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3,3,4,4,5,5-Hexafluoro-1,2-bis(5-formyl-2-*n*-heptyl-3-thienyl)cyclopent-1-ene: a new photochromic diarylethene compound

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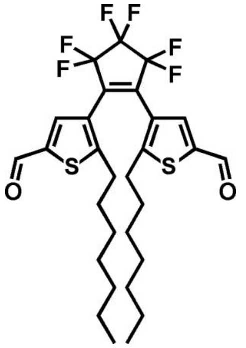
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.062; wR factor = 0.181; data-to-parameter ratio = 15.0.

The title compound, $C_{29}H_{34}F_6O_2S_2$, is a new C_2-symmetric photochromic dithienylethene. In the crystal structure, the molecule, lying on a crystallographic twofold rotation axis, adopts a photoactive antiparallel conformation. The distance between the two reactive thiophene ring C atoms is 3.743 (2) Å. The dihedral angle between the central cyclopentene ring and the adjacent thiophene rings is 43.4 (3)°.

Related literature

For related literature, see: Dürr & Bouas-Laurent (1990); Irie (2000); Kobatake *et al.* (2004); Pu *et al.* (2005); Tian & Yang (2004); Woodward & Hoffmann (1970); Zheng *et al.* (2007).



Experimental

Crystal data

$C_{29}H_{34}F_6O_2S_2$
M_r = 592.68
Monoclinic, $C2/c$
a = 20.929 (7) Å
b = 8.945 (3) Å
c = 17.232 (6) Å
β = 109.905 (4)°
V = 3033.4 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 291 (2) K
0.49 × 0.48 × 0.47 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\min}$ = 0.893, $T_{\max}$ = 0.897
10891 measured reflections
2816 independent reflections
2357 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.181
S = 1.05
2816 reflections
188 parameters
244 restraints
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\min}$ = −0.36 e Å^{-3}

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2194).

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supplementary materials

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3,3,4,4,5,5-Hexafluoro-1,2-bis(5-formyl-2-*n*-heptyl-3-thienyl)cyclopent-1-ene: a new photochromic diarylethene compound

S. Zhu, Y. Rao, G. Liu, Y. Xie and S. Pu

Comment

Organic photochromic materials have attracted much attention owing their potential application to optical memory media and optical switches (Dürr & Bouas-Laurent, 1990; Irie, 2000; Tian & Yang, 2004). In addition, dithienylethenes bearing formyl groups are of special interest because the formyl group can be easily functionalized by some simple reactions (Pu *et al.*, 2005; Zheng *et al.*, 2007). In this work, a new dithienylethene with formyl groups, (Ia), was synthesized and its structure presented.

The molecular structure of (Ia), Fig. 1 and Table 1, has 2-fold symmetry and packs in a photoactive anti-parallel conformation. In the hexafluorocyclopentene ring, the C13=C13^i double bond, 1.350 (5) Å, links the thiophene rings; i: $2 - x, y, -z + 1/2$.

The two heptyl groups are located on different sides of the double bond and this configuration is crucial to allow the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970). The dihedral angles between the hexafluorocyclopentene ring and the two thiophene rings is 47.37 (3)°. The distance between the two reactive C4 atoms, C4···C4^i, is 3.743 (2) Å. This distance indicates that the crystal can undergo photochromism because the photochromic reactivity of crystals depends on the distance between the reactive C atoms being less than 4.2 Å (Kobatake *et al.*, 2004).

Crystals of (Ib) show photochromism in accordance with the expected ring closure, to form (Ib); Scheme 2. Upon irradiation with 313 nm light, the colorless single crystals of (Ia) turned green quickly. When the green crystal was dissolved in hexane, the solution also showed a green color, with an absorption maximum at 632 nm, consistent with the presence of the closed-ring isomer, (Ib). Upon irradiation with visible light with a wavelength greater than 510 nm, the green crystal can return to its initial colorless state, and the absorption spectrum of the hexane solution containing the colorless crystal is the same as that of solution of the open-ring form, (Ia), with the absorption maximum at 261 nm.

Experimental

The title compound, (Ia) was originally derived from thiophene, (1); Scheme 3. Firstly, 2-heptylthiophene derivative (2) was obtained in high yield by reacting thiophene (1) (5.0 g, 59.42 mmol) with 1-bromoheptane (49.52 mmol) in the presence of n-BuLi/hexane solution (23.77 ml, 59.42 mmol) at 195 K. Then, 5-heptylthiophene-2-carbaldehyde (3) (8.99 g, 42.73 mmol) was obtained in 71.9% yield by the acylation of 2-heptylthiophene (2) (10.83 g, 59.42 mmol) with DMF/POCl3. 3-Bromo-2-heptyl-5-formylthiophene (4) (7.10 g, 24.56 mmol), was obtained in 57.5% yield by bromination of (3) (8.99 g, 42.73 mmol) in acetic acid at room temperature. The dioxolane acetal (5) (4.37 g, 13.10 mmol) was prepared in 53.3% yield by refluxing under Dean-Stark conditions in the presence of (4) (7.10 g, 24.56 mmol), glycol (8.17 ml, 143.3 mmol), and *p*-toluenesulfonic acid (0.07 g) in benzene (200 ml). To a stirred solution of (5) (4.37 g, 13.10 mmol) in THF (100 ml) was added dropwise a 2.5 mol/*L* n-BuLi (5.24 ml, 13.10 mmol) at 195 K under a N_2 atmosphere. Stirring was continued for 40 minutes, perfluorocyclopentene (0.90 ml, 6.05 mmol) was slowly added to the reaction mixture, and the mixture was stirred for 3.0 h at 195 K. The reaction was stopped by the addition of water. Through a series of routine operations, 1,2-bis{2-heptyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (1.20 g, 1.82 mmol), was obtained in 25.2% yield. Finally, the title compound (Ia) was produced in 81.3% yield by hydrolyzing (6), and the colorless crystals were obtained by slow vapor diffusion of the mixture of chloroform and hexane(chloroform/hexane = 1/3); m.p. 328.7 K-329.2 K. Analysis found: C 58.86, H 5.69, F 19.43, O 5.43, S 10.98; $C_{29}H_{34}F_6O_2S_2$ requires: C 58.77, H 5.78, F 19.23, O 5.40, S 10.82. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, 6H, J = 6.8 Hz), δ 1.17 (s, 12H), δ 1.25–1.26 (m, 4H), δ 1.36 (s, 4H), δ 2.23 (t, 4H, J = 7.4 Hz), δ 7.73 (s, 2H), δ 9.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.99, 22.54, 28.82, 29.13, 29.80, 30.95, 31.56, 124.89, 135.45, 136.69, 142.23, 158.29, 181.78. IR (KBr, cm-1): 943, 977, 996, 1086, 1125, 1193, 1321, 1271, 1327, 1384, 1462, 1544, 2857, 2960, 3097.

Refinement

The H atoms were allowed to ride on their parent atoms with C—H = 0.93–0.97 Å, and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$ or $1.5U_{\rm eq}$(methyl-C). The methyl groups were treated as rigid groups and allowed to rotate about the C—C bond. The CF_3 group was found to be disordered over two positions. From anisotropic refinement, the site occupancies for the primed and unprimed F atoms were 0.539 (5):0.461.

Figures

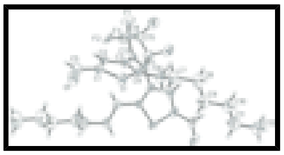


Fig. 1. The molecular structure of (Ia) with 35% probability ellipsoids, showing the atomic numbering scheme. The molecule has crystallographic 2-fold symmetry and the unlebelled atoms are related by 2 − *x*, *y*, −*z* + 1/2.

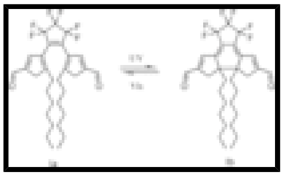


Fig. 2. Interconversion of compound (Ia) and compound (Ib).

Fig. 3. Synthesis of compound (Ia).

3,3,4,4,5,5-Hexafluoro-1,2-bis(5-formyl-2-n-heptyl-3-thienyl)cyclopent-1-ene

Crystal data

$C_{29}H_{34}F_6O_2S_2$

$M_r = 592.68$

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

$a = 20.929$ (7) Å

$b = 8.945$ (3) Å

$c = 17.232$ (6) Å

$F_{000} = 1240$

$D_x = 1.298$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 4940 reflections

θ = 2.5–28.3°

μ = 0.24 mm^{-1}

T = 291 (2) K

$\beta = 109.905\ (4)^\circ$

$V = 3033.4\ (18)\ \text{Å}^3$

$Z = 4$

Block, yellow

$0.49 \times 0.48 \times 0.47$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.893$, $T_{\max} = 0.897$

10891 measured reflections

2816 independent reflections

2357 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 25.5^\circ$

$\theta_{\min} = 2.5^\circ$

$h = -25 \rightarrow 25$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.181$

$S = 1.05$

2816 reflections

188 parameters

244 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

$w = 1/[\sigma^2(F_o^2) + (0.0872P)^2 + 4.7076P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.62$ e Å^{-3}

$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	$U_{\text{iso}}*/U_{\text{eq}}$	Occ. (<1)
F1	1.0631 (4)	0.6550 (10)	0.1574 (4)	0.0940 (14)	0.461 (5)

F2	1.1096 (4)	0.6430 (12)	0.2892 (5)	0.0907 (17)	0.461 (5)
F3	1.0407 (3)	0.7837 (6)	0.3284 (4)	0.0925 (10)	0.461 (5)
F1'	1.0266 (3)	0.6557 (8)	0.1389 (4)	0.0940 (14)	0.539 (5)
F2'	1.1124 (3)	0.6621 (10)	0.2556 (5)	0.0907 (17)	0.539 (5)
F3'	0.9726 (2)	0.8465 (5)	0.2076 (4)	0.0925 (10)	0.539 (5)
S1	1.08117 (4)	0.09048 (9)	0.15338 (5)	0.0627 (3)	
O1	1.23276 (12)	0.0233 (3)	0.20361 (19)	0.0937 (9)	
C1	1.14975 (13)	0.1952 (4)	0.21100 (19)	0.0578 (7)	
C2	1.13026 (13)	0.3251 (3)	0.23615 (19)	0.0530 (7)	
H2	1.1607	0.3966	0.2669	0.064*	
C3	1.05849 (12)	0.3415 (3)	0.21070 (17)	0.0476 (6)	
C4	1.02487 (13)	0.2223 (3)	0.16359 (18)	0.0511 (6)	
C5	1.21892 (16)	0.1423 (4)	0.2270 (2)	0.0712 (9)	
H5	1.2546	0.2039	0.2571	0.085*	
C6	0.94978 (14)	0.1969 (4)	0.1237 (2)	0.0626 (8)	
H6A	0.9274	0.2934	0.1116	0.075*	
H6B	0.9332	0.1469	0.1631	0.075*	
C7	0.92932 (17)	0.1061 (5)	0.0454 (2)	0.0785 (10)	
H7A	0.9482	0.0063	0.0580	0.094*	
H7B	0.9486	0.1514	0.0072	0.094*	
C8	0.85209 (17)	0.0942 (5)	0.0037 (2)	0.0839 (11)	
H8A	0.8340	0.1942	−0.0108	0.101*	
H8B	0.8429	0.0388	−0.0473	0.101*	
C9	0.81418 (19)	0.0210 (6)	0.0535 (3)	0.0902 (11)	
H9A	0.8190	0.0826	0.1015	0.108*	
H9B	0.8354	−0.0747	0.0731	0.108*	
C10	0.73906 (19)	−0.0048 (5)	0.0079 (3)	0.0872 (11)	
H10A	0.7191	0.0894	−0.0165	0.105*	
H10B	0.7346	−0.0739	−0.0370	0.105*	
C11	0.6991 (2)	−0.0630 (7)	0.0565 (3)	0.1104 (16)	
H11A	0.7044	0.0052	0.1020	0.132*	
H11B	0.7186	−0.1580	0.0800	0.132*	
C12	0.6247 (2)	−0.0859 (7)	0.0122 (3)	0.1195 (18)	
H12A	0.6033	0.0089	−0.0059	0.179*	
H12B	0.6048	−0.1318	0.0489	0.179*	
H12C	0.6183	−0.1495	−0.0347	0.179*	
C13	1.02544 (13)	0.4699 (3)	0.23425 (18)	0.0487 (6)	
C14	1.04707 (16)	0.6270 (4)	0.2242 (2)	0.0671 (8)	
C15	1.0000	0.7277 (5)	0.2500	0.0718 (12)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.117 (4)	0.0690 (15)	0.121 (3)	−0.015 (4)	0.073 (3)	0.013 (2)
F2	0.0505 (12)	0.052 (2)	0.175 (5)	−0.0202 (11)	0.047 (3)	0.005 (4)
F3	0.091 (2)	0.048 (2)	0.133 (3)	0.0038 (14)	0.030 (2)	0.0042 (19)
F1'	0.117 (4)	0.0690 (15)	0.121 (3)	−0.015 (4)	0.073 (3)	0.013 (2)
F2'	0.0505 (12)	0.052 (2)	0.175 (5)	−0.0202 (11)	0.047 (3)	0.005 (4)

F3'	0.091 (2)	0.048 (2)	0.133 (3)	0.0038 (14)	0.030 (2)	0.0042 (19)
S1	0.0457 (4)	0.0577 (5)	0.0877 (6)	0.0065 (3)	0.0266 (4)	−0.0105 (4)
O1	0.0540 (14)	0.101 (2)	0.122 (2)	0.0308 (14)	0.0251 (14)	−0.0024 (17)
C1	0.0372 (13)	0.0638 (17)	0.0755 (18)	0.0038 (12)	0.0234 (12)	0.0096 (14)
C2	0.0359 (12)	0.0528 (15)	0.0725 (17)	−0.0019 (11)	0.0215 (12)	0.0059 (13)
C3	0.0366 (12)	0.0456 (13)	0.0634 (15)	−0.0016 (10)	0.0206 (11)	0.0041 (11)
C4	0.0386 (13)	0.0505 (15)	0.0677 (16)	0.0031 (11)	0.0224 (12)	−0.0022 (12)
C5	0.0433 (15)	0.081 (2)	0.089 (2)	0.0160 (15)	0.0233 (15)	0.0069 (18)
C6	0.0417 (14)	0.0649 (18)	0.0811 (19)	0.0002 (13)	0.0206 (13)	−0.0169 (15)
C7	0.0537 (17)	0.098 (3)	0.081 (2)	0.0004 (17)	0.0191 (15)	−0.0204 (19)
C8	0.0565 (18)	0.107 (3)	0.080 (2)	−0.0011 (18)	0.0139 (16)	−0.021 (2)
C9	0.0603 (19)	0.115 (3)	0.085 (2)	0.001 (2)	0.0105 (17)	−0.008 (2)
C10	0.064 (2)	0.098 (3)	0.092 (2)	−0.0039 (19)	0.0181 (18)	−0.006 (2)
C11	0.080 (3)	0.144 (4)	0.097 (3)	−0.021 (3)	0.017 (2)	0.016 (3)
C12	0.081 (3)	0.154 (5)	0.118 (4)	−0.024 (3)	0.028 (3)	0.025 (3)
C13	0.0378 (12)	0.0408 (13)	0.0652 (16)	−0.0025 (10)	0.0148 (11)	0.0004 (11)
C14	0.0612 (17)	0.0490 (16)	0.097 (2)	−0.0090 (13)	0.0343 (16)	0.0020 (15)
C15	0.064 (2)	0.041 (2)	0.101 (3)	0.000	0.017 (2)	0.000

Geometric parameters (Å, °)

F1—C14	1.327 (6)	C7—H7B	0.9700
F2—C14	1.411 (7)	C8—C9	1.503 (6)
F3—C15	1.421 (6)	C8—H8A	0.9700
F1'—C14	1.407 (6)	C8—H8B	0.9700
F2'—C14	1.326 (6)	C9—C10	1.517 (5)
F3'—C15	1.307 (5)	C9—H9A	0.9700
F3'—F3'$^{\mathrm{i}}$	1.519 (11)	C9—H9B	0.9700
S1—C1	1.718 (3)	C10—C11	1.465 (6)
S1—C4	1.718 (3)	C10—H10A	0.9700
O1—C5	1.208 (4)	C10—H10B	0.9700
C1—C2	1.351 (4)	C11—C12	1.497 (6)
C1—C5	1.457 (4)	C11—H11A	0.9700
C2—C3	1.422 (3)	C11—H11B	0.9700
C2—H2	0.9300	C12—H12A	0.9600
C3—C4	1.379 (4)	C12—H12B	0.9600
C3—C13	1.468 (4)	C12—H12C	0.9600
C4—C6	1.503 (4)	C13—C13$^{\mathrm{i}}$	1.350 (5)
C5—H5	0.9300	C13—C14	1.505 (4)
C6—C7	1.508 (5)	C14—C15	1.509 (4)
C6—H6A	0.9700	C15—F3'$^{\mathrm{i}}$	1.307 (5)
C6—H6B	0.9700	C15—F3$^{\mathrm{i}}$	1.421 (6)
C7—C8	1.533 (5)	C15—C14$^{\mathrm{i}}$	1.510 (4)
C7—H7A	0.9700		
C15—F3'—F3'$^{\mathrm{i}}$	54.5 (3)	C9—C10—H10A	108.1
C4—S1—C1	91.94 (14)	C11—C10—H10B	108.1
C2—C1—C5	127.4 (3)	C9—C10—H10B	108.1
C2—C1—S1	111.7 (2)	H10A—C10—H10B	107.3

C5—C1—S1	120.9 (3)	C10—C11—C12	117.0 (4)
C1—C2—C3	113.1 (3)	C10—C11—H11A	108.0
C1—C2—H2	123.5	C12—C11—H11A	108.0
C3—C2—H2	123.5	C10—C11—H11B	108.0
C4—C3—C2	112.1 (2)	C12—C11—H11B	108.0
C4—C3—C13	125.0 (2)	H11A—C11—H11B	107.3
C2—C3—C13	122.9 (2)	C11—C12—H12A	109.5
C3—C4—C6	129.1 (2)	C11—C12—H12B	109.5
C3—C4—S1	111.14 (19)	H12A—C12—H12B	109.5
C6—C4—S1	119.8 (2)	C11—C12—H12C	109.5
O1—C5—C1	123.9 (3)	H12A—C12—H12C	109.5
O1—C5—H5	118.0	H12B—C12—H12C	109.5
C1—C5—H5	118.0	C13$^{\text{i}}$—C13—C3	128.44 (14)
C4—C6—C7	115.1 (2)	C13$^{\text{i}}$—C13—C14	110.86 (16)
C4—C6—H6A	108.5	C3—C13—C14	120.7 (2)
C7—C6—H6A	108.5	F2'—C14—F1	77.3 (4)
C4—C6—H6B	108.5	F2'—C14—F1'	106.7 (4)
C7—C6—H6B	108.5	F1—C14—F2	103.3 (4)
H6A—C6—H6B	107.5	F1'—C14—F2	133.0 (4)
C6—C7—C8	113.0 (3)	F2'—C14—C13	118.9 (4)
C6—C7—H7A	109.0	F1—C14—C13	116.8 (5)
C8—C7—H7A	109.0	F1'—C14—C13	107.2 (4)
C6—C7—H7B	109.0	F2—C14—C13	103.7 (5)
C8—C7—H7B	109.0	F2'—C14—C15	115.1 (5)
H7A—C7—H7B	107.8	F1—C14—C15	121.7 (5)
C9—C8—C7	116.1 (3)	F1'—C14—C15	101.7 (4)
C9—C8—H8A	108.3	F2—C14—C15	103.1 (5)
C7—C8—H8A	108.3	C13—C14—C15	105.7 (2)
C9—C8—H8B	108.3	F3'$^{\text{i}}$—C15—F3'	71.1 (6)
C7—C8—H8B	108.3	F3$^{\text{i}}$—C15—F3	138.7 (6)
H8A—C8—H8B	107.4	F3'$^{\text{i}}$—C15—C14	116.4 (2)
C8—C9—C10	115.2 (3)	F3'—C15—C14	121.8 (3)
C8—C9—H9A	108.5	F3$^{\text{i}}$—C15—C14	99.8 (3)
C10—C9—H9A	108.5	F3—C15—C14	104.6 (3)
C8—C9—H9B	108.5	F3'$^{\text{i}}$—C15—C14$^{\text{i}}$	121.8 (3)
C10—C9—H9B	108.5	F3'—C15—C14$^{\text{i}}$	116.4 (2)
H9A—C9—H9B	107.5	F3$^{\text{i}}$—C15—C14$^{\text{i}}$	104.6 (3)
C11—C10—C9	116.7 (4)	F3—C15—C14$^{\text{i}}$	99.8 (3)
C11—C10—H10A	108.1	C14—C15—C14$^{\text{i}}$	106.8 (3)

C4—S1—C1—C2	−0.5 (2)	C3—C13—C14—F2	−74.9 (5)
C4—S1—C1—C5	−179.8 (3)	C13$^{\text{i}}$—C13—C14—C15	−2.7 (4)
C5—C1—C2—C3	−179.3 (3)	C3—C13—C14—C15	177.0 (2)
S1—C1—C2—C3	1.4 (3)	F3'$^{\text{i}}$—F3'—C15—F3$^{\text{i}}$	−166.3 (8)
C1—C2—C3—C4	−1.9 (4)	F3'$^{\text{i}}$—F3'—C15—F3	7.9 (5)
C1—C2—C3—C13	176.8 (3)	F3'$^{\text{i}}$—F3'—C15—C14	−109.9 (4)

C2—C3—C4—C6	−178.9 (3)	F3'^{i}—F3'—C15—C14^{i}	116.8 (3)
C13—C3—C4—C6	2.3 (5)	F2'—C14—C15—F3'^{i}	7.4 (5)
C2—C3—C4—S1	1.5 (3)	F1—C14—C15—F3'^{i}	−82.8 (5)
C13—C3—C4—S1	−177.2 (2)	F1'—C14—C15—F3'^{i}	−107.6 (4)
C1—S1—C4—C3	−0.6 (2)	F2—C14—C15—F3'^{i}	32.1 (5)
C1—S1—C4—C6	179.8 (3)	C13—C14—C15—F3'^{i}	140.7 (4)
C2—C1—C5—O1	178.8 (3)	F2'—C14—C15—F3'	90.6 (6)
S1—C1—C5—O1	−1.9 (5)	F1—C14—C15—F3'	0.4 (7)
C3—C4—C6—C7	150.0 (3)	F1'—C14—C15—F3'	−24.4 (5)
S1—C4—C6—C7	−30.5 (4)	F2—C14—C15—F3'	115.3 (5)
C4—C6—C7—C8	−175.4 (3)	C13—C14—C15—F3'	−136.1 (4)
C6—C7—C8—C9	−60.8 (5)	F2'—C14—C15—F3^{i}	119.1 (5)
C7—C8—C9—C10	−173.7 (4)	F1—C14—C15—F3^{i}	28.9 (6)
C8—C9—C10—C11	−174.4 (4)	F1'—C14—C15—F3^{i}	4.2 (5)
C9—C10—C11—C12	178.9 (5)	F2—C14—C15—F3^{i}	143.8 (5)
C4—C3—C13—C13^{i}	47.4 (5)	C13—C14—C15—F3^{i}	−107.6 (3)
C2—C3—C13—C13^{i}	−131.2 (4)	F2'—C14—C15—F3	−27.2 (5)
C4—C3—C13—C14	−132.3 (3)	F1—C14—C15—F3	−117.4 (5)
C2—C3—C13—C14	49.0 (4)	F1'—C14—C15—F3	−142.2 (4)
C13^{i}—C13—C14—F2'	128.5 (5)	F2—C14—C15—F3	−2.5 (5)
C3—C13—C14—F2'	−51.8 (6)	C13—C14—C15—F3	106.1 (4)
C13^{i}—C13—C14—F1	−141.7 (5)	F2'—C14—C15—C14^{i}	−132.4 (4)
C3—C13—C14—F1	38.0 (6)	F1—C14—C15—C14^{i}	137.4 (5)
C13^{i}—C13—C14—F1'	−110.6 (4)	F1'—C14—C15—C14^{i}	112.7 (3)
C3—C13—C14—F1'	69.2 (4)	F2—C14—C15—C14^{i}	−107.6 (4)
C13^{i}—C13—C14—F2	105.4 (6)	C13—C14—C15—C14^{i}	0.93 (13)

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

Fig. 1

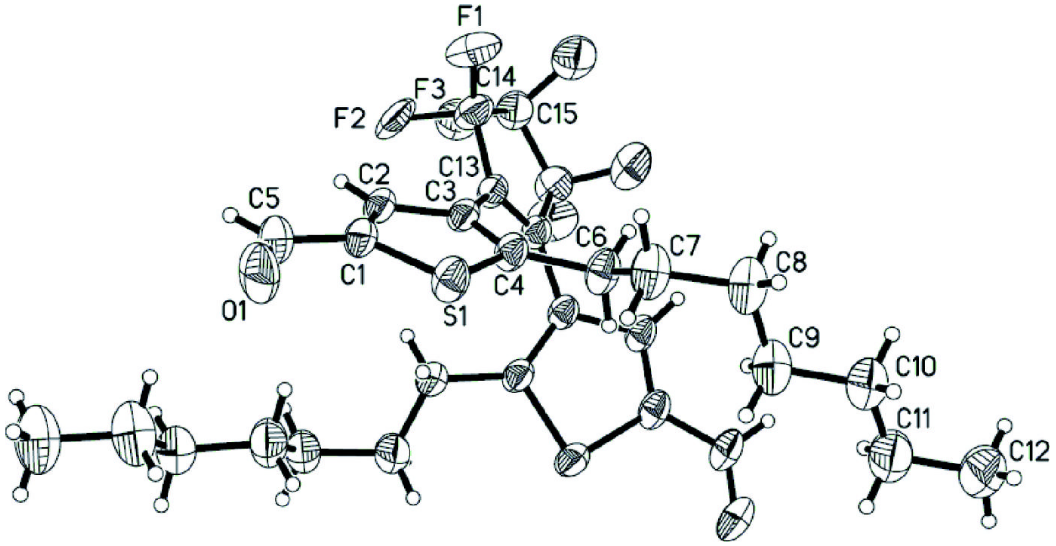


Fig. 2

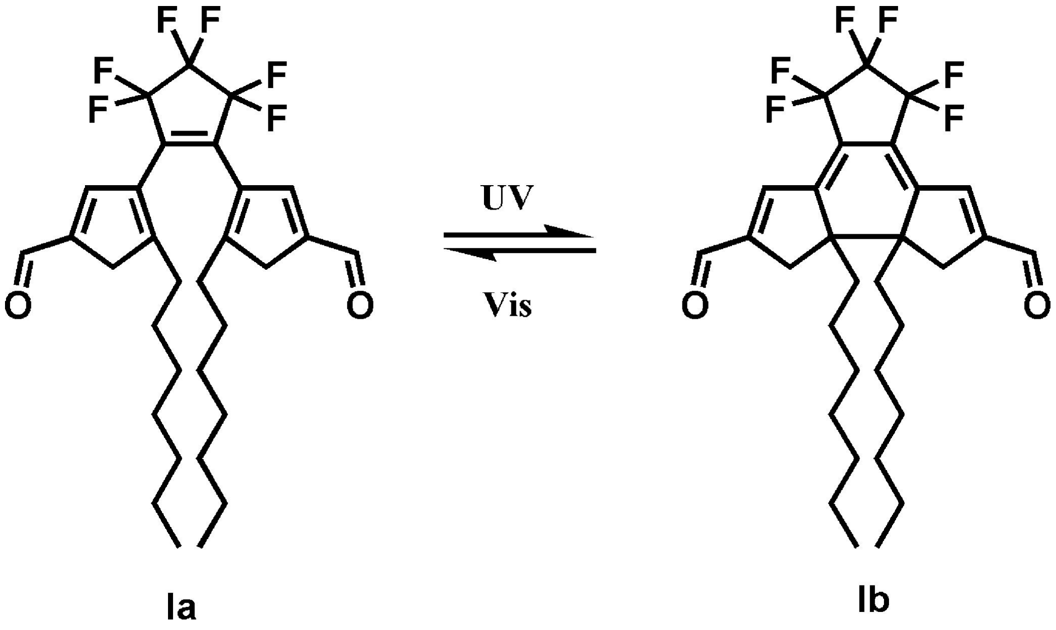
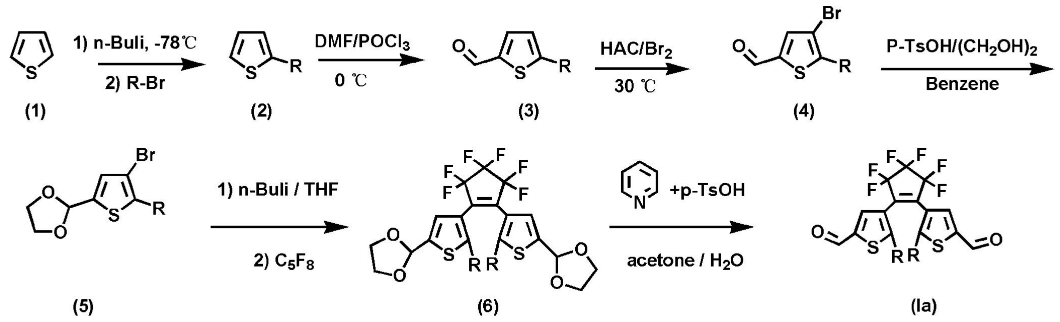


Fig. 3


(1)
1) n-Buli, -78℃
2) R-Br
(2)
DMF/POCl3
0 ℃
(3)
HAC/Br2
30 ℃
Br
(4)
P-TsOH/(CH2OH)2
Benzene
(5)
1) n-Buli / THF
2) C5F8
(6)
+p-TsOH
acetone / H2O
(Ia)
S
R
O
F
N

R = C_7H_{15}