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ISSN 2414-3146

The 2:1 charge-transfer complex of 4,6-dimethyldibenzothiophene and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane

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Received 15 December 2017
Accepted 12 January 2018

Edited by H. Ishida, Okayama University, Japan

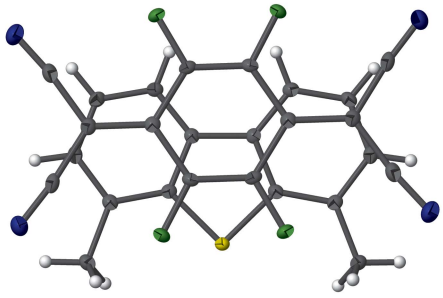
Keywords: crystal structure; charge-transfer complex; 4,6-dimethyldibenzothiophene; 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane.

CCDC reference: 1816551

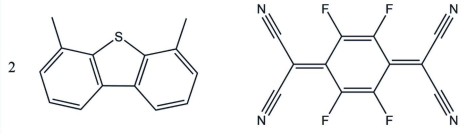
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $2C_{14}H_{12}S{\cdot}C_{12}N_4F_4$, was obtained by using 4,6-dimethyldibenzothiophene (DMDBT) as an electron donor and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (F_4TCNQ) as an electron acceptor. The asymmetric unit consists of one DMDBT molecule and one half of an F_4TCNQ molecule, which lies on an inversion centre. In the crystal, the DMDBT and F_4TCNQ molecules form a 2:1 unit *via* a charge-transfer interaction, with a centroid–centroid distance of 3.3681 (15) Å between the five-membered ring of DMDBT and the six-membered ring of F_4TCNQ. An F···F contact [2.911 (1) Å] is also observed.

3D view



Chemical scheme



Structure description

4,6-Dimethyldibenzothiophene (DMDBT) is one of the sulfur compounds contained in light oil. Hydrodesulfurization is used to remove the sulfur compounds in light oil. However, DMDBT is difficult to desulfurize because the two methyl groups interfere with the reaction of hydrodesulfurization. Although Milenkovic *et al.* (1999) succeeded in desulfurizing from light oil by the formation of charge-transfer complexes using 2,4,5,7-tetranitro-9-fluorene (TNF) as an electron acceptor, the crystal structure of DMDBT–TNF was not determined. The crystal structures of DMDBT and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (F_4TCNQ) have been determined by Meille *et al.* (1996) and Krupskaya *et al.* (2015), respectively. In this study, we obtained a novel complex using DMDBT as a donor and F_4TCNQ as an acceptor, and determined the crystal structure.

The asymmetric unit consists of one DMDBT molecule and one half of an F_4TCNQ molecule, which lies on an inversion centre (Fig. 1). A donor–acceptor–donor 2:1 unit is

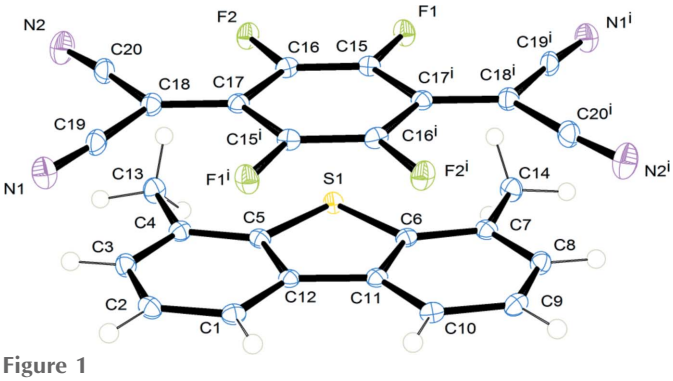


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres. [Symmetry code: (i) $-x+2, -y+1, -z$.]

formed *via* a charge-transfer interaction (Fig. 2); the centroid–centroid distance between the five-membered ring of DMDBT and the six-membered ring of F_4TCNQ is 3.3681 (15) Å. The units are stacked in a column along [110]. An F···F contact [2.911 (1) Å] is also observed (Fig. 3).

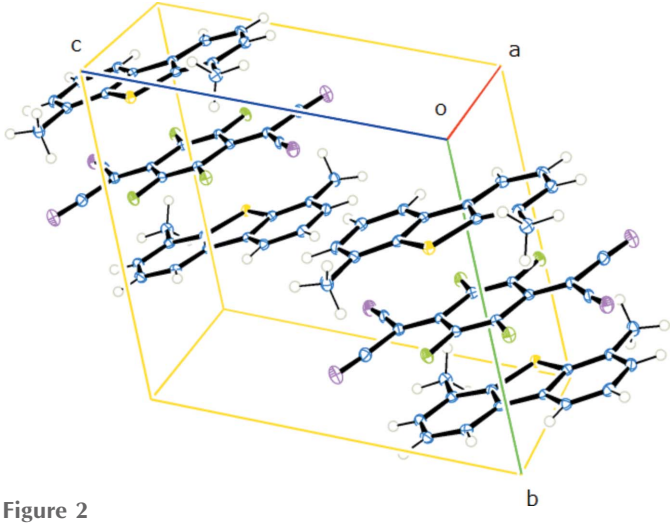


Figure 2
A packing diagram of the title compound, showing the 2:1 electron donor and acceptor unit.

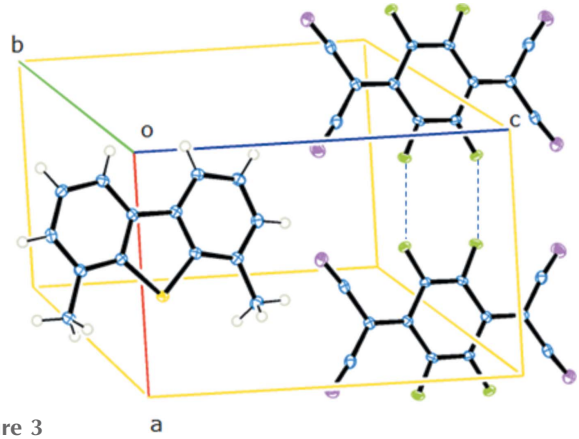


Figure 3
A packing diagram of the title compound, showing the F···F contacts as blue dashed lines.

Table 1
Experimental details.

Crystal data	
Chemical formula	$2C_{14}H_{12}S{\cdot}C_{12}F_4N_4$
M_r	700.77
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	93
a, b, c (Å)	7.570 (2), 10.206 (3), 11.549 (4)
α, β, γ (°)	113.400 (2), 90.010 (3), 108.607 (3)
V (Å^3)	767.8 (4)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.24
Crystal size (mm)	0.42 × 0.10 × 0.02
Data collection	
Diffractometer	Rigaku Saturn724
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.854, 0.995
No. of measured, independent and observed [$F^2 > 2\sigma(F^2)$] reflections	6222, 3311, 2887
R_{int}	0.021
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.644
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.091, 1.03
No. of reflections	3311
No. of parameters	228
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.25

Computer programs: *CrystalClear* (Rigaku, 2008), *SIR2014* (Burla *et al.*, 2012), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2016) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

The title complex was obtained by mixing an acetonitrile solution (3 ml) of DMDBT (2.2 mg) with an acetonitrile solution (2.5 ml) of F_4TCNQ (2.7 mg), and then concentrating the solution for one day. The obtained black complex showed new charge-transfer bands around 600 nm in the UV–vis absorption spectrum, which were not observed for the raw materials.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Funding information

This work was supported by JSPS KAKENHI grant No. JP17KT0100.

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full crystallographic data

IUCrData (2018). **3**, x180077 [https://doi.org/10.1107/S2414314618000779]

The 2:1 charge-transfer complex of 4,6-dimethyldibenzothiophene and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane

Takuya Fujii and Hideo Yamakado

Bis[6,10-dimethyl-8-thiatricyclo[7.4.0.0^{2,7}]trideca-1(9),2,4,6,10,12-hexaene] 2-[4-(dicyanomethylidene)-2,3,5,6-tetrafluorocyclohexa-2,5-dien-1-ylidene]propanedinitrile

Crystal data

$2C_{14}H_{12}S{\cdot}C_{12}F_4N_4$
M_r = 700.77
Triclinic, $P\overline{1}$
a = 7.570 (2) Å
b = 10.206 (3) Å
c = 11.549 (4) Å
α = 113.400 (2)°
β = 90.010 (3)°
γ = 108.607 (3)°
V = 767.8 (4) Å^3
Z = 1
$F(000)$ = 360.00
D_x = 1.516 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 2475 reflections
θ = 3.7–27.5°
μ = 0.24 mm^{-1}
T = 93 K
Prism, black
0.42 × 0.10 × 0.02 mm

Data collection

Rigaku Saturn724 diffractometer
Detector resolution: 28.445 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.854, T_{max} = 0.995
6222 measured reflections
3311 independent reflections
2887 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.021
θ_{max} = 27.3°, θ_{min} = 3.7°
h = −8→9
k = −13→13
l = −14→12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 1.03
3311 reflections
228 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.4352P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.50372 (5)	0.19776 (4)	0.00985 (3)	0.01267 (11)
F1	0.66794 (11)	0.46548 (10)	−0.11943 (8)	0.01555 (19)
F2	0.73704 (12)	0.60156 (10)	0.13100 (8)	0.0156 (2)
N1	1.37660 (19)	0.69718 (16)	0.40939 (13)	0.0196 (3)
N2	0.8594 (2)	0.75756 (17)	0.42387 (13)	0.0234 (3)
C1	1.0005 (2)	0.24541 (16)	0.16420 (14)	0.0134 (3)
H1	1.106198	0.219533	0.132407	0.016*
C2	1.0013 (2)	0.31783 (17)	0.29404 (14)	0.0144 (3)
H2	1.107384	0.340458	0.351784	0.017*
C3	0.8466 (2)	0.35811 (16)	0.34113 (14)	0.0149 (3)
H3	0.850956	0.408757	0.430689	0.018*
C4	0.6867 (2)	0.32626 (16)	0.26081 (14)	0.0135 (3)
C5	0.6874 (2)	0.25106 (16)	0.12964 (14)	0.0123 (3)
C6	0.6322 (2)	0.12100 (16)	−0.10872 (14)	0.0120 (3)
C7	0.5684 (2)	0.05155 (16)	−0.24017 (14)	0.0134 (3)
C8	0.6910 (2)	−0.00336 (16)	−0.31948 (14)	0.0150 (3)
H8	0.652923	−0.051750	−0.409160	0.018*
C9	0.8694 (2)	0.01070 (17)	−0.27078 (14)	0.0151 (3)
H9	0.949518	−0.027864	−0.327803	0.018*
C10	0.9300 (2)	0.08007 (16)	−0.14069 (14)	0.0134 (3)
H10	1.050959	0.089629	−0.108152	0.016*
C11	0.8102 (2)	0.13592 (16)	−0.05784 (14)	0.0119 (3)
C12	0.8422 (2)	0.21067 (15)	0.08018 (13)	0.0116 (3)
C13	0.5213 (2)	0.36983 (18)	0.31136 (15)	0.0174 (3)
H13A	0.514343	0.452297	0.290378	0.026*
H13B	0.536587	0.404189	0.404152	0.026*
H13C	0.405198	0.281435	0.272533	0.026*
C14	0.3773 (2)	0.03761 (17)	−0.29078 (15)	0.0167 (3)
H14A	0.371282	0.139434	−0.266854	0.025*
H14B	0.280501	−0.018362	−0.254580	0.025*
H14C	0.355357	−0.017344	−0.383911	0.025*
C15	0.83036 (19)	0.48166 (16)	−0.06107 (14)	0.0114 (3)
C16	0.86612 (19)	0.55144 (16)	0.06696 (14)	0.0117 (3)
C17	1.03840 (19)	0.57591 (15)	0.13883 (13)	0.0113 (3)
C18	1.0752 (2)	0.64812 (16)	0.26997 (14)	0.0131 (3)
C19	1.2464 (2)	0.67300 (16)	0.34279 (14)	0.0146 (3)

C20	0.9484 (2)	0.70676 (17)	0.35044 (14)	0.0156 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01041 (17)	0.01487 (18)	0.01270 (18)	0.00466 (13)	0.00217 (13)	0.00553 (13)
F1	0.0113 (4)	0.0217 (5)	0.0136 (4)	0.0073 (3)	−0.0004 (3)	0.0062 (4)
F2	0.0127 (4)	0.0201 (4)	0.0142 (4)	0.0091 (3)	0.0050 (3)	0.0048 (3)
N1	0.0190 (7)	0.0225 (7)	0.0150 (6)	0.0063 (5)	0.0002 (5)	0.0064 (5)
N2	0.0234 (7)	0.0268 (7)	0.0163 (7)	0.0101 (6)	0.0058 (6)	0.0045 (6)
C1	0.0128 (7)	0.0123 (7)	0.0163 (7)	0.0044 (5)	0.0037 (6)	0.0072 (6)
C2	0.0128 (7)	0.0155 (7)	0.0158 (7)	0.0039 (5)	0.0001 (5)	0.0081 (6)
C3	0.0173 (7)	0.0144 (7)	0.0123 (7)	0.0041 (6)	0.0026 (6)	0.0059 (6)
C4	0.0136 (7)	0.0123 (7)	0.0150 (7)	0.0039 (5)	0.0040 (5)	0.0067 (5)
C5	0.0113 (6)	0.0114 (6)	0.0145 (7)	0.0023 (5)	0.0014 (5)	0.0070 (5)
C6	0.0116 (6)	0.0093 (6)	0.0147 (7)	0.0024 (5)	0.0026 (5)	0.0057 (5)
C7	0.0132 (7)	0.0107 (7)	0.0153 (7)	0.0020 (5)	0.0012 (5)	0.0063 (5)
C8	0.0172 (7)	0.0127 (7)	0.0126 (7)	0.0036 (6)	0.0011 (6)	0.0040 (5)
C9	0.0154 (7)	0.0129 (7)	0.0163 (7)	0.0060 (6)	0.0046 (6)	0.0047 (6)
C10	0.0125 (7)	0.0119 (7)	0.0166 (7)	0.0045 (5)	0.0026 (5)	0.0065 (5)
C11	0.0123 (7)	0.0087 (6)	0.0139 (7)	0.0017 (5)	0.0014 (5)	0.0054 (5)
C12	0.0134 (7)	0.0093 (6)	0.0131 (7)	0.0034 (5)	0.0030 (5)	0.0061 (5)
C13	0.0156 (7)	0.0225 (8)	0.0156 (7)	0.0089 (6)	0.0051 (6)	0.0076 (6)
C14	0.0146 (7)	0.0174 (7)	0.0156 (7)	0.0042 (6)	−0.0007 (6)	0.0055 (6)
C15	0.0089 (6)	0.0115 (6)	0.0140 (7)	0.0032 (5)	0.0012 (5)	0.0059 (5)
C16	0.0101 (6)	0.0114 (6)	0.0148 (7)	0.0045 (5)	0.0049 (5)	0.0060 (5)
C17	0.0119 (7)	0.0096 (6)	0.0128 (7)	0.0028 (5)	0.0026 (5)	0.0056 (5)
C18	0.0138 (7)	0.0118 (7)	0.0122 (7)	0.0032 (5)	0.0024 (5)	0.0047 (5)
C19	0.0183 (7)	0.0134 (7)	0.0100 (7)	0.0040 (6)	0.0040 (6)	0.0040 (5)
C20	0.0166 (7)	0.0149 (7)	0.0119 (7)	0.0032 (6)	−0.0007 (6)	0.0041 (6)

Geometric parameters (Å, º)

S1—C5	1.7500 (15)	C8—C9	1.405 (2)
S1—C6	1.7520 (15)	C8—H8	0.9500
F1—C15	1.3322 (17)	C9—C10	1.384 (2)
F2—C16	1.3350 (15)	C9—H9	0.9500
N1—C19	1.148 (2)	C10—C11	1.4003 (19)
N2—C20	1.147 (2)	C10—H10	0.9500
C1—C2	1.383 (2)	C11—C12	1.448 (2)
C1—C12	1.400 (2)	C13—H13A	0.9800
C1—H1	0.9500	C13—H13B	0.9800
C2—C3	1.402 (2)	C13—H13C	0.9800
C2—H2	0.9500	C14—H14A	0.9800
C3—C4	1.393 (2)	C14—H14B	0.9800
C3—H3	0.9500	C14—H14C	0.9800
C4—C5	1.401 (2)	C15—C16	1.344 (2)
C4—C13	1.5015 (19)	C15—C17^{i}	1.4466 (19)

C5—C12	1.4105 (19)	C16—C17	1.442 (2)
C6—C7	1.402 (2)	C17—C18	1.377 (2)
C6—C11	1.408 (2)	C18—C20	1.438 (2)
C7—C8	1.393 (2)	C18—C19	1.439 (2)
C7—C14	1.502 (2)		

C5—S1—C6	91.18 (7)	C10—C11—C12	128.65 (13)
C2—C1—C12	119.20 (13)	C6—C11—C12	112.03 (12)
C2—C1—H1	120.4	C1—C12—C5	119.36 (13)
C12—C1—H1	120.4	C1—C12—C11	128.77 (13)
C1—C2—C3	120.50 (14)	C5—C12—C11	111.87 (13)
C1—C2—H2	119.7	C4—C13—H13A	109.5
C3—C2—H2	119.7	C4—C13—H13B	109.5
C4—C3—C2	122.11 (14)	H13A—C13—H13B	109.5
C4—C3—H3	118.9	C4—C13—H13C	109.5
C2—C3—H3	118.9	H13A—C13—H13C	109.5
C3—C4—C5	116.59 (13)	H13B—C13—H13C	109.5
C3—C4—C13	122.05 (13)	C7—C14—H14A	109.5
C5—C4—C13	121.35 (13)	C7—C14—H14B	109.5
C4—C5—C12	122.23 (13)	H14A—C14—H14B	109.5
C4—C5—S1	125.29 (11)	C7—C14—H14C	109.5
C12—C5—S1	112.48 (11)	H14A—C14—H14C	109.5
C7—C6—C11	122.66 (13)	H14B—C14—H14C	109.5
C7—C6—S1	124.90 (11)	F1—C15—C16	118.90 (12)
C11—C6—S1	112.45 (11)	F1—C15—C17^{i}	118.30 (12)
C8—C7—C6	116.35 (13)	C16—C15—C17^{i}	122.80 (13)
C8—C7—C14	122.58 (14)	F2—C16—C15	118.70 (13)
C6—C7—C14	121.07 (13)	F2—C16—C17	118.20 (12)
C7—C8—C9	121.94 (14)	C15—C16—C17	123.10 (13)
C7—C8—H8	119.0	C18—C17—C16	123.02 (13)
C9—C8—H8	119.0	C18—C17—C15^{i}	122.88 (13)
C10—C9—C8	120.80 (13)	C16—C17—C15^{i}	114.10 (13)
C10—C9—H9	119.6	C17—C18—C20	124.50 (13)
C8—C9—H9	119.6	C17—C18—C19	123.55 (13)
C9—C10—C11	118.93 (13)	C20—C18—C19	111.96 (13)
C9—C10—H10	120.5	N1—C19—C18	174.55 (15)
C11—C10—H10	120.5	N2—C20—C18	173.74 (16)
C10—C11—C6	119.32 (13)		

C12—C1—C2—C3	−0.9 (2)	C7—C6—C11—C12	−179.64 (12)
C1—C2—C3—C4	0.7 (2)	S1—C6—C11—C12	0.22 (15)
C2—C3—C4—C5	0.2 (2)	C2—C1—C12—C5	0.4 (2)
C2—C3—C4—C13	−179.84 (13)	C2—C1—C12—C11	−179.92 (13)
C3—C4—C5—C12	−0.7 (2)	C4—C5—C12—C1	0.5 (2)
C13—C4—C5—C12	179.28 (13)	S1—C5—C12—C1	−179.87 (11)
C3—C4—C5—S1	179.65 (11)	C4—C5—C12—C11	−179.28 (13)
C13—C4—C5—S1	−0.3 (2)	S1—C5—C12—C11	0.39 (15)
C6—S1—C5—C4	179.43 (13)	C10—C11—C12—C1	0.1 (2)

C6—S1—C5—C12	−0.22 (11)	C6—C11—C12—C1	179.90 (14)
C5—S1—C6—C7	179.85 (13)	C10—C11—C12—C5	179.81 (14)
C5—S1—C6—C11	0.00 (11)	C6—C11—C12—C5	−0.39 (17)
C11—C6—C7—C8	0.2 (2)	F1—C15—C16—F2	0.2 (2)
S1—C6—C7—C8	−179.66 (11)	C17^{i}—C15—C16—F2	179.72 (12)
C11—C6—C7—C14	179.91 (13)	F1—C15—C16—C17	−179.32 (12)
S1—C6—C7—C14	0.1 (2)	C17^{i}—C15—C16—C17	0.2 (2)
C6—C7—C8—C9	−0.4 (2)	F2—C16—C17—C18	0.1 (2)
C14—C7—C8—C9	179.90 (14)	C15—C16—C17—C18	179.65 (13)
C7—C8—C9—C10	0.2 (2)	F2—C16—C17—C15^{i}	−179.71 (11)
C8—C9—C10—C11	0.2 (2)	C15—C16—C17—C15^{i}	−0.2 (2)
C9—C10—C11—C6	−0.4 (2)	C16—C17—C18—C20	0.2 (2)
C9—C10—C11—C12	179.42 (14)	C15^{i}—C17—C18—C20	−179.97 (13)
C7—C6—C11—C10	0.2 (2)	C16—C17—C18—C19	179.89 (13)
S1—C6—C11—C10	−179.95 (11)	C15^{i}—C17—C18—C19	−0.3 (2)

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