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2,3,5,6-Tetrafluoro-1,4-bis({[(thiophen-2-yl)methylidene]amino}methyl)benzene

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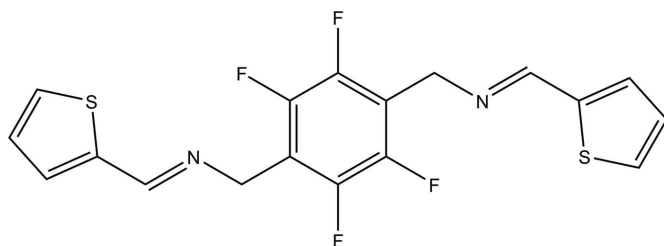
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.090; data-to-parameter ratio = 13.1.

In the title compound, $\text{C}_{18}\text{H}_{12}\text{F}_4\text{N}_2\text{S}_2$, a bis-thiophenyl Schiff base ligand with a perfluorinated aromatic core, the complete molecule is generated by crystallographic inversion symmetry. The thiophene and tetrafluorinated benzene rings are oriented at a dihedral angle of $77.38(4)^\circ$. The crystal structure exhibits $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds, resulting in supramolecular chains along the c -axis direction.

Related literature

For background information on thiophene-based Schiff base ligands, see: Hee & Soon (2007); Fang *et al.* (2001). For fluorine-functionalized complexes, see Chen *et al.* (2012). Zhang *et al.* (2011) describe the synthesis of the title compound.



Experimental

Crystal data

$\text{C}_{18}\text{H}_{12}\text{F}_4\text{N}_2\text{S}_2$
 $M_r = 396.42$
 Monoclinic, $P2_1/c$

$a = 15.500(7)$ Å
 $b = 4.865(2)$ Å
 $c = 11.713(6)$ Å

$\beta = 95.371(9)^\circ$
 $V = 879.3(7)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.35$ mm⁻¹
 $T = 296$ K
 $0.24 \times 0.22 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.921$, $T_{\max} = 0.934$

6136 measured reflections
 1541 independent reflections
 1427 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.090$
 $S = 1.02$
 1541 reflections

118 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5}\cdots\text{F1}^i$	0.93	2.56	3.446 (2)	159
$\text{C6}-\text{H6B}\cdots\text{F1}^i$	0.97	2.63	3.542 (2)	156

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

Data collection: APEX2 (Bruker, 2007); cell refinement: APEX2 and SAINT (Bruker, 2007); data reduction: SAINT (Bruker, 2007); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 2005); software used to prepare material for publication: SHELXTL.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IM2454).

References

- Brandenburg, K. (2005). DIAMOND. Crystal Impact GbR, Bonn, Germany.
 Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chen, S.-C., Zhang, Z.-H., Xu, H., Gao, H.-B., Qin, R.-R., Chen, Q., He, M.-Y. & Du, M. (2012). *Inorg. Chem. Commun.* **15**, 180–184.
 Fang, X., Watkin, J. G., Scott, B. L. & Kubas, G. J. (2001). *Organometallics*, **20**, 3351–3354.
 Hee, K. L. & Soon, W. L. (2007). *Bull. Korean Chem. Soc.* **28**, 421–426.
 Sheldrick, G. M. (2003). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Zhang, Z.-H., Chen, S.-C., He, M.-Y., Li, C., Chen, Q. & Du, M. (2011). *Cryst. Growth Des.* **11**, 5171–5175.

supplementary materials

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2,3,5,6-Tetrafluoro-1,4-bis(1-(thiophen-2-yl)methylidene)amino)methyl)benzene

Ning Gao, Hai-Kun Luo, Rui-Rui Qin and Ming-Yang He

1. Comment

In the past decade, thiophen-based bidentate Schiff base ligands have been utilized intensively to assemble various coordination compounds with intriguing structural features and potential applications (Hee & Soon, 2007; Fang *et al.*, 2001). As part of our ongoing studies of the effect of fluorine substitution on crystal structures of coordination polymers (Chen *et al.*, 2012), herein, we wish to report the crystal structure of the title compound, 2,3,5,6-tetrafluoro-1,4-bis(1-(1-thiophen-2-yl)methyleneaminomethyl)benzene, (I).

A perspective view of (I), including the atomic numbering scheme, is shown in Fig. 1. (I) crystallizes around a crystallographic centre with a half molecule in the asymmetric unit. Bond lengths and angles are within normal ranges. The terminal thiophenyl groups are coplanar, and they form a dihedral angle of $77.38(4)^\circ$ with the central tetrafluorinated benzene ring. Intermolecular C—H \cdots F hydrogen-bonding interactions link the adjacent molecules to generate one-dimensional supramolecular chains along the *c* axis (see Fig. 2).

2. Experimental

Compound (I) was synthesized and purified according to the method described by Zhang *et al.* (2011) through a condensation of 2,3,5,6-tetrafluoro-1,4-benzenedimethanamine with thiophene-2-carboxaldehyde (yied 75%). ^1H NMR (CDCl_3): δ 2.71 (s, 4H, CH_2), 7.19 (s, 2H, CH), 7.58 (s, 2H, CH), 7.84 (s, 2H, CH), 8.02 (s, 2H, CH).

Colourless needle-like single crystals (m.p. 452.3—452.6 K) suitable for X-ray analysis were obtained by dissolving (I) (20.0 mg) in dichloromethane (6 ml) solution and then slowly evaporating the solvent at room temperature for a period of about one week.

3. Refinement

All H atoms bound to carbon were assigned to calculated positions, with C—H = 0.97 Å (methylene) and 0.93 Å (aromatic and imine), and refined using a riding model, with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$.

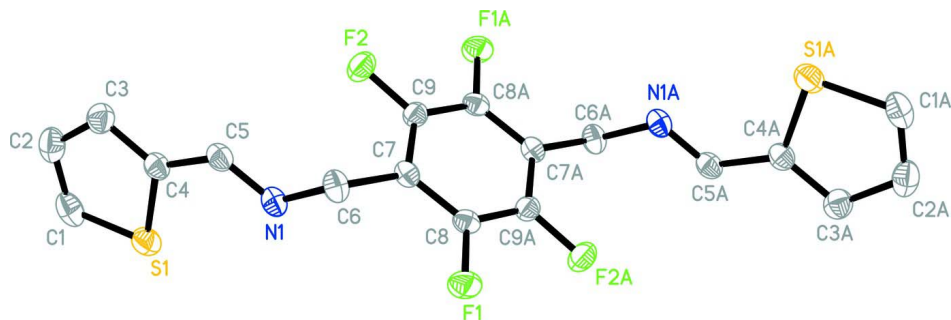


Figure 1

Molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

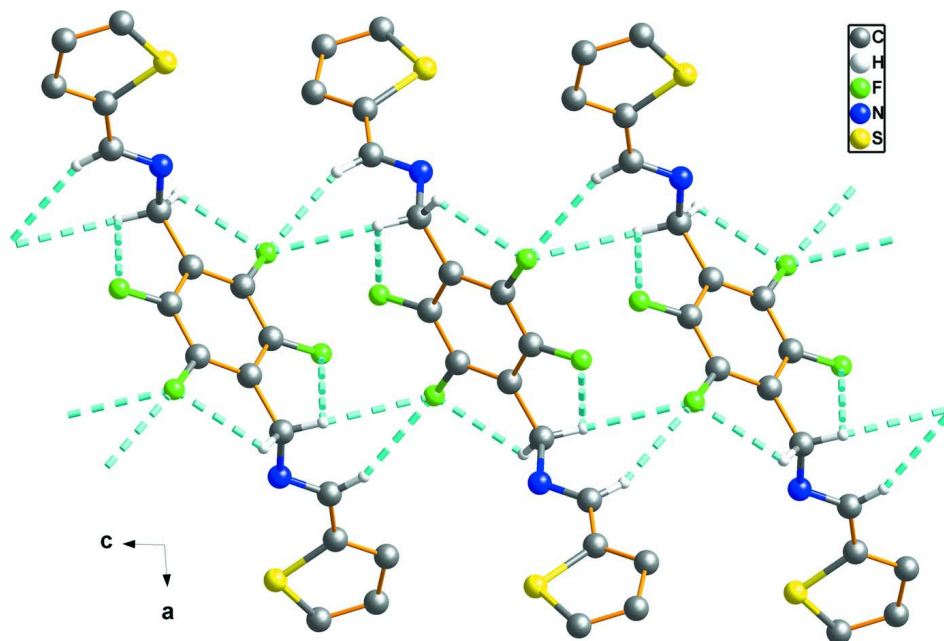


Figure 2

View of the one-dimensional supramolecular chain structure constructed via intermolecular C—H...F hydrogen-bonding interactions (irrelative hydrogen atoms are omitted for clarity).

2,3,5,6-Tetrafluoro-1,4-bis(2-(thiophen-2-yl)methylideneamino)methylbenzene

Crystal data

$C_{18}H_{12}F_4N_2S_2$

$M_r = 396.42$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1 ybc$

$a = 15.500$ (7) Å

$b = 4.865$ (2) Å

$c = 11.713$ (6) Å

$\beta = 95.371$ (9)°

$V = 879.3$ (7) Å³

$Z = 2$

$F(000) = 404$

$D_x = 1.497$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5195 reflections

$\theta = 2.6$ – 31.7 °

$\mu = 0.35$ mm⁻¹

$T = 296$ K

Shape, colourless

$0.24 \times 0.22 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD diffractometer	6136 measured reflections
Radiation source: fine-focus sealed tube	1541 independent reflections
Graphite monochromator	1427 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.018$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.921$, $T_{\text{max}} = 0.934$	$h = -18 \rightarrow 17$
	$k = -5 \rightarrow 5$
	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.297P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
1541 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
118 parameters	$\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.28 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.43101 (11)	0.7020 (4)	0.85018 (19)	0.0605 (5)
H1	0.4750	0.8166	0.8818	0.073*
C2	0.40375 (12)	0.6938 (4)	0.73736 (18)	0.0610 (5)
H2	0.4266	0.8036	0.6826	0.073*
C3	0.33673 (12)	0.5000 (4)	0.71153 (16)	0.0531 (4)
H3	0.3110	0.4671	0.6378	0.064*
C4	0.31367 (10)	0.3652 (3)	0.80758 (13)	0.0427 (4)
C5	0.24772 (9)	0.1542 (3)	0.81301 (13)	0.0428 (4)
H5	0.2214	0.0838	0.7446	0.051*
C6	0.15903 (10)	-0.1584 (3)	0.89660 (15)	0.0464 (4)
H6A	0.1831	-0.3231	0.9338	0.056*
H6B	0.1440	-0.2005	0.8162	0.056*
C7	0.07804 (9)	-0.0748 (3)	0.95097 (13)	0.0376 (3)
C8	0.05197 (9)	-0.2024 (3)	1.04813 (12)	0.0388 (3)
C9	0.02329 (9)	0.1316 (3)	0.90476 (12)	0.0388 (3)
F1	0.10088 (7)	-0.4083 (2)	1.09813 (8)	0.0566 (3)
F2	0.04382 (6)	0.2659 (2)	0.80981 (8)	0.0549 (3)

N1	0.22433 (8)	0.0614 (3)	0.90663 (12)	0.0445 (3)
S1	0.37524 (3)	0.47708 (10)	0.92848 (4)	0.05398 (19)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0407 (9)	0.0496 (10)	0.0913 (15)	-0.0038 (8)	0.0063 (9)	-0.0024 (10)
C2	0.0532 (10)	0.0521 (10)	0.0809 (14)	0.0022 (9)	0.0229 (9)	0.0114 (10)
C3	0.0513 (10)	0.0576 (11)	0.0517 (10)	0.0049 (8)	0.0108 (8)	0.0013 (8)
C4	0.0354 (7)	0.0451 (9)	0.0477 (9)	0.0048 (6)	0.0052 (6)	-0.0031 (7)
C5	0.0349 (7)	0.0481 (9)	0.0453 (9)	0.0027 (7)	0.0031 (6)	-0.0075 (7)
C6	0.0391 (8)	0.0437 (9)	0.0575 (10)	-0.0013 (7)	0.0107 (7)	-0.0063 (7)
C7	0.0327 (7)	0.0371 (8)	0.0427 (8)	-0.0012 (6)	0.0024 (6)	-0.0045 (6)
C8	0.0366 (7)	0.0355 (8)	0.0429 (8)	0.0042 (6)	-0.0033 (6)	0.0009 (6)
C9	0.0409 (8)	0.0389 (8)	0.0365 (8)	-0.0034 (6)	0.0030 (6)	0.0009 (6)
F1	0.0541 (6)	0.0549 (6)	0.0601 (6)	0.0183 (5)	0.0013 (5)	0.0136 (5)
F2	0.0608 (6)	0.0565 (6)	0.0492 (6)	0.0035 (5)	0.0144 (4)	0.0145 (5)
N1	0.0341 (7)	0.0488 (8)	0.0510 (8)	-0.0003 (6)	0.0056 (6)	-0.0053 (6)
S1	0.0457 (3)	0.0584 (3)	0.0562 (3)	-0.00403 (19)	-0.0039 (2)	-0.0020 (2)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.350 (3)	C6—N1	1.469 (2)
C1—S1	1.713 (2)	C6—C7	1.515 (2)
C1—H1	0.9300	C6—H6A	0.9700
C2—C3	1.414 (3)	C6—H6B	0.9700
C2—H2	0.9300	C7—C8	1.389 (2)
C3—C4	1.378 (2)	C7—C9	1.391 (2)
C3—H3	0.9300	C8—F1	1.3555 (17)
C4—C5	1.454 (2)	C8—C9 ⁱ	1.380 (2)
C4—S1	1.7202 (17)	C9—F2	1.3531 (18)
C5—N1	1.270 (2)	C9—C8 ⁱ	1.380 (2)
C5—H5	0.9300		
C2—C1—S1	112.19 (15)	N1—C6—H6A	109.4
C2—C1—H1	123.9	C7—C6—H6A	109.4
S1—C1—H1	123.9	N1—C6—H6B	109.4
C1—C2—C3	112.68 (17)	C7—C6—H6B	109.4
C1—C2—H2	123.7	H6A—C6—H6B	108.0
C3—C2—H2	123.7	C8—C7—C9	115.32 (13)
C4—C3—C2	112.58 (17)	C8—C7—C6	122.69 (14)
C4—C3—H3	123.7	C9—C7—C6	121.97 (14)
C2—C3—H3	123.7	F1—C8—C9 ⁱ	118.11 (13)
C3—C4—C5	127.50 (15)	F1—C8—C7	119.36 (13)
C3—C4—S1	110.81 (13)	C9 ⁱ —C8—C7	122.51 (14)
C5—C4—S1	121.70 (12)	F2—C9—C8 ⁱ	118.72 (13)
N1—C5—C4	123.20 (14)	F2—C9—C7	119.11 (13)
N1—C5—H5	118.4	C8 ⁱ —C9—C7	122.16 (14)
C4—C5—H5	118.4	C5—N1—C6	116.10 (14)
N1—C6—C7	111.25 (13)	C1—S1—C4	91.74 (10)

S1—C1—C2—C3	-0.6 (2)	C6—C7—C8—C9 ⁱ	-177.86 (14)
C1—C2—C3—C4	0.7 (2)	C8—C7—C9—F2	-179.81 (13)
C2—C3—C4—C5	-179.95 (15)	C6—C7—C9—F2	-1.4 (2)
C2—C3—C4—S1	-0.37 (19)	C8—C7—C9—C8 ⁱ	-0.5 (2)
C3—C4—C5—N1	-172.30 (16)	C6—C7—C9—C8 ⁱ	177.88 (14)
S1—C4—C5—N1	8.2 (2)	C4—C5—N1—C6	-177.93 (14)
N1—C6—C7—C8	-113.68 (16)	C7—C6—N1—C5	-120.34 (16)
N1—C6—C7—C9	68.1 (2)	C2—C1—S1—C4	0.36 (15)
C9—C7—C8—F1	179.22 (13)	C3—C4—S1—C1	0.02 (14)
C6—C7—C8—F1	0.8 (2)	C5—C4—S1—C1	179.62 (14)
C9—C7—C8—C9 ⁱ	0.5 (2)		

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C6—H6A...F1	0.97	2.44	2.873 (3)	107
C5—H5...F1 ⁱⁱ	0.93	2.56	3.446 (2)	159
C6—H6B...F1 ⁱⁱ	0.97	2.63	3.542 (2)	156

Symmetry code: (ii) $x, -y-1/2, z-1/2$.