular hydrogen bonds to occur [C3—H3···O1 (molecule *A*) and C16—H16···O14 (molecule *B*) in **1**; C3—H3···O1 in **2**] (Fig. 1 and Tables 1 and 2), forming an *S*(6) ring motif with the carbonyl O and cyano N atoms consequently exhibiting an *anti*-configuration to each other. The conformation of the ethene bond is always *E* [C2═C3 = 1.363 (2) Å (molecule *A*) and C15═C16 = 1.3625 (19) (molecule *B*) in **1**; C2═C3 = 1.3592 (18) Å in **2**].

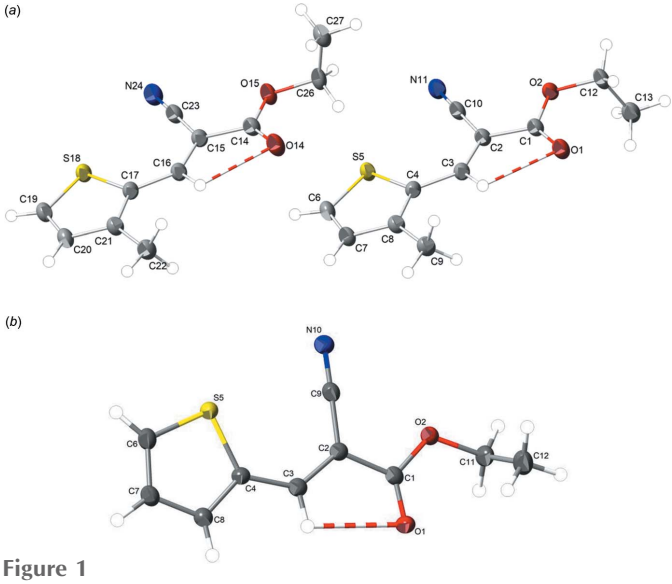


Figure 1
Molecular structures of compounds (*a*) **1** and (*b*) **2** with the atom-labelling scheme (displacement ellipsoids at 50% probability level). Intramolecular C—H···O interactions are presented as red–white multi-band cylinders.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1	0.95	2.43	2.8136 (19)	104
C16—H16···O14	0.95	2.38	2.7829 (19)	105
C19—H19···O1^{i}	0.95	2.34	3.2708 (19)	165
C22—H22*A*···O15^{ii}	0.98	2.59	3.292 (2)	128

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

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1	0.964 (19)	2.444 (19)	2.7998 (18)	101.5 (14)
C3—H3···O1^{i}	0.964 (19)	2.45 (2)	3.3436 (18)	153.4 (15)
C6—H6···N10^{ii}	0.99 (2)	2.49 (2)	3.465 (2)	169.1 (18)
C8—H8···O1^{i}	0.94 (2)	2.50 (2)	3.3047 (19)	143.6 (17)

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

Derivative **2** is a polymorph of ethyl (*E*)-2-cyano-3-(thiophen-2-yl)acrylate (CSD refcode GEHYEA; Castro Agudelo *et al.*, 2017). It shows a similar structure to **1**, which has an extra methyl substituent on the thiophene ring. In compound **1** and the two polymorphs of **2**, all thiophene-based cyanoacrylate non-H atoms, except for the ethyl group, lie in the same plane. It is also noteworthy that in the polymorph, the ethyl fragment occurs in more than one conformation, thus resulting in disorder, which is absent in **1** and **2**.

3. Supramolecular features

In the crystal of **1**, the *A* and *B* molecules each form layers parallel to the *ac* plane, Fig. 2*a*. The layers built up from chains of *B* molecules are connected *via* C—H···O hydrogen bonds along the *a* axis. These chains are further connected through C—H···O interactions with stacks of molecules *A* along the *c* axis. In the *b*-axis direction, interlayered interactions through van der Waals forces and/or weak dipolar interactions generate a three-dimensional network. In the crystal of **2**, inversion dimers are assembled along the *c* axis through C—H···O interactions, Fig. 2*b*. Adjacent dimers (along the *c* axis) are further connected through C—H···N interactions, leading to infinite chains propagating along the *c*-axis direction. The resulting chains interact via van der Waals forces to form sheets parallel to the *ac* plane (Fig. 2*b*). The sheets are connected through van der Waals forces and/or weak dipolar interactions, thus consolidating the three-dimensional framework structure. Compounds **1**, **2** and the polymorph of **2** (Castro Agudelo *et al.*, 2017) show no apparent degree of π–π stacking.

The polymorph of **2** shows a similar crystal packing arrangement, the molecules being connected *via* C—H···O/N interactions, generating centrosymmetric dimers. Chains of

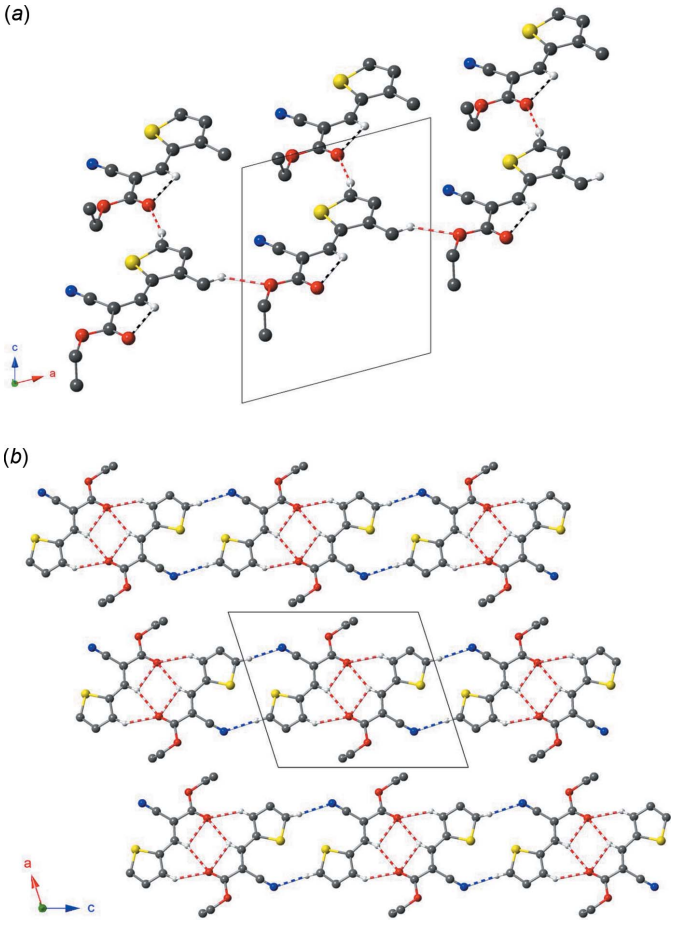


Figure 2
(*a*) Partial packing diagram for **1** showing layers of *A* and *B* molecules parallel to the *ac* plane, and connected *via* C—H···O intermolecular interactions (shown as multi-band cylinders). (*b*) The intramolecular (black and white) and intermolecular (red and white) interactions in **2** forming chains of dimeric species connected *via* C—H···O and C—H···N interactions. In both figures, hydrogen atoms not involved in interactions are omitted for clarity.

molecules are further connected by van der Waals forces into sheets.

4. Database survey

Castro Agudelo *et al.* (2017) reported a recent survey on the Cambridge Structural Database [CSD Version 5.37 with two updates; Groom *et al.*, 2016] for hits containing the complete thiophene-based cyanoacrylate fragment, together with the possibility of other five-membered rings and/or the presence of a saturated chain longer than the ethyl fragment. They found three hits containing the main part of the title compounds, the thiophene-cyanoacrylate, with additional and/or longer substituents, namely ethyl-3-(3-chloro-4-cyano-5-{[4-(dimethylamino)phenyl]diazenyl}-2-thienyl)-2-cyanoacrylate (UMUYAE; Xu *et al.*, 2016), octyl-2-cyano-3-(4,6-dibromo-7,7-dimethyl-7*H*-thieno[3′,4′:4,5]silolo[2,3-*b*]thiophen-2-yl)-acrylate (QUSKAS; Liu *et al.*, 2016) and ethyl-2-cyano-3-(3,3‴-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophen-5-yl)acrylate (AVUFON; Miyazaki *et al.*, 2011). In all derivatives AVUFON, UMUYAE and QUSKAS, the non-H thiophene-based acrylate fragment is almost planar except for the methyl group (or the longer alkyl chain in QUSKAS) being slightly out of the plane. The crystal lattices of AVUFON, UMUYAE and QUSKAS are stabilized by C—H···O/S, C—H···O/N and C—H···N/S intermolecular interactions, respectively.

A further search of the CSD for other five-membered rings instead of thiophene provided six hits. Of them, the following three are very similar to the title compounds: ethyl-(2*E*)-2-cyano-3-(1-methyl-1*H*-pyrrol-2-yl)prop-2-enoate (AYUGEH; Asiri *et al.*, 2011), (*E*)-ethyl-2-cyano-3-(1*H*-pyrrol-2-yl)acrylate (EVIZEP; Yuvaraj *et al.*, 2011) and (*E*)-ethyl-2-cyano-3-(furan-2-yl)acrylate (ZAQKIN; Kalkhambkar *et al.*, 2012). In both AYUGEH and EVIZEP, all the non-H atoms are nearly in the same plane, while in ZAQKIN the furan-based cyanoacrylate moiety lies in the same plane except for the methyl groups, which are slightly out of plane. As far as crystal packing is concerned, the molecules in EVIZEP and ZAQKIN are linked into dimers *via* N—H···O and C—H···O hydrogen bonds, respectively, while in AYUGEH the molecules are linked into tapes *via* both C—H···O and C—H···N interactions. The tapes are further interconnected by C—H···π interactions into a three-dimensional structure.

5. Synthesis and crystallization

All reagents and solvent were purchased from Aldrich and used without further purifications. The title compounds were synthesized as outlined in Fig. 3.

In a 250 ml round-bottom flask connected with a condenser, a mixture of the corresponding thiophene-2-carboxaldehyde (1 mmol), ethylcyanoacetate (1.1 mmol) and ammonium acetate (8 mmol) in absolute ethanol was refluxed for 6 h. The reaction was monitored using thin layer chromatography (TLC plates coated with silica gel). After completion, the reaction mixture was cooled to room temperature, and the obtained yellowish-brown precipitate was filtered off, washed with cooled water, dried and recrystallized from ethanol solution to give the final products as pale-yellow crystals (90% yield for both **1** and **2**).

Ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate (**1**): m.p. 381–382 K, ^{1}H NMR (CD_2Cl_2, 300 MHz): δ (ppm) = 1.39 (*t*, *J* = 7.12, 3H, CH_2CH_3), 2.48 (*s*, 3H, CH_3-3′), 4.36 (*q*, *J* = 7.12, 2H, CH_2CH_3), 7.07 (*d*, *J* = 5.01,1H, H-4′), 7.74 (*d*, *J* = 5.01, 1H, H-5′), 8.46 (*s*, 1H, H-3). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ (ppm) = 14.4 (CH_2CH_3), 14.9 (CH_3-3′), 62.7 (CH_2CH_3), 98.0 (C-2), 116.4 (CN), 131.2 (C-2′), 131.4 (C-4′), 134.3 (C-5′), 145.0 (C-3),

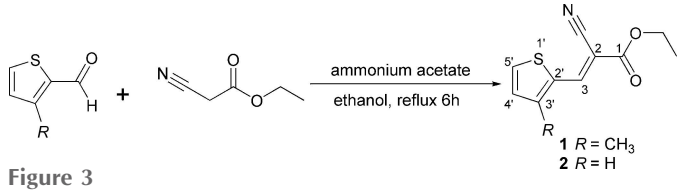


Figure 3
Syntheis of the title compounds.

Table 3
Experimental details.

	1	2
Crystal data		
Chemical formula	$C_{11}H_{11}NO_2S$	$C_{10}H_9NO_2S$
M_r	221.27	207.24
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
Temperature (K)	100	100
a, b, c (Å)	9.2784 (2), 10.7925 (3), 11.6696 (2)	11.5907 (3), 6.6883 (2), 13.4837 (3)
α, β, γ (°)	74.464 (2), 74.179 (2), 85.073 (2)	90, 107.859 (2), 90
V (Å^3)	1083.11 (4)	994.92 (5)
Z	4	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	2.49	2.68
Crystal size (mm)	0.26 × 0.24 × 0.11	0.32 × 0.20 × 0.20
Data collection		
Diffractometer	Stoe STADIVARI	Stoe STADIVARI
Absorption correction	Multi-scan (*LANA*; Stoe & Cie, 2016)	Multi-scan (*LANA*; Stoe & Cie, 2016)
T_{min}, T_{max}	0.074, 0.546	0.051, 0.168
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21624, 4399, 3911	10400, 2048, 1974
R_{int}	0.032	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.630	0.630
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.122, 1.10	0.033, 0.100, 1.09
No. of reflections	4399	2048
No. of parameters	275	164
H-atom treatment	H-atom parameters constrained	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.49	0.29, −0.28

Computer programs: *X-AREA Pilatus*, *Recipe* and *Integrate* (Stoe & Cie, 2016) *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *DIAMOND* (Crystal Impact, 2014).

149.9 (C-3′), 163.4 (C-1). (+)-ESIMS m/z = 244 ([M + Na]$^+$, 100%), 465 ([2M + Na]$^+$, 16%).

Ethyl (*E*)-2-cyano-3-(thiophen-2-yl)acrylate (**2**): mp. 371–372 K, ^{1}H NMR (CD_2Cl_2, 300 MHz): δ (ppm) = 1.39 (*t*, J = 7.12, 3H, CH_2CH_3), 4.37 (*q*, J = 7.12, 2H, CH_2CH_3), 7.27 (*t*, J = 4.44,1H, H-4′), 7.85 (*d*, J = 4.36, 2H, H-3′,5′), 8.38 (*s*, 1H, H-3). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ (ppm) = 14.4 (CH_2CH_3), 62.9 (CH_2CH_3), 99.8 (C-2), 116.1 (CN), 129.0 (C-4′), 135.5 (C-5′), 136.5 (C-2′), 137.8 (C-3′), 146.9 (C-3), 162.9 (C-1). (+)-ESIMS m/z = 230 ([M + Na]$^+$, 100%), 237 ([2M + Na]$^+$, 11%).

6. Refinement

Detailed crystal data and structure refinement for the title compounds are listed in Table 3. In **1**, C-bound hydrogen atoms were included in calculated positions (0.95–0.99 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C-methyl). Methyl groups were allowed to rotate to fit best the electron density. All hydrogen atoms in **2** were located in difference-Fourier maps and refined isotropically.

Funding information

The authors thank Al al-Bayt University for financial support. Thanks are also due to the DFG (Deutsche Forschungsgemeinschaft) for financial support (research visit fellowship to Dr Mahmoud Al-Refai).

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supporting information

Acta Cryst. (2019). E**75**, 1357-1361 [https://doi.org/10.1107/S2056989019011435]

Synthesis, characterization, crystal structure and supramolecularity of ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate and a new polymorph of ethyl (*E*)-2-cyano-3-(thiophen-2-yl)acrylate

Mahmoud Al-Refai, Basem F. Ali, Ala'a B. Said, Armin Geyer, Michael Marsch and Klaus Harms

Computing details

For both structures, data collection: *X-AREA Pilatus* (Stoe & Cie, 2016); cell refinement: *X-AREA Recipe* (Stoe & Cie, 2015); data reduction: *X-AREA Integrate* (Stoe & Cie, 2016) and *LANA* (Stoe & Cie, 2016); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Crystal Impact, 2014); software used to prepare material for publication: *X-AREA* (Stoe & Cie, 2016).

Ethyl (*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylate (1)

Crystal data

$C_{11}H_{11}NO_2S$
$M_r = 221.27$
Triclinic, $P\overline{1}$
$a = 9.2784$ (2) Å
$b = 10.7925$ (3) Å
$c = 11.6696$ (2) Å
$\alpha = 74.464$ (2)°
$\beta = 74.179$ (2)°
$\gamma = 85.073$ (2)°
$V = 1083.11$ (4) Å^3
$Z = 4$
$F(000) = 464$
$D_x = 1.357$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54186$ Å
Cell parameters from 24144 reflections
$\theta = 4.3$–$76.6°$
$\mu = 2.49$ mm^{-1}
$T = 100$ K
Plate, colourless
0.26 × 0.24 × 0.11 mm

Data collection

Stoe STADIVARI diffractometer
Radiation source: GeniX 3D HF Cu
Detector resolution: 5.81 pixels mm^{-1}
rotation method, ω scans
Absorption correction: multi-scan (*LANA*; Stoe & Cie, 2016)
$T_{min} = 0.074$, $T_{max} = 0.546$
21624 measured reflections
4399 independent reflections
3911 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 76.1°$, $\theta_{min} = 4.3°$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.122$
$S = 1.10$
4399 reflections
275 parameters
0 restraints
Primary atom site location: dual

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 0.1177P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} = 0.001$
H-atom parameters constrained	$\Delta\rho_{max} = 0.37$ e Å^{-3}
	$\Delta\rho_{min} = -0.49$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.50743 (12)	0.18612 (11)	−0.05309 (9)	0.0282 (2)
C1	0.41104 (16)	0.24976 (14)	−0.00171 (13)	0.0244 (3)
O2	0.26787 (11)	0.25753 (11)	−0.00683 (9)	0.0272 (2)
C2	0.43611 (16)	0.33079 (14)	0.07627 (13)	0.0241 (3)
C3	0.57815 (16)	0.33732 (14)	0.08609 (13)	0.0237 (3)
H3	0.651544	0.290986	0.038820	0.028*
C4	0.63437 (16)	0.40276 (14)	0.15613 (13)	0.0237 (3)
S5	0.52472 (4)	0.48985 (3)	0.25473 (3)	0.02482 (13)
C6	0.67767 (17)	0.52373 (15)	0.29500 (13)	0.0279 (3)
H6	0.673143	0.573149	0.352151	0.033*
C7	0.80743 (16)	0.47210 (15)	0.23616 (13)	0.0271 (3)
H7	0.902616	0.481512	0.248382	0.033*
C8	0.78481 (16)	0.40304 (14)	0.15496 (13)	0.0253 (3)
C9	0.90876 (16)	0.33949 (15)	0.07698 (14)	0.0288 (3)
H9A	1.002445	0.344255	0.098973	0.043*
H9B	0.920518	0.383536	−0.010108	0.043*
H9C	0.884318	0.249167	0.091128	0.043*
C10	0.30968 (16)	0.39583 (15)	0.13711 (13)	0.0260 (3)
N11	0.20792 (14)	0.44850 (13)	0.18585 (12)	0.0307 (3)
C12	0.22775 (17)	0.18030 (16)	−0.07799 (14)	0.0293 (3)
H12A	0.311397	0.179597	−0.151655	0.035*
H12B	0.138713	0.218888	−0.106211	0.035*
C13	0.19407 (17)	0.04420 (16)	−0.00130 (15)	0.0335 (3)
H13A	0.154960	−0.003295	−0.046871	0.050*
H13B	0.119282	0.045515	0.076064	0.050*
H13C	0.286108	0.002013	0.016692	0.050*
O14	0.39990 (12)	0.67602 (12)	0.40403 (10)	0.0326 (3)
C14	0.29946 (16)	0.72830 (15)	0.46523 (13)	0.0262 (3)
O15	0.15438 (11)	0.72446 (11)	0.46857 (10)	0.0285 (2)
C15	0.32273 (16)	0.80391 (14)	0.54804 (13)	0.0251 (3)
C16	0.46568 (16)	0.81134 (14)	0.55532 (12)	0.0246 (3)
H16	0.538142	0.766223	0.506059	0.029*
C17	0.52508 (16)	0.87543 (14)	0.62444 (13)	0.0245 (3)
S18	0.42127 (4)	0.96642 (3)	0.72124 (3)	0.02552 (13)

C19	0.57711 (17)	0.99953 (15)	0.75821 (13)	0.0282 (3)
H19	0.575810	1.050830	0.813150	0.034*
C20	0.70388 (17)	0.94398 (15)	0.69991 (13)	0.0279 (3)
H20	0.800387	0.952569	0.710077	0.033*
C22	0.79644 (17)	0.80089 (16)	0.54916 (14)	0.0306 (3)
H22A	0.894192	0.818438	0.558037	0.046*
H22B	0.796091	0.829397	0.462132	0.046*
H22C	0.777504	0.708354	0.579387	0.046*
C21	0.67641 (16)	0.87201 (15)	0.62249 (13)	0.0258 (3)
C23	0.19658 (16)	0.86371 (15)	0.61513 (13)	0.0271 (3)
N24	0.09612 (15)	0.91263 (14)	0.67014 (12)	0.0324 (3)
C26	0.11875 (17)	0.65600 (15)	0.38777 (14)	0.0300 (3)
H26A	0.017243	0.619428	0.424811	0.036*
H26B	0.191159	0.584110	0.378726	0.036*
C27	0.12498 (19)	0.74571 (17)	0.26288 (14)	0.0360 (4)
H27A	0.092643	0.700287	0.212052	0.054*
H27B	0.227878	0.775245	0.222919	0.054*
H27C	0.058482	0.819932	0.272496	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0258 (5)	0.0336 (6)	0.0305 (5)	0.0029 (4)	−0.0085 (4)	−0.0166 (4)
C1	0.0237 (7)	0.0275 (8)	0.0244 (6)	0.0005 (5)	−0.0079 (5)	−0.0096 (6)
O2	0.0232 (5)	0.0346 (6)	0.0320 (5)	0.0020 (4)	−0.0115 (4)	−0.0185 (4)
C2	0.0237 (7)	0.0268 (8)	0.0249 (6)	0.0014 (5)	−0.0086 (5)	−0.0101 (6)
C3	0.0238 (7)	0.0258 (7)	0.0237 (6)	0.0005 (5)	−0.0065 (5)	−0.0098 (5)
C4	0.0230 (7)	0.0265 (8)	0.0253 (6)	0.0019 (5)	−0.0076 (5)	−0.0121 (5)
S5	0.0228 (2)	0.0302 (2)	0.0267 (2)	0.00155 (14)	−0.00801 (14)	−0.01489 (15)
C6	0.0293 (7)	0.0315 (8)	0.0290 (7)	−0.0017 (6)	−0.0115 (6)	−0.0135 (6)
C7	0.0253 (7)	0.0313 (8)	0.0291 (7)	−0.0012 (6)	−0.0101 (6)	−0.0115 (6)
C8	0.0244 (7)	0.0282 (8)	0.0251 (6)	0.0002 (5)	−0.0071 (5)	−0.0095 (6)
C9	0.0226 (7)	0.0357 (9)	0.0311 (7)	0.0029 (6)	−0.0068 (6)	−0.0149 (6)
C10	0.0256 (7)	0.0302 (8)	0.0280 (6)	0.0005 (6)	−0.0117 (5)	−0.0126 (6)
N11	0.0263 (6)	0.0384 (8)	0.0342 (6)	0.0030 (5)	−0.0103 (5)	−0.0190 (6)
C12	0.0282 (7)	0.0361 (9)	0.0325 (7)	0.0023 (6)	−0.0134 (6)	−0.0188 (6)
C13	0.0303 (7)	0.0382 (9)	0.0393 (8)	−0.0019 (6)	−0.0111 (6)	−0.0194 (7)
O14	0.0289 (5)	0.0416 (7)	0.0359 (6)	0.0049 (5)	−0.0102 (4)	−0.0239 (5)
C14	0.0258 (7)	0.0296 (8)	0.0264 (7)	0.0007 (6)	−0.0088 (5)	−0.0105 (6)
O15	0.0249 (5)	0.0360 (6)	0.0312 (5)	−0.0003 (4)	−0.0092 (4)	−0.0175 (4)
C15	0.0252 (7)	0.0285 (8)	0.0248 (6)	0.0017 (5)	−0.0076 (5)	−0.0116 (5)
C16	0.0255 (7)	0.0277 (8)	0.0232 (6)	0.0005 (5)	−0.0068 (5)	−0.0106 (5)
C17	0.0247 (7)	0.0278 (8)	0.0242 (6)	0.0014 (5)	−0.0068 (5)	−0.0121 (5)
S18	0.0248 (2)	0.0310 (2)	0.0255 (2)	0.00185 (14)	−0.00731 (14)	−0.01494 (15)
C19	0.0319 (7)	0.0306 (8)	0.0273 (7)	−0.0015 (6)	−0.0111 (6)	−0.0124 (6)
C20	0.0281 (7)	0.0322 (8)	0.0283 (7)	−0.0023 (6)	−0.0108 (6)	−0.0119 (6)
C22	0.0261 (7)	0.0364 (9)	0.0325 (7)	0.0043 (6)	−0.0077 (6)	−0.0158 (6)
C21	0.0245 (7)	0.0294 (8)	0.0259 (7)	0.0005 (6)	−0.0073 (5)	−0.0105 (6)

C23	0.0268 (7)	0.0312 (8)	0.0278 (7)	0.0002 (6)	−0.0105 (6)	−0.0117 (6)
N24	0.0272 (6)	0.0403 (8)	0.0342 (7)	0.0025 (5)	−0.0078 (5)	−0.0178 (6)
C26	0.0300 (7)	0.0338 (9)	0.0337 (8)	−0.0012 (6)	−0.0112 (6)	−0.0179 (6)
C27	0.0377 (8)	0.0441 (10)	0.0341 (8)	−0.0029 (7)	−0.0139 (6)	−0.0179 (7)

Geometric parameters (Å, º)

O1—C1	1.2057 (17)	O14—C14	1.2081 (18)
C1—O2	1.3404 (17)	C14—O15	1.3399 (17)
C1—C2	1.4912 (19)	C14—C15	1.4876 (19)
O2—C12	1.4545 (16)	O15—C26	1.4593 (16)
C2—C3	1.363 (2)	C15—C16	1.3625 (19)
C2—C10	1.4298 (19)	C15—C23	1.428 (2)
C3—C4	1.4296 (19)	C16—C17	1.4282 (19)
C3—H3	0.9500	C16—H16	0.9500
C4—C8	1.3925 (19)	C17—C21	1.3955 (19)
C4—S5	1.7375 (14)	C17—S18	1.7339 (14)
S5—C6	1.7068 (14)	S18—C19	1.7076 (15)
C6—C7	1.368 (2)	C19—C20	1.366 (2)
C6—H6	0.9500	C19—H19	0.9500
C7—C8	1.4181 (19)	C20—C21	1.421 (2)
C7—H7	0.9500	C20—H20	0.9500
C8—C9	1.4997 (19)	C22—C21	1.499 (2)
C9—H9A	0.9800	C22—H22A	0.9800
C9—H9B	0.9800	C22—H22B	0.9800
C9—H9C	0.9800	C22—H22C	0.9800
C10—N11	1.1517 (19)	C23—N24	1.153 (2)
C12—C13	1.509 (2)	C26—C27	1.508 (2)
C12—H12A	0.9900	C26—H26A	0.9900
C12—H12B	0.9900	C26—H26B	0.9900
C13—H13A	0.9800	C27—H27A	0.9800
C13—H13B	0.9800	C27—H27B	0.9800
C13—H13C	0.9800	C27—H27C	0.9800
O1—C1—O2	124.91 (13)	O14—C14—O15	124.76 (13)
O1—C1—C2	124.13 (13)	O14—C14—C15	123.55 (13)
O2—C1—C2	110.96 (12)	O15—C14—C15	111.68 (12)
C1—O2—C12	116.44 (11)	C14—O15—C26	116.44 (11)
C3—C2—C10	123.99 (13)	C16—C15—C23	123.75 (13)
C3—C2—C1	117.90 (13)	C16—C15—C14	117.06 (13)
C10—C2—C1	118.10 (12)	C23—C15—C14	119.19 (12)
C2—C3—C4	130.33 (14)	C15—C16—C17	130.94 (14)
C2—C3—H3	114.8	C15—C16—H16	114.5
C4—C3—H3	114.8	C17—C16—H16	114.5
C8—C4—C3	123.93 (13)	C21—C17—C16	123.66 (14)
C8—C4—S5	111.36 (10)	C21—C17—S18	111.12 (11)
C3—C4—S5	124.71 (11)	C16—C17—S18	125.22 (11)
C6—S5—C4	91.34 (7)	C19—S18—C17	91.77 (7)

C7—C6—S5	112.77 (11)	C20—C19—S18	112.44 (11)
C7—C6—H6	123.6	C20—C19—H19	123.8
S5—C6—H6	123.6	S18—C19—H19	123.8
C6—C7—C8	112.84 (13)	C19—C20—C21	113.02 (13)
C6—C7—H7	123.6	C19—C20—H20	123.5
C8—C7—H7	123.6	C21—C20—H20	123.5
C4—C8—C7	111.68 (13)	C21—C22—H22A	109.5
C4—C8—C9	124.57 (13)	C21—C22—H22B	109.5
C7—C8—C9	123.75 (13)	H22A—C22—H22B	109.5
C8—C9—H9A	109.5	C21—C22—H22C	109.5
C8—C9—H9B	109.5	H22A—C22—H22C	109.5
H9A—C9—H9B	109.5	H22B—C22—H22C	109.5
C8—C9—H9C	109.5	C17—C21—C20	111.66 (13)
H9A—C9—H9C	109.5	C17—C21—C22	124.81 (13)
H9B—C9—H9C	109.5	C20—C21—C22	123.53 (13)
N11—C10—C2	179.8 (2)	N24—C23—C15	178.96 (15)
O2—C12—C13	110.63 (12)	O15—C26—C27	110.46 (12)
O2—C12—H12A	109.5	O15—C26—H26A	109.6
C13—C12—H12A	109.5	C27—C26—H26A	109.6
O2—C12—H12B	109.5	O15—C26—H26B	109.6
C13—C12—H12B	109.5	C27—C26—H26B	109.6
H12A—C12—H12B	108.1	H26A—C26—H26B	108.1
C12—C13—H13A	109.5	C26—C27—H27A	109.5
C12—C13—H13B	109.5	C26—C27—H27B	109.5
H13A—C13—H13B	109.5	H27A—C27—H27B	109.5
C12—C13—H13C	109.5	C26—C27—H27C	109.5
H13A—C13—H13C	109.5	H27A—C27—H27C	109.5
H13B—C13—H13C	109.5	H27B—C27—H27C	109.5

O1—C1—O2—C12	1.4 (2)	O14—C14—O15—C26	−2.6 (2)
C2—C1—O2—C12	−178.63 (12)	C15—C14—O15—C26	178.16 (12)
O1—C1—C2—C3	2.7 (2)	O14—C14—C15—C16	−1.2 (2)
O2—C1—C2—C3	−177.20 (13)	O15—C14—C15—C16	178.04 (13)
O1—C1—C2—C10	−176.67 (14)	O14—C14—C15—C23	179.03 (15)
O2—C1—C2—C10	3.39 (18)	O15—C14—C15—C23	−1.8 (2)
C10—C2—C3—C4	1.6 (3)	C23—C15—C16—C17	−0.5 (3)
C1—C2—C3—C4	−177.78 (14)	C14—C15—C16—C17	179.71 (15)
C2—C3—C4—C8	−178.52 (15)	C15—C16—C17—C21	179.19 (16)
C2—C3—C4—S5	2.4 (2)	C15—C16—C17—S18	−0.6 (2)
C8—C4—S5—C6	−0.81 (12)	C21—C17—S18—C19	0.10 (12)
C3—C4—S5—C6	178.37 (14)	C16—C17—S18—C19	179.92 (14)
C4—S5—C6—C7	0.29 (12)	C17—S18—C19—C20	−0.07 (13)
S5—C6—C7—C8	0.30 (17)	S18—C19—C20—C21	0.02 (18)
C3—C4—C8—C7	−178.06 (14)	C16—C17—C21—C20	−179.93 (14)
S5—C4—C8—C7	1.12 (16)	S18—C17—C21—C20	−0.11 (17)
C3—C4—C8—C9	2.5 (2)	C16—C17—C21—C22	−0.4 (2)
S5—C4—C8—C9	−178.36 (12)	S18—C17—C21—C22	179.43 (12)
C6—C7—C8—C4	−0.93 (19)	C19—C20—C21—C17	0.1 (2)

C6—C7—C8—C9	178.56 (14)	C19—C20—C21—C22	−179.49 (14)
C1—O2—C12—C13	83.60 (15)	C14—O15—C26—C27	−88.66 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1	0.95	2.43	2.8136 (19)	104
C16—H16···O14	0.95	2.38	2.7829 (19)	105
C19—H19···O1^{i}	0.95	2.34	3.2708 (19)	165
C22—H22*A*···O15^{ii}	0.98	2.59	3.292 (2)	128

Symmetry codes: (i) *x*, *y*+1, *z*+1; (ii) *x*+1, *y*, *z*.

Ethyl (*E*)-2-cyano-3-(thiophen-2-yl)acrylate (2)

Crystal data

$C_{10}H_9NO_2S$
M_r = 207.24
Monoclinic, $P2_1/c$
a = 11.5907 (3) Å
b = 6.6883 (2) Å
c = 13.4837 (3) Å
β = 107.859 (2)°
V = 994.92 (5) Å^3
Z = 4
F(000) = 432
D_x = 1.384 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54186 Å
Cell parameters from 15380 reflections
θ = 3.5–76.4°
μ = 2.68 mm^{-1}
T = 100 K
Block, colourless
0.32 × 0.20 × 0.20 mm

Data collection

Stoe STADIVARI diffractometer
Radiation source: GeniX 3D HF Cu
Detector resolution: 5.81 pixels mm^{-1}
rotation method, *ω* scans
Absorption correction: multi-scan (*LANA*; Stoe & Cie, 2016)
T_{min} = 0.051, T_{max} = 0.168
10400 measured reflections
2048 independent reflections
1974 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 76.3°, θ_{min} = 6.8°
h = −14→14
k = −8→8
l = −16→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.100
S = 1.09
2048 reflections
164 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.2209P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: SHELXL-2018/3 (Sheldrick 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0030 (6)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.67411 (9)	0.47068 (14)	0.54042 (8)	0.0266 (3)
C1	0.72087 (12)	0.46539 (17)	0.47233 (11)	0.0214 (3)
O2	0.84079 (8)	0.45263 (13)	0.48771 (8)	0.0238 (2)
C2	0.65241 (12)	0.46897 (17)	0.35943 (11)	0.0211 (3)
C3	0.52935 (12)	0.47114 (18)	0.33171 (11)	0.0215 (3)
H3	0.4938 (17)	0.475 (2)	0.3876 (14)	0.025 (4)*
C4	0.44161 (12)	0.47115 (17)	0.23001 (11)	0.0210 (3)
S5	0.47197 (3)	0.46815 (5)	0.11198 (2)	0.02218 (16)
C6	0.32131 (13)	0.47018 (18)	0.04368 (12)	0.0250 (3)
H6	0.301 (2)	0.470 (3)	−0.0329 (19)	0.044 (6)*
C7	0.24983 (13)	0.47201 (19)	0.10750 (12)	0.0256 (3)
H7	0.158 (2)	0.472 (3)	0.0817 (19)	0.053 (6)*
C8	0.31729 (13)	0.47269 (18)	0.21394 (12)	0.0229 (3)
H8	0.2819 (18)	0.476 (2)	0.2678 (16)	0.031 (5)*
C9	0.71814 (12)	0.46836 (18)	0.28517 (11)	0.0223 (3)
H9	0.8744 (14)	0.354 (3)	0.6320 (12)	0.026 (4)*
N10	0.76940 (11)	0.46866 (17)	0.22440 (10)	0.0272 (3)
H10	0.9901 (15)	0.379 (3)	0.5923 (13)	0.029 (4)*
C11	0.91574 (13)	0.4415 (2)	0.59654 (12)	0.0277 (3)
H11	0.8636 (16)	0.712 (3)	0.6428 (13)	0.039 (5)*
C12	0.94012 (13)	0.6466 (3)	0.64456 (12)	0.0355 (3)
H12	0.9946 (17)	0.630 (3)	0.7176 (16)	0.051 (5)*
H13	0.9802 (15)	0.731 (3)	0.6063 (14)	0.044 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0208 (5)	0.0392 (6)	0.0210 (5)	0.0009 (4)	0.0081 (4)	0.0005 (4)
C1	0.0179 (6)	0.0224 (6)	0.0235 (7)	−0.0005 (4)	0.0055 (5)	−0.0001 (4)
O2	0.0170 (5)	0.0334 (5)	0.0205 (5)	0.0013 (3)	0.0050 (4)	0.0002 (3)
C2	0.0196 (6)	0.0236 (6)	0.0203 (7)	0.0004 (4)	0.0062 (5)	0.0002 (4)
C3	0.0205 (7)	0.0220 (7)	0.0225 (7)	0.0002 (4)	0.0071 (5)	−0.0001 (4)
C4	0.0202 (7)	0.0236 (6)	0.0203 (7)	−0.0006 (4)	0.0077 (5)	−0.0004 (4)
S5	0.0193 (2)	0.0285 (2)	0.0190 (2)	−0.00064 (10)	0.00624 (14)	−0.00010 (10)
C6	0.0221 (6)	0.0269 (7)	0.0234 (7)	−0.0009 (5)	0.0033 (5)	0.0002 (5)
C7	0.0196 (6)	0.0290 (7)	0.0264 (8)	−0.0006 (5)	0.0046 (5)	0.0004 (5)
C8	0.0210 (7)	0.0240 (6)	0.0236 (7)	−0.0003 (4)	0.0068 (5)	−0.0001 (4)
C9	0.0178 (6)	0.0245 (7)	0.0231 (7)	0.0000 (4)	0.0040 (5)	0.0003 (4)
N10	0.0213 (6)	0.0371 (7)	0.0236 (6)	0.0006 (4)	0.0073 (5)	0.0007 (4)

C11	0.0195 (6)	0.0398 (7)	0.0212 (7)	0.0042 (5)	0.0024 (5)	0.0014 (5)
C12	0.0229 (6)	0.0484 (9)	0.0318 (8)	0.0018 (6)	0.0032 (5)	−0.0091 (7)

Geometric parameters (Å, º)

O1—C1	1.2012 (18)	C6—H6	0.99 (2)
C1—O2	1.3438 (15)	C7—C8	1.408 (2)
C1—C2	1.4855 (19)	C7—H7	1.01 (2)
O2—C11	1.4600 (16)	C8—H8	0.938 (19)
C2—C3	1.3592 (18)	C9—N10	1.1501 (19)
C2—C9	1.4322 (18)	C11—C12	1.506 (2)
C3—C4	1.4350 (19)	C11—H9	0.969 (16)
C3—H3	0.964 (18)	C11—H10	0.976 (16)
C4—C8	1.3899 (19)	C12—H11	0.982 (18)
C4—S5	1.7323 (14)	C12—H12	1.00 (2)
S5—C6	1.7062 (15)	C12—H13	0.974 (19)
C6—C7	1.365 (2)		
O1—C1—O2	124.87 (13)	C6—C7—H7	124.0 (14)
O1—C1—C2	123.94 (12)	C8—C7—H7	123.2 (14)
O2—C1—C2	111.18 (11)	C4—C8—C7	112.58 (13)
C1—O2—C11	115.27 (10)	C4—C8—H8	123.9 (13)
C3—C2—C9	123.10 (13)	C7—C8—H8	123.5 (13)
C3—C2—C1	117.88 (12)	N10—C9—C2	178.99 (14)
C9—C2—C1	119.01 (11)	O2—C11—C12	111.16 (12)
C2—C3—C4	129.73 (13)	O2—C11—H9	107.1 (10)
C2—C3—H3	116.7 (11)	C12—C11—H9	113.1 (10)
C4—C3—H3	113.5 (11)	O2—C11—H10	103.1 (10)
C8—C4—C3	123.09 (13)	C12—C11—H10	111.3 (10)
C8—C4—S5	110.48 (11)	H9—C11—H10	110.5 (13)
C3—C4—S5	126.43 (10)	C11—C12—H11	110.2 (11)
C6—S5—C4	91.90 (7)	C11—C12—H12	107.6 (13)
C7—C6—S5	112.23 (11)	H11—C12—H12	111.4 (15)
C7—C6—H6	131.8 (13)	C11—C12—H13	111.0 (11)
S5—C6—H6	116.0 (13)	H11—C12—H13	107.7 (15)
C6—C7—C8	112.81 (12)	H12—C12—H13	109.0 (15)
O1—C1—O2—C11	1.03 (17)	C2—C3—C4—S5	0.03 (19)
C2—C1—O2—C11	−178.07 (10)	C8—C4—S5—C6	0.27 (9)
O1—C1—C2—C3	−2.45 (17)	C3—C4—S5—C6	179.99 (11)
O2—C1—C2—C3	176.65 (10)	C4—S5—C6—C7	−0.31 (10)
O1—C1—C2—C9	178.04 (11)	S5—C6—C7—C8	0.27 (14)
O2—C1—C2—C9	−2.85 (15)	C3—C4—C8—C7	−179.90 (11)
C9—C2—C3—C4	0.7 (2)	S5—C4—C8—C7	−0.17 (13)
C1—C2—C3—C4	−178.77 (11)	C6—C7—C8—C4	−0.06 (16)
C2—C3—C4—C8	179.71 (12)	C1—O2—C11—C12	−83.41 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1	0.964 (19)	2.444 (19)	2.7998 (18)	101.5 (14)
C3—H3···O1^{i}	0.964 (19)	2.45 (2)	3.3436 (18)	153.4 (15)
C6—H6···N10^{ii}	0.99 (2)	2.49 (2)	3.465 (2)	169.1 (18)
C8—H8···O1^{i}	0.94 (2)	2.50 (2)	3.3047 (19)	143.6 (17)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*.