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(E)-3-(2,3,4,5,6-Pentafluorostyryl)-thiopheneSébastien Clément,^a Olivier Coulembier,^b Franck Meyer,^b Matthias Zeller^c and Christophe M. L. Vande Velde^{d*}

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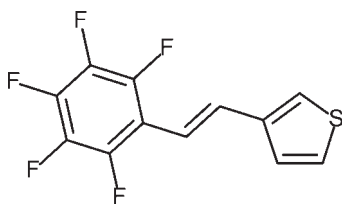
Received 28 February 2010; accepted 17 March 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.086; wR factor = 0.186; data-to-parameter ratio = 18.7.

The reaction of thiophene-3-carboxaldehyde and perfluorobenzyltriphenylphosphonium bromide in the presence of sodium hydride gave the title compound, $\text{C}_{12}\text{H}_5\text{F}_5\text{S}$, in 70% yield. The thiophene and perfluorophenyl groups form a dihedral angle of 5.4 (2)°. The structure is characterized by a head-to-tail organization in a columnar arrangement due to π - π interactions between the thiophene and pentafluorophenyl rings with centroid-centroid distances in the range 3.698 (2)- 3.802 (2) Å.

Related literature

For electronic materials with high conductivity due to complementary groups, see: Yamamoto *et al.* (2009); Hoeben *et al.* (2005). For a bottom-up approach to rational design of electronic materials, see: Lu & Lieber (2007). For thiophene derivatives used in solar cells or oLEDs, see: Osaka & McCullough (2008); Mishra *et al.* (2009). For the structure of 2,5-dibromo-3-(2,3,4,5,6-pentafluorostyryl)thiophene, see: Clément *et al.* (2010).



Experimental

Crystal data

$\text{C}_{12}\text{H}_5\text{F}_5\text{S}$
 $M_r = 276.22$
 Monoclinic, $P2_1/c$
 $a = 5.8097$ (15) Å
 $b = 24.581$ (6) Å
 $c = 7.3224$ (18) Å
 $\beta = 94.953$ (4)°

$V = 1041.8$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.36$ mm⁻¹
 $T = 100$ K
 $0.31 \times 0.21 \times 0.05$ mm

Data collection

Bruker SMART APEX area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.637$, $T_{\max} = 0.746$

5781 measured reflections
 3056 independent reflections
 2513 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.086$
 $wR(F^2) = 0.186$
 $S = 1.21$
 3056 reflections

163 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.73$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.58$ e Å⁻³

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2740).

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supporting information

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(E)-3-(2,3,4,5,6-Pentafluorostyryl)thiophene

Sébastien Clément, Olivier Coulembier, Franck Meyer, Matthias Zeller and Christophe M. L. Vande Velde

S1. Comment

The development of new electronic devices is currently performed through the engineering of organic electronic materials composed of π -conjugated polymers. The incorporation of unsaturated systems with complementary groups takes advantage of high electronic conductivity supplemented by a supramolecular organization at the nanoscale (Yamamoto *et al.*, 2009, Hoeben *et al.*, 2005). Therefore, the rational design of new building blocks has arisen as an essential pathway to fulfill the bottom-up approach (Lu & Lieber, 2007). As a preliminary milestone, we report the structure of (E)-3-(perfluorostyryl)thiophene (**1**), an intermediate aiming at the preparation of polythiophenes with self-complementary groups. These thiophene derivatives could find applications in electronic devices with solar cell or organic light emitting diode (oLED) properties (Osaka & McCullough, 2008; Mishra *et al.*, 2009). The structure of **1** is shown in Figure 1.

(E)-3-(perfluorostyryl)thiophene crystallizes in the space group $P2_1/c$ and exhibits an almost planar molecular geometry - a slight rotation of $5.4 (2)^\circ$ between the L.S. planes of the thiophene and perfluorophenyl groups is observed. The π - π stacking between the aromatic rings arranges the unsaturated compound in alternating orientations within one column due to opposite dipole moments. The distance between the thiophene-perfluorophenyl centres for successive pairs is in the range $3.698 (2)$ - $3.802 (2)$ Å.

The orientation of the double bonds of successive molecules in the columns is perpendicular, in contrast with 2,5-dibromo-3-(perfluorostyryl)thiophene (Clément *et al.*, 2010), where they are parallel, due to a different arrangement of the molecules with regard to the symmetry elements in the cell, although the space group is identical.

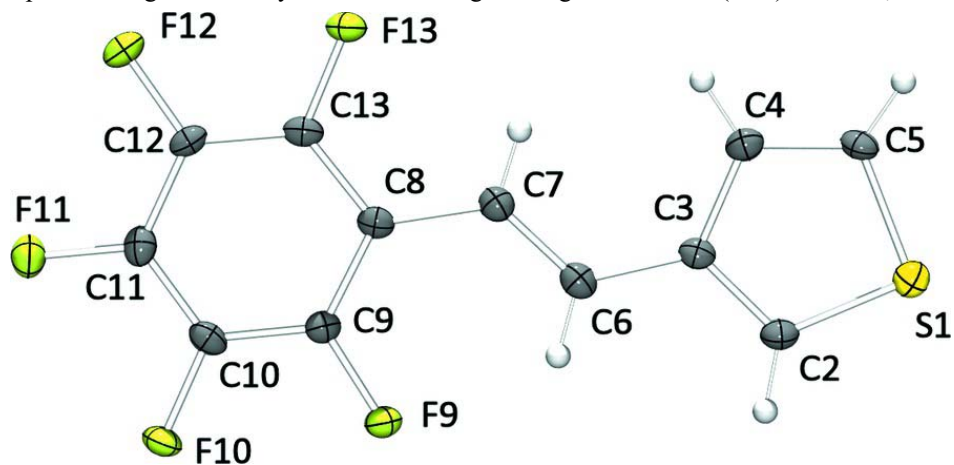
Neighboring columns in **1** are closely packed, with the molecules in neighboring columns shifted up or down by approximately half the intermolecular distance. Between columns, there are also short S—S contacts and 2 F—F interactions. For a list of short contacts, see the "Geometric parameters" table.

S2. Experimental

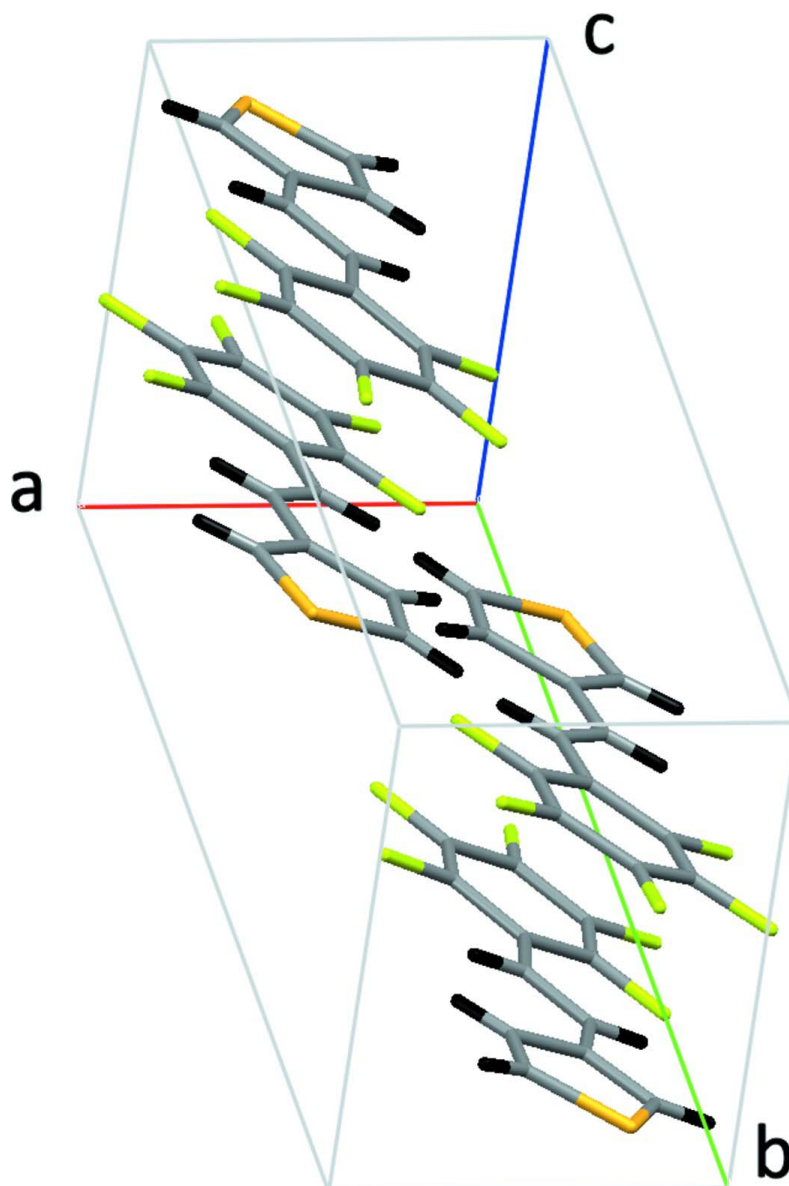
Perfluorobenzyltriphenylphosphonium bromide (800 mg, 1.53 mmol) and sodium hydride (80 mg, 2 mmol) are stirred in 5 ml of DMF during 15 min. Then, thiophenecarboxaldehyde (0.13 ml, 1.53 mmol) is added and the mixture is heated at 50°C . After 16 h, the reaction is hydrolyzed and the solid residue is filtered off. The compound is purified by chromatography on silica gel with hexane/ CH_2Cl_2 (4:1) to give (E)-3-(perfluorostyryl)thiophene in 70% yield. Crystals of **1** were obtained by slow evaporation of a saturated dichloromethane solution. ^1H NMR (300 MHz, CDCl_3): δ 7.43 (d, 1 H, $\text{CH}=\text{}$, $^3J_{\text{H}-\text{H}} = 16.5$, vinyl-*H*), 7.37 (m, 3 H, 3 H_{ar}), 6.82 (d, 1 H, $\text{CH}=\text{}$, $^3J_{\text{H}-\text{H}} = 16.5$, vinyl-*H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 145.7 (C-8, C-12), 142.3 (C-10), 138.8 (C-9, C-11), 130.5, 126.1, 124.3, 123.8 (C-1, C-2, C-3, C-4, C-5, C-6); 111.8 (C-7); ^{19}F NMR (CDCl_3): δ -140.9 (2 F, F_{ortho}), -154.4 (1 F, F_{para}), -162.9 (2 F, F_{meta}); ESI-MS (m/z): 276(100, M^+), 257 (92, $\text{M}^+ - \text{F}$).

S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with $d(\text{C-H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

The structure of 1 with displacement ellipsoids drawn at the 50% probability level.

**Figure 2**

A view of the packing of **1**.

(*E*)-3-(2,3,4,5,6-Pentafluorostyryl)thiophene

Crystal data

$C_{12}H_5F_5S$

$M_r = 276.22$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 5.8097\ (15)\ \text{\AA}$

$b = 24.581\ (6)\ \text{\AA}$

$c = 7.3224\ (18)\ \text{\AA}$

$\beta = 94.953\ (4)^\circ$

$V = 1041.8\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 552$

$D_x = 1.761\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2814 reflections

$\theta = 2.9\text{--}31.1^\circ$

$\mu = 0.36\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Plate, colourless

$0.31 \times 0.21 \times 0.05\ \text{mm}$

Data collection

Bruker SMART APEX area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2008)
 $T_{\min} = 0.637$, $T_{\max} = 0.746$

5781 measured reflections
3056 independent reflections
2513 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 31.2^\circ$, $\theta_{\text{min}} = 1.7^\circ$
 $h = -5 \rightarrow 8$
 $k = -25 \rightarrow 35$
 $l = -10 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.086$
 $wR(F^2) = 0.186$
 $S = 1.21$
3056 reflections
163 parameters
0 restraints
3 constraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0193P)^2 + 5.9694P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.73 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.58 \text{ e } \text{\AA}^{-3}$

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.22542 (18)	0.54717 (4)	0.56342 (15)	0.0219 (2)
F9	-0.0433 (4)	0.80297 (10)	0.4285 (3)	0.0200 (5)
F10	-0.0888 (4)	0.91035 (10)	0.4229 (3)	0.0211 (5)
F12	0.6511 (4)	0.93050 (10)	0.7310 (3)	0.0218 (5)
F13	0.6987 (4)	0.82233 (10)	0.7475 (3)	0.0205 (5)
F11	0.2579 (5)	0.97589 (10)	0.5694 (4)	0.0244 (5)
C4	0.4895 (7)	0.62804 (17)	0.6462 (5)	0.0181 (7)
H4	0.6168	0.6489	0.6883	0.022*
C13	0.5023 (6)	0.84305 (17)	0.6626 (5)	0.0160 (7)
C3	0.2770 (6)	0.65098 (16)	0.5703 (5)	0.0154 (7)
C8	0.3328 (6)	0.80732 (16)	0.5885 (5)	0.0154 (7)
C12	0.4805 (6)	0.89877 (16)	0.6571 (5)	0.0162 (7)
C11	0.2808 (7)	0.92176 (16)	0.5756 (5)	0.0188 (8)
C9	0.1336 (7)	0.83262 (16)	0.5062 (5)	0.0161 (7)
C6	0.2239 (7)	0.70861 (16)	0.5483 (5)	0.0183 (7)
H6	0.0793	0.7182	0.4934	0.022*

C10	0.1082 (7)	0.88846 (17)	0.5015 (5)	0.0185 (8)
C7	0.3708 (7)	0.74870 (16)	0.6022 (5)	0.0178 (7)
H7	0.5149	0.7378	0.6548	0.021*
C2	0.1186 (7)	0.61079 (17)	0.5195 (5)	0.0179 (7)
H2	-0.0301	0.6177	0.4670	0.022*
C5	0.4880 (7)	0.57227 (17)	0.6512 (5)	0.0177 (7)
H5	0.6123	0.5509	0.6961	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0228 (5)	0.0195 (5)	0.0229 (5)	-0.0009 (4)	-0.0003 (4)	-0.0008 (4)
F9	0.0164 (11)	0.0213 (12)	0.0216 (12)	-0.0008 (9)	-0.0019 (9)	-0.0022 (9)
F10	0.0163 (11)	0.0242 (13)	0.0219 (12)	0.0053 (9)	-0.0039 (9)	0.0004 (10)
F12	0.0203 (11)	0.0239 (13)	0.0210 (12)	-0.0070 (10)	-0.0004 (9)	-0.0039 (10)
F13	0.0150 (10)	0.0257 (13)	0.0199 (12)	0.0008 (9)	-0.0033 (9)	-0.0005 (9)
F11	0.0309 (13)	0.0179 (12)	0.0240 (13)	0.0007 (10)	0.0003 (10)	-0.0014 (10)
C4	0.0169 (16)	0.0215 (19)	0.0159 (16)	-0.0013 (14)	0.0018 (13)	-0.0014 (15)
C13	0.0131 (15)	0.024 (2)	0.0107 (15)	0.0005 (14)	0.0010 (12)	0.0007 (14)
C3	0.0158 (16)	0.0196 (19)	0.0107 (15)	0.0011 (13)	0.0010 (13)	-0.0002 (13)
C8	0.0136 (16)	0.0198 (19)	0.0133 (16)	0.0009 (13)	0.0035 (13)	0.0000 (14)
C12	0.0150 (16)	0.0206 (19)	0.0129 (16)	-0.0048 (14)	0.0013 (13)	-0.0023 (14)
C11	0.026 (2)	0.0166 (19)	0.0137 (17)	0.0001 (15)	0.0035 (15)	-0.0014 (14)
C9	0.0158 (16)	0.0185 (19)	0.0141 (16)	-0.0014 (14)	0.0013 (13)	0.0011 (14)
C6	0.0206 (17)	0.0199 (19)	0.0148 (17)	0.0032 (15)	0.0028 (13)	0.0011 (14)
C10	0.0163 (17)	0.023 (2)	0.0170 (17)	0.0047 (14)	0.0036 (14)	0.0018 (15)
C7	0.0201 (17)	0.0189 (19)	0.0144 (16)	0.0018 (14)	0.0010 (14)	-0.0002 (14)
C2	0.0156 (17)	0.022 (2)	0.0152 (16)	-0.0009 (14)	-0.0018 (13)	-0.0003 (14)
C5	0.0170 (17)	0.022 (2)	0.0133 (16)	0.0035 (14)	-0.0020 (13)	-0.0002 (14)

Geometric parameters (Å, °)

S1—C2	1.703 (4)	C3—C2	1.380 (5)
S1—C5	1.718 (4)	C3—C6	1.456 (5)
F9—C9	1.345 (4)	C8—C9	1.403 (5)
F10—C10	1.348 (4)	C8—C7	1.460 (5)
F12—C12	1.338 (4)	C12—C11	1.379 (6)
F13—C13	1.350 (4)	C11—C10	1.370 (6)
F11—C11	1.338 (5)	C9—C10	1.381 (6)
C4—C5	1.371 (6)	C6—C7	1.341 (6)
C4—C3	1.425 (5)	C6—H6	0.9300
C4—H4	0.9300	C7—H7	0.9300
C13—C12	1.376 (6)	C2—H2	0.9300
C13—C8	1.394 (5)	C5—H5	0.9300
S1...S1 ⁱ	3.5611 (17)	F10...H5 ⁱⁱⁱ	2.49
F9...F13 ⁱⁱ	2.921 (3)	H5...F11 ^{iv}	2.59
F10...F12 ⁱⁱ	2.865 (3)	H2...F13 ⁱⁱⁱ	2.61

F10...C12 ⁱⁱ	3.166 (4)	C3...C9 ^v	3.392 (5)
F10...C5 ⁱⁱⁱ	3.056 (5)	C3...C13 ^{vi}	3.365 (5)
C2—S1—C5	92.19 (19)	F9—C9—C10	116.9 (3)
C5—C4—C3	113.5 (4)	F9—C9—C8	120.9 (3)
C5—C4—H4	123.3	C10—C9—C8	122.3 (4)
C3—C4—H4	123.3	C7—C6—C3	124.0 (4)
F13—C13—C12	117.4 (3)	C7—C6—H6	118.0
F13—C13—C8	118.8 (4)	C3—C6—H6	118.0
C12—C13—C8	123.7 (4)	F10—C10—C11	119.8 (4)
C2—C3—C4	110.9 (4)	F10—C10—C9	119.5 (4)
C2—C3—C6	122.5 (4)	C11—C10—C9	120.7 (4)
C4—C3—C6	126.6 (4)	C6—C7—C8	128.1 (4)
C13—C8—C9	114.6 (4)	C6—C7—H7	116.0
C13—C8—C7	119.8 (3)	C8—C7—H7	116.0
C9—C8—C7	125.5 (4)	C3—C2—S1	112.5 (3)
F12—C12—C13	120.3 (3)	C3—C2—H2	123.7
F12—C12—C11	120.2 (4)	S1—C2—H2	123.7
C13—C12—C11	119.5 (4)	C4—C5—S1	110.9 (3)
F11—C11—C10	120.9 (4)	C4—C5—H5	124.6
F11—C11—C12	120.0 (4)	S1—C5—H5	124.6
C10—C11—C12	119.1 (4)		
C5—C4—C3—C2	0.0 (5)	C2—C3—C6—C7	177.5 (4)
C5—C4—C3—C6	179.3 (4)	C4—C3—C6—C7	-1.7 (6)
F13—C13—C8—C9	178.9 (3)	F11—C11—C10—F10	-0.7 (6)
C12—C13—C8—C9	-0.1 (6)	C12—C11—C10—F10	179.4 (3)
F13—C13—C8—C7	-0.6 (5)	F11—C11—C10—C9	179.2 (4)
C12—C13—C8—C7	-179.6 (4)	C12—C11—C10—C9	-0.6 (6)
F13—C13—C12—F12	1.1 (5)	F9—C9—C10—F10	0.7 (5)
C8—C13—C12—F12	-179.9 (3)	C8—C9—C10—F10	-179.0 (3)
F13—C13—C12—C11	-178.5 (3)	F9—C9—C10—C11	-179.3 (3)
C8—C13—C12—C11	0.5 (6)	C8—C9—C10—C11	1.1 (6)
F12—C12—C11—F11	0.4 (6)	C3—C6—C7—C8	-179.1 (4)
C13—C12—C11—F11	-180.0 (4)	C13—C8—C7—C6	176.1 (4)
F12—C12—C11—C10	-179.7 (4)	C9—C8—C7—C6	-3.3 (7)
C13—C12—C11—C10	-0.1 (6)	C4—C3—C2—S1	0.1 (4)
C13—C8—C9—F9	179.7 (3)	C6—C3—C2—S1	-179.2 (3)
C7—C8—C9—F9	-0.9 (6)	C5—S1—C2—C3	-0.2 (3)
C13—C8—C9—C10	-0.7 (6)	C3—C4—C5—S1	-0.2 (4)
C7—C8—C9—C10	178.8 (4)	C2—S1—C5—C4	0.2 (3)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $x-1, -y+3/2, z-1/2$; (iv) $-x+1, y-1/2, -z+3/2$; (v) $x, -y+3/2, z+1/2$; (vi) $x, -y+3/2, z-1/2$.