Debora Cobo,[a] Jairo Quiroga,[a] Justo Cobo,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.094
Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

(E)-3-(4-Chlorophenyl)-2-(2-thienyl)acrylonitrile: chains built from C—H···N hydrogen bonds

In the title compound, $C_{13}H_8ClNS$, the thiophene ring is disordered over two orientations. The molecules are linked into C(5) chains by a single C—H···N hydrogen bond.
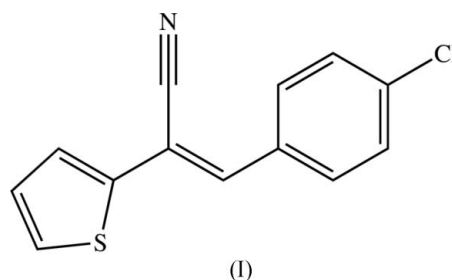
Comment

The title compound, (I), was prepared for use as an intermediate in the synthesis of new fused heterocyclic systems.

(I)

The thiophene rings are disordered over two orientations corresponding to a 180° rotation about the C2—C22 bond (Fig. 1); the two conformers have unequal occupancy, with refined site-occupancy factors for the major and minor conformers of 0.802 (3) and 0.198 (3), respectively. The bond distances show no unexpected values; in particular, the C—N and C—C distances for the nitrile unit (Table 1) are typical, where the mean values (Allen *et al.*, 1987) are 1.136 and 1.427 Å, respectively. The bond angles at C2 deviate significantly from regular trigonal geometry, while the C—C—N fragment is not quite linear. While both orientations of the thiophene unit are almost coplanar with the central C═C double bond, the 4-chlorophenyl ring is twisted well out of this plane. Thus, the dihedral angles between the plane of the central space unit C22—C2═C3—C31 and the planes of the adjacent rings are as follows: thiophene ring (major orientation) 5.7 (2)°, thiophene ring (minor orientation) 4.9 (5)° and aryl ring 38.2 (2)°.

The molecules are linked by a single C—H···N hydrogen bond (Table 2) into C(5) (Bernstein *et al.*, 1995) chains generated by the *n*-glide planes and running parallel to the [10$\bar{1}$] direction (Fig. 2). Two such chains, related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent chains: in particular π–π stacking interactions, and C—H···π(arene) and C—H···π(thiophene) hydrogen bonds are all absent.

Experimental

A solution of 2-thiopheneacetonitrile (2.87 mmol) and potassium *tert*-butoxide (0.53 mmol) in anhydrous ethanol (3 ml) was stirred at

organic papers

room temperature for 15 min; a solution of 4-chlorobenzaldehyde (2.87 mmol) in anhydrous ethanol (3 ml) was then added. The resulting precipitate was collected by filtration, washed with ethanol, dried and finally crystallized from dimethylformamide to give yellow crystals suitable for single-crystal X-ray diffraction.

Crystal data

$C_{13}H_8ClNS$	$D_x = 1.453$ Mg m^{-3}
$M_r = 245.72$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2552
$a = 3.8142$ (2) Å	reflections
$b = 23.6852$ (8) Å	$\theta = 3.4$–27.5°
$c = 12.5319$ (5) Å	$\mu = 0.49$ mm^{-1}
$\beta = 97.2160$ (16)°	$T = 120$ (2) K
$V = 1123.17$ (8) Å^3	Block, yellow
$Z = 4$	$0.30 \times 0.20 \times 0.12$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer	2552 independent reflections
	2132 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan ($SADABS$; Sheldrick, 2003)	$\theta_{max} = 27.5$°
	$h = -4 \rightarrow 4$
$T_{min} = 0.866$, $T_{max} = 0.943$	$k = -30 \rightarrow 25$
11691 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.9116P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2552 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -1.02$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.147 (3)	C2—C3	1.346 (3)
C1—C2	1.448 (3)		
N1—C1—C2	176.2 (2)	C1—C2—C22	114.88 (15)
C1—C2—C3	120.69 (17)	C3—C2—C22	124.33 (15)
C3—C2—C22—S21	4.2 (3)	C2—C3—C31—C32	37.9 (3)
C3—C2—C22—S21A	−177.4 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N1^i	0.95	2.53	3.438 (2)	161

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. It was apparent at an early stage that the thiophene unit was disordered over two sets of sites related by a rotation of 180° about the exocyclic C—C bond; the geometry of the minor orientation was restrained to match that of the major orientation, and the anisotropic displacement parameters for corresponding atoms in the two orientations were constrained to be equal. The deepest hole in the difference map is located 0.33 Å from the minor-occupancy atom S21A.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure:
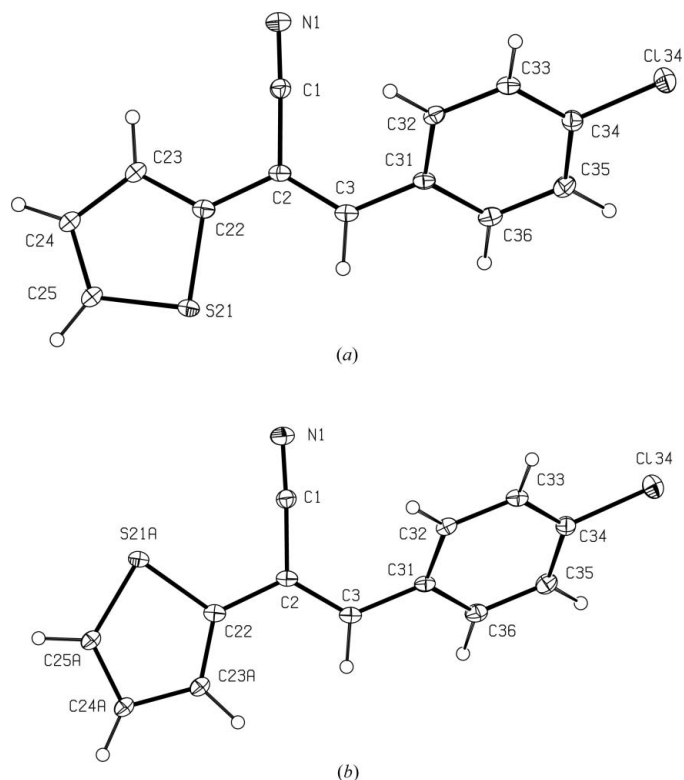

Figure 1
The molecule of compound (I), showing the atom-labelling scheme for (*a*) the major conformer and (*b*) the minor conformer. Displacement ellipsoids are drawn at the 30% probability level.
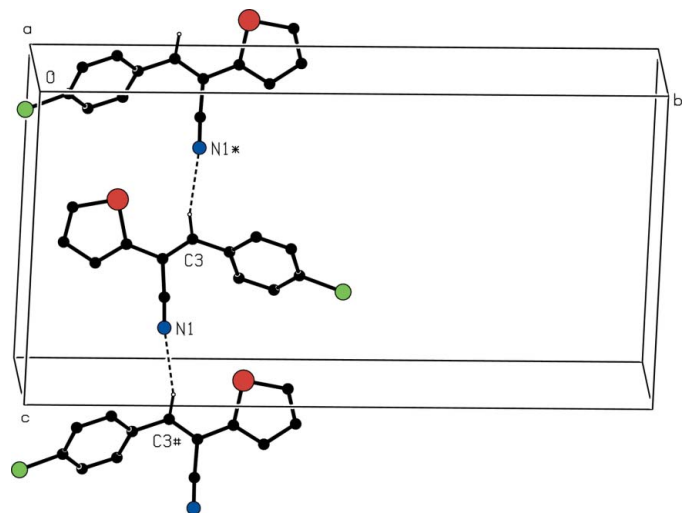
Figure 2
Part of the crystal structure of compound (I), showing the formation of a $C(5)$ chain along [10$\bar{1}$] generated by the *n*-glide plane at $y = 0.25$. For the sake of clarity, H atoms not involved in the motif shown have been omitted, and only the major conformer is shown. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$) and ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), respectively.

OSCAIL (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

References

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.

Bernstein, J. Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307-326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

(*E*)-3-(4-Chlorophenyl)-2-(2-thienyl)acrylonitrile: chains built from C—H···N hydrogen bonds

Debora Cobo, Jairo Quiroga, Justo Cobo, John N. Low and Christopher Glidewell

(*E*)-3-(4-Chlorophenyl)-2-(2-thienyl)acrylonitrile

Crystal data

$C_{13}H_8ClNS$	$F(000) = 504$
$M_r = 245.72$	$D_x = 1.453$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2552 reflections
$a = 3.8142$ (2) Å	$\theta = 3.4$–$27.5°$
$b = 23.6852$ (8) Å	$\mu = 0.49$ mm^{-1}
$c = 12.5319$ (5) Å	$T = 120$ K
$\beta = 97.2160$ (16)°	Needle, yellow
$V = 1123.17$ (8) Å^3	$0.30 \times 0.20 \times 0.12$ mm
$Z = 4$	

Data collection

Bruker–Nonius 95mm CCD camera on κ goniostat diffractometer	$T_{min} = 0.866$, $T_{max} = 0.943$
	11691 measured reflections
	2552 independent reflections
Radiation source: Bruker-Nonius FR91 rotating anode	2132 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.033$
Detector resolution: 9.091 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
φ and ω scans	$h = -4 \rightarrow 4$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$k = -30 \rightarrow 25$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.094$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.9116P]$ where $P = (F_o^2 + 2F_c^2)/3$
2552 reflections	
145 parameters	$(\Delta/\sigma)_{max} = 0.001$
10 restraints	$\Delta\rho_{max} = 0.55$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -1.02$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$	Occ. (<1)
Cl34	0.34216 (14)	0.50512 (2)	0.68406 (4)	0.02927 (16)	
S21	0.7644 (2)	0.14768 (3)	0.45758 (5)	0.0204 (2)	0.802 (3)
S21A	0.5909 (9)	0.10747 (8)	0.66549 (18)	0.0204 (2)	0.198 (3)
N1	0.3752 (5)	0.22435 (8)	0.80736 (14)	0.0314 (4)	
C1	0.4690 (5)	0.22378 (8)	0.72392 (15)	0.0219 (4)	
C2	0.5721 (5)	0.21992 (8)	0.61686 (14)	0.0187 (4)	
C3	0.5864 (5)	0.26641 (8)	0.55581 (15)	0.0209 (4)	
C22	0.6355 (5)	0.16265 (6)	0.58077 (9)	0.0197 (4)	
C23	0.5928 (8)	0.11359 (6)	0.63458 (17)	0.0224 (4)	0.802 (3)
C24	0.6664 (9)	0.06308 (5)	0.57986 (16)	0.0224 (4)	0.802 (3)
C25	0.7582 (9)	0.07648 (5)	0.48227 (16)	0.0224 (4)	0.802 (3)
C23A	0.748 (5)	0.1471 (4)	0.4861 (7)	0.0224 (4)	0.198 (3)
C24A	0.773 (4)	0.0881 (4)	0.4667 (8)	0.0224 (4)	0.198 (3)
C25A	0.683 (4)	0.0664 (4)	0.5601 (7)	0.0224 (4)	0.198 (3)
C31	0.5370 (5)	0.32511 (8)	0.58827 (15)	0.0197 (4)	
C32	0.6649 (5)	0.34480 (8)	0.69114 (15)	0.0206 (4)	
C33	0.6102 (5)	0.40037 (8)	0.71952 (15)	0.0214 (4)	
C35	0.3042 (5)	0.41834 (9)	0.54241 (16)	0.0242 (4)	
C34	0.4250 (5)	0.43614 (8)	0.64543 (16)	0.0214 (4)	
C36	0.3651 (5)	0.36295 (9)	0.51405 (16)	0.0240 (4)	
H3	0.6335	0.2606	0.4840	0.025*	
H23	0.5187	0.1131	0.7042	0.027*	0.802 (3)
H24	0.6530	0.0259	0.6075	0.027*	0.802 (3)
H25	0.8142	0.0490	0.4319	0.027*	0.802 (3)
H23A	0.8073	0.1743	0.4356	0.027*	0.198 (3)
H24A	0.8360	0.0691	0.4051	0.027*	0.198 (3)
H25A	0.6705	0.0265	0.5671	0.027*	0.198 (3)
H32	0.7899	0.3199	0.7418	0.025*	
H33	0.6990	0.4138	0.7892	0.026*	
H35	0.1815	0.4436	0.4919	0.029*	
H36	0.2885	0.3506	0.4428	0.029*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl34	0.0301 (3)	0.0250 (3)	0.0326 (3)	0.0034 (2)	0.0032 (2)	−0.0020 (2)
S21	0.0216 (3)	0.0241 (3)	0.0164 (4)	0.0006 (2)	0.0054 (3)	−0.0021 (3)
S21A	0.0216 (3)	0.0241 (3)	0.0164 (4)	0.0006 (2)	0.0054 (3)	−0.0021 (3)
N1	0.0406 (11)	0.0332 (10)	0.0224 (9)	0.0029 (8)	0.0122 (8)	0.0017 (8)
C1	0.0225 (10)	0.0228 (10)	0.0208 (10)	0.0023 (8)	0.0045 (8)	0.0016 (8)
C2	0.0154 (9)	0.0268 (10)	0.0140 (8)	0.0014 (7)	0.0021 (7)	−0.0008 (7)
C3	0.0192 (9)	0.0284 (10)	0.0153 (9)	−0.0007 (8)	0.0037 (7)	−0.0017 (8)
C22	0.0147 (9)	0.0274 (10)	0.0165 (9)	0.0015 (7)	0.0004 (7)	−0.0010 (8)
C23	0.0249 (7)	0.0234 (7)	0.0188 (8)	−0.0008 (6)	0.0026 (7)	0.0052 (6)
C24	0.0249 (7)	0.0234 (7)	0.0188 (8)	−0.0008 (6)	0.0026 (7)	0.0052 (6)

C25	0.0249 (7)	0.0234 (7)	0.0188 (8)	−0.0008 (6)	0.0026 (7)	0.0052 (6)
C23A	0.0249 (7)	0.0234 (7)	0.0188 (8)	−0.0008 (6)	0.0026 (7)	0.0052 (6)
C24A	0.0249 (7)	0.0234 (7)	0.0188 (8)	−0.0008 (6)	0.0026 (7)	0.0052 (6)
C25A	0.0249 (7)	0.0234 (7)	0.0188 (8)	−0.0008 (6)	0.0026 (7)	0.0052 (6)
C31	0.0174 (9)	0.0253 (10)	0.0174 (9)	−0.0009 (7)	0.0057 (7)	−0.0001 (8)
C32	0.0187 (9)	0.0254 (10)	0.0181 (9)	0.0008 (8)	0.0038 (7)	0.0044 (8)
C33	0.0187 (9)	0.0284 (10)	0.0175 (9)	−0.0018 (8)	0.0039 (7)	−0.0011 (8)
C35	0.0229 (10)	0.0275 (11)	0.0218 (9)	0.0011 (8)	0.0009 (8)	0.0054 (8)
C34	0.0178 (9)	0.0224 (10)	0.0248 (10)	0.0001 (7)	0.0062 (8)	0.0004 (8)
C36	0.0256 (10)	0.0296 (11)	0.0166 (9)	−0.0018 (8)	0.0018 (8)	0.0008 (8)

Geometric parameters (Å, º)

C1—N1	1.147 (3)	C24A—C25A	1.3622 (11)
C1—C2	1.448 (3)	C24A—H24A	0.95
C2—C3	1.346 (3)	C25A—H25A	0.95
C2—C22	1.460 (2)	C3—C31	1.467 (3)
C22—C23A	1.3620 (11)	C3—H3	0.95
C22—C23	1.3635 (10)	C31—C36	1.395 (3)
C22—S21A	1.7058 (10)	C31—C32	1.400 (3)
C22—S21	1.7151 (9)	C32—C33	1.386 (3)
S21—C25	1.7153	C32—H32	0.95
C23—C24	1.4244 (10)	C33—C34	1.383 (3)
C23—H23	0.95	C33—H33	0.95
C24—C25	1.3516	C35—C34	1.381 (3)
C24—H24	0.95	C35—C36	1.386 (3)
C25—H25	0.95	C35—H35	0.95
S21A—C25A	1.7125 (11)	C34—Cl34	1.744 (2)
C23A—C24A	1.4240 (11)	C36—H36	0.95
C23A—H23A	0.95		
N1—C1—C2	176.2 (2)	C25A—C24A—H24A	129.4
C1—C2—C3	120.69 (17)	C23A—C24A—H24A	129.4
C1—C2—C22	114.88 (15)	C24A—C25A—S21A	123.1 (8)
C3—C2—C22	124.33 (15)	C24A—C25A—H25A	118.5
C23A—C22—C23	105.7 (5)	S21A—C25A—H25A	118.5
C23A—C22—C2	127.1 (5)	C2—C3—C31	127.00 (17)
C23—C22—C2	127.15 (12)	C2—C3—H3	116.5
C23A—C22—S21A	113.7 (5)	C31—C3—H3	116.5
C2—C22—S21A	119.07 (12)	C36—C31—C32	118.72 (18)
C23—C22—S21	109.55 (13)	C36—C31—C3	119.34 (17)
C2—C22—S21	123.26 (11)	C32—C31—C3	121.92 (17)
S21A—C22—S21	117.65 (12)	C33—C32—C31	120.42 (18)
C22—S21—C25	91.65 (8)	C33—C32—H32	119.8
C22—C23—C24	115.77 (15)	C31—C32—H32	119.8
C22—C23—H23	122.1	C34—C33—C32	119.33 (18)
C24—C23—H23	122.1	C34—C33—H33	120.3
C25—C24—C23	109.12 (9)	C32—C33—H33	120.3

C25—C24—H24	125.4	C34—C35—C36	118.79 (18)
C23—C24—H24	125.4	C34—C35—H35	120.6
C24—C25—S21	113.90 (6)	C36—C35—H35	120.6
C24—C25—H25	123.0	C35—C34—C33	121.51 (18)
S21—C25—H25	123.0	C35—C34—Cl34	119.64 (15)
C22—S21A—C25A	84.8 (4)	C33—C34—Cl34	118.84 (15)
C22—C23A—C24A	116.7 (8)	C35—C36—C31	121.13 (18)
C22—C23A—H23A	121.7	C35—C36—H36	119.4
C24A—C23A—H23A	121.7	C31—C36—H36	119.4
C25A—C24A—C23A	101.2 (9)		
C3—C2—C22—C23A	6.4 (10)	S21—C22—S21A—C25A	−4.4 (7)
C1—C2—C22—C23A	−177.1 (10)	C23—C22—C23A—C24A	2.9 (17)
C3—C2—C22—C23	−173.3 (2)	C2—C22—C23A—C24A	−176.8 (11)
C1—C2—C22—C23	3.2 (3)	S21A—C22—C23A—C24A	6.8 (19)
C1—C2—C22—S21A	−1.0 (3)	S21—C22—C23A—C24A	−151 (11)
C3—C2—C22—S21	4.2 (3)	C22—C23A—C24A—C25A	−2.9 (17)
C3—C2—C22—S21A	−177.4 (2)	C23A—C24A—C25A—S21A	−2.3 (13)
C1—C2—C22—S21	−179.31 (14)	C22—S21A—C25A—C24A	5.1 (9)
C23A—C22—S21—C25	26 (10)	C1—C2—C3—C31	5.9 (3)
C23—C22—S21—C25	−0.2 (2)	C22—C2—C3—C31	−177.85 (18)
C2—C22—S21—C25	−178.08 (19)	C2—C3—C31—C36	−143.7 (2)
S21A—C22—S21—C25	3.55 (17)	C2—C3—C31—C32	37.9 (3)
C23A—C22—C23—C24	−1.1 (8)	C36—C31—C32—C33	2.2 (3)
C2—C22—C23—C24	178.7 (2)	C3—C31—C32—C33	−179.30 (17)
S21A—C22—C23—C24	−157.0 (16)	C31—C32—C33—C34	0.6 (3)
S21—C22—C23—C24	0.9 (4)	C36—C35—C34—C33	1.3 (3)
C22—C23—C24—C25	−1.3 (3)	C36—C35—C34—Cl34	−178.44 (15)
C23—C24—C25—S21	1.13 (13)	C32—C33—C34—C35	−2.4 (3)
C22—S21—C25—C24	−0.59 (9)	C32—C33—C34—Cl34	177.34 (14)
C23A—C22—S21A—C25A	−6.2 (12)	C34—C35—C36—C31	1.6 (3)
C23—C22—S21A—C25A	19.2 (12)	C32—C31—C36—C35	−3.4 (3)
C2—C22—S21A—C25A	177.2 (6)	C3—C31—C36—C35	178.13 (18)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N1[i]	0.95	2.53	3.438 (2)	161

Symmetry code: (i) x+1/2, −y+1/2, z−1/2.