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2,5-Bis{[(–)-(*S*)-1-(4-methylphenyl)ethyl]iminomethyl}thiophene

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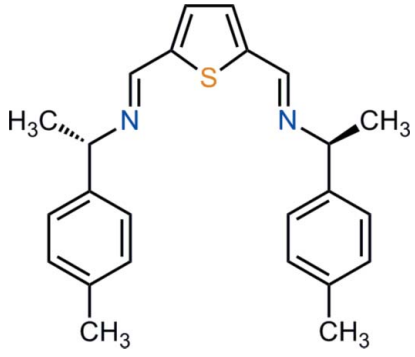
Key indicators: single-crystal X-ray study; T = 298 K, P = 0.0 kPa; mean σ(C–C) = 0.008 Å; R factor = 0.052; wR factor = 0.155; data-to-parameter ratio = 14.1.

The title chiral bis-aldimine, $C_{24}H_{26}N_2S$, was synthesized using a solvent-free Schiff condensation. The molecule displays crystallographic C_2 symmetry, with the S atom lying on the twofold axis parallel to [100]. As a consequence of the (*S*,*S*) stereochemistry, the tolyl groups are oriented towards opposite faces of the thiophene core, giving a twisted conformation for the whole molecule. Molecules are arranged in the crystal in a herringbone-like pattern, without any significant intermolecular contacts.

Related literature

For the solvent-free approach in organic synthesis, see: Tanaka & Toda (2000). For the structure of a chiral bis-aldimine compound, see: Espinosa Leija *et al.* (2009). For structures of thiophenes substituted in positions 2 and 5 by imine functionalities, see: Skene & Dufresne (2006); Fridman & Kaftory (2007); de Lima *et al.* (2010); Kudyakova *et al.* (2011, 2012).



Experimental

Crystal data

$C_{24}H_{26}N_2S$
M_r = 374.53
Orthorhombic, $P22_12_1$
a = 6.278 (3) Å
b = 7.900 (3) Å
c = 21.500 (7) Å
V = 1066.4 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.16 mm^{-1}
T = 298 K
0.50 × 0.32 × 0.10 mm

Data collection

Bruker P4 diffractometer
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
T_{min} = 0.754, T_{max} = 0.985
3046 measured reflections
1767 independent reflections
1352 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
3 standard reflections
every 97 reflections
intensity decay: 2.5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.155
S = 1.06
1767 reflections
125 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack x determined using 412 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons & Flack, 2004)
Absolute structure parameter: −0.08 (18)

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2315).

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Acta Cryst. (2013). E**69**, o1428 [doi:10.1107/S1600536813021685]

2,5-Bis{[(–)-(*S*)-1-(4-methylphenyl)ethyl]iminomethyl}thiophene

Sylvain Bernès, Guadalupe Hernández-Téllez, Manju Sharma, Oscar Portillo-Moreno and René Gutiérrez

S1. Comment

In the last few years, our attention has been focused on the synthesis and structure of chiral bis-imines (*e.g.* Espinosa Leija *et al.*, 2009), mostly due to their versatile coordination behavior and interesting properties as ligands for building of chiral metal complexes. Along this line, the title compound was synthesized through a Schiff condensation between a low-melting point dialdehyde and a liquid amine having a high boiling-point (above 200 °C), which also serves as a solvent for the reaction. No other solvents were used for the reaction (Tanaka & Toda, 2000).

The crude compound crystallized from CH_2Cl_2, allowing to determine its chiral purity and crystal structure. The obtained bis-aldimine is the expected (*S*,*S*) diastereoisomer, with imine bonds in the common *E* configuration (Fig. 1). The molecule is placed on the 2-fold axis of space group $P22_12_1$, with the S atom lying on the symmetry axis. The resulting molecular conformation displays the C_2 symmetry, with imine arms oriented towards opposite sides of the central thiophene core ring. Other thiophenes substituted in positions 2 and 5 by imine groups have been characterized (*e.g.* Skene & Dufresne, 2006; Fridman & Kaftory, 2007; de Lima *et al.*, 2010; Kudyakova *et al.*, 2011, 2012). However, all were achiral compounds, and only one actually presented a crystallographic C_2 symmetry (space group $C2/c$, Kudyakova *et al.*, 2011), as in the title compound.

The molecules are arranged in the crystal in such a way they form a herringbone-like structure (Fig. 2). However, no actual supramolecular pattern is formed in the solid-state, since no intermolecular contacts of significant strength are present.

S2. Experimental

Under solvent-free conditions, a mixture of 2,5-thiophenedicarboxaldehyde (100 mg, 0.71 mmol) and (*S*)-(–)-1-(4-methylphenyl)ethylamine (192 mg, 1.42 mmol) in a 1:2 molar ratio were mixed at room temperature, giving a brownish solid. The crude was recrystallized from CH_2Cl_2, affording colorless crystals of the title compound, in 91% yield. *M*.p. 150–152 °C. Spectroscopic data: $[\alpha]^{25}_D$ = +59.9 (c 1, $CHCl_3$). IR (KBr): 1624 cm^{-1} (C═N). ^{1}H-NMR (400 MHz, $CDCl_3$/TMS, p.p.m.): δ = 1.54–1.55 (d, 6H, CHC*H*$_3$), 2.33 (s, 6H, PhC*H*$_3$), 4.46, 4.51 (q, 2H, C*H*), 7.13–7.29 (m, 10H, Ar), 8.34 (s, 2H, *H*C═N). ^{13}C-NMR (100 MHz, $CDCl_3$/TMS, p.p.m.): δ = 21.0 (C*C*H$_3$), 30.9 (Ph*C*H$_3$), 69.0 (*C*HCH$_3$), 126.5 (Ar), 129.0 (Ar), 129.7 (Ar), 136.4 (Ar), 141.9 (Ar), 145.1 (Ar), 152.2 (H*C*═N). MS—EI: *m*/*z* = 374 (M^+).

S3. Refinement

All C-bonded H atoms were placed in idealized positions and refined as riding to their carrier C atoms, with bond lengths fixed to 0.93 (aromatic CH), 0.96 (methyl CH_3), and 0.98 Å (methine CH). Isotropic displacement parameters were calculated as U_{iso}(H) = 1.5U_{eq}(C7, C14) for methyl groups and U_{iso}(H) = 1.2U_{eq}(carrier C) for other H atoms. The absolute configuration was assigned from the known configuration of the chiral amine used as starting material. The absolute

structure was confirmed through the Parsons-Flack test (Parsons & Flack, 2004).

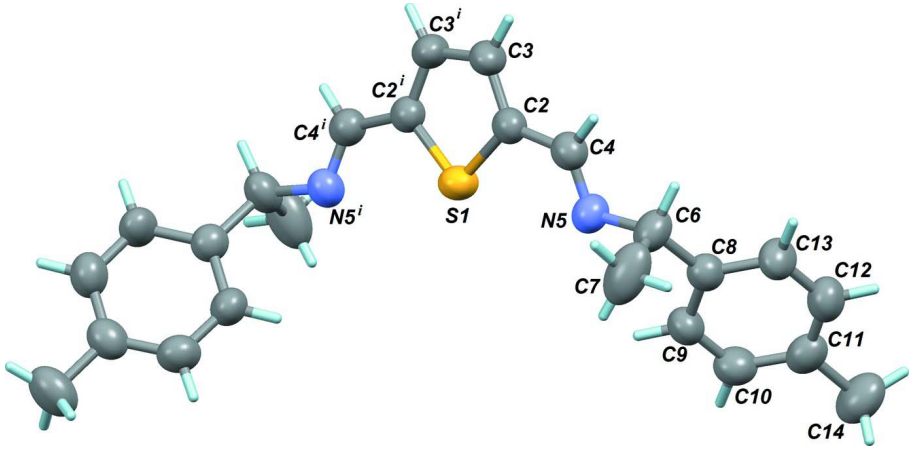

Figure 1

The title molecule with displacement ellipsoids for non-H atoms shown at the 50% probability level. The asymmetric unit consists of half of the molecule, and symmetry code to generate equivalent atoms is $i = x, 1 - y, 2 - z$.

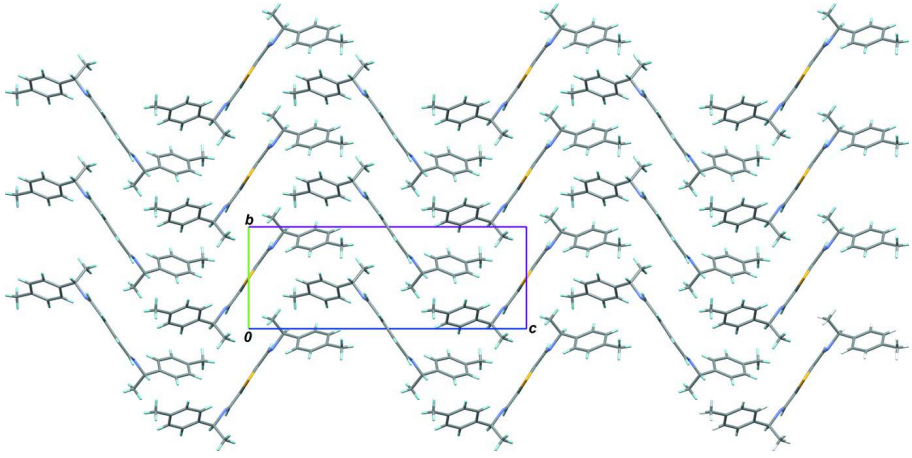

Figure 2

Part of the crystal structure, viewed along the *a*-axis.

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Crystal data

$C_{24}H_{26}N_2S$
$M_r = 374.53$
Orthorhombic, $P22_12_1$
Hall symbol: P 2bc 2
$a = 6.278$ (3) Å
$b = 7.900$ (3) Å
$c = 21.500$ (7) Å
$V = 1066.4$ (7) Å^3
$Z = 2$
$F(000) = 400$
$D_x = 1.166$ Mg m^{-3}
Melting point: 423 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 71 reflections
$\theta = 4.2$–12.3°
$\mu = 0.16$ mm^{-1}
$T = 298$ K
Plate, colourless
0.50 × 0.32 × 0.10 mm

Data collection

Bruker P4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$2\theta/\omega$ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
T_{min} = 0.754, T_{max} = 0.985
3046 measured reflections
1767 independent reflections
1352 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 25.1°, θ_{min} = 1.9°
$h = -7\rightarrow5$
$k = -9\rightarrow9$
$l = -25\rightarrow25$
3 standard reflections every 97 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.155
S = 1.06
1767 reflections
125 parameters
0 restraints
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.760P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack x determined using 412 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons & Flack, 2004)
Absolute structure parameter: −0.08 (18)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.6440 (3)	0.5000	1.0000	0.0580 (5)
C2	0.8347 (8)	0.3700 (6)	0.9686 (2)	0.0536 (12)
C3	1.0327 (8)	0.4251 (7)	0.9825 (2)	0.0645 (15)
H3B	1.1562	0.3696	0.9701	0.077*
C4	0.7765 (9)	0.2268 (7)	0.9303 (2)	0.0579 (13)
H4A	0.8834	0.1535	0.9172	0.069*
N5	0.5897 (7)	0.1971 (6)	0.91410 (19)	0.0578 (11)
C6	0.5569 (9)	0.0468 (7)	0.8745 (2)	0.0651 (15)
H6B	0.6951	0.0064	0.8594	0.078*
C7	0.4544 (14)	−0.0898 (8)	0.9141 (3)	0.099 (2)
H7B	0.5485	−0.1196	0.9476	0.148*
H7C	0.4271	−0.1879	0.8890	0.148*
H7D	0.3226	−0.0483	0.9309	0.148*
C8	0.4176 (8)	0.0904 (6)	0.8199 (2)	0.0540 (12)
C9	0.2393 (8)	0.1892 (7)	0.8261 (2)	0.0605 (14)
H9B	0.2074	0.2369	0.8645	0.073*
C10	0.1074 (9)	0.2188 (8)	0.7765 (3)	0.0665 (14)
H10A	−0.0132	0.2855	0.7822	0.080*
C11	0.1489 (9)	0.1524 (7)	0.7186 (3)	0.0627 (13)
C12	0.3281 (10)	0.0573 (7)	0.7125 (2)	0.0697 (15)
H12D	0.3618	0.0133	0.6736	0.084*
C13	0.4616 (9)	0.0235 (8)	0.7617 (2)	0.0657 (14)

H13D	0.5812	−0.0441	0.7559	0.079*
C14	0.0019 (11)	0.1849 (9)	0.6647 (3)	0.091 (2)
H14A	0.0789	0.1720	0.6265	0.136*
H14B	−0.0533	0.2980	0.6675	0.136*
H14C	−0.1138	0.1055	0.6659	0.136*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0456 (10)	0.0627 (11)	0.0658 (10)	0.000	0.000	−0.0035 (10)
C2	0.051 (3)	0.062 (3)	0.048 (2)	0.001 (3)	0.001 (2)	−0.004 (2)
C3	0.046 (3)	0.085 (4)	0.062 (3)	0.005 (3)	0.002 (2)	−0.018 (3)
C4	0.056 (3)	0.063 (3)	0.055 (3)	0.005 (3)	0.002 (2)	−0.004 (3)
N5	0.059 (3)	0.057 (3)	0.057 (2)	0.002 (2)	−0.007 (2)	−0.006 (2)
C6	0.068 (3)	0.064 (4)	0.064 (3)	0.006 (3)	−0.017 (3)	−0.011 (3)
C7	0.151 (7)	0.063 (4)	0.082 (4)	−0.013 (4)	−0.040 (5)	0.012 (3)
C8	0.055 (3)	0.048 (3)	0.059 (3)	0.000 (2)	0.001 (2)	−0.005 (2)
C9	0.056 (3)	0.068 (3)	0.057 (3)	0.004 (3)	0.006 (2)	−0.009 (3)
C10	0.056 (3)	0.063 (3)	0.080 (3)	0.007 (3)	0.000 (3)	−0.005 (3)
C11	0.064 (3)	0.055 (3)	0.068 (3)	−0.009 (3)	−0.010 (3)	0.000 (3)
C12	0.080 (4)	0.069 (4)	0.059 (3)	0.000 (3)	−0.002 (3)	−0.009 (3)
C13	0.064 (3)	0.066 (3)	0.067 (3)	0.015 (3)	−0.003 (2)	−0.018 (3)
C14	0.098 (5)	0.087 (5)	0.088 (4)	−0.005 (4)	−0.032 (4)	0.008 (4)

Geometric parameters (Å, º)

S1—C2	1.716 (5)	C8—C9	1.371 (7)
S1—C2^{i}	1.716 (5)	C8—C13	1.387 (7)
C2—C3	1.350 (7)	C9—C10	1.370 (7)
C2—C4	1.446 (7)	C9—H9B	0.9300
C3—C3^{i}	1.403 (10)	C10—C11	1.377 (8)
C3—H3B	0.9300	C10—H10A	0.9300
C4—N5	1.246 (6)	C11—C12	1.359 (8)
C4—H4A	0.9300	C11—C14	1.502 (8)
N5—C6	1.475 (7)	C12—C13	1.374 (8)
C6—C8	1.504 (7)	C12—H12D	0.9300
C6—C7	1.518 (9)	C13—H13D	0.9300
C6—H6B	0.9800	C14—H14A	0.9600
C7—H7B	0.9600	C14—H14B	0.9600
C7—H7C	0.9600	C14—H14C	0.9600
C7—H7D	0.9600		
C2—S1—C2^{i}	91.5 (3)	C9—C8—C6	122.0 (5)
C3—C2—C4	127.6 (5)	C13—C8—C6	120.1 (5)
C3—C2—S1	111.2 (4)	C10—C9—C8	121.1 (5)
C4—C2—S1	121.1 (4)	C10—C9—H9B	119.5
C2—C3—C3^{i}	113.0 (3)	C8—C9—H9B	119.5
C2—C3—H3B	123.5	C9—C10—C11	121.6 (5)

C3^{i}—C3—H3B	123.5	C9—C10—H10A	119.2
N5—C4—C2	123.0 (5)	C11—C10—H10A	119.2
N5—C4—H4A	118.5	C12—C11—C10	117.0 (5)
C2—C4—H4A	118.5	C12—C11—C14	122.0 (6)
C4—N5—C6	116.4 (4)	C10—C11—C14	121.0 (6)
N5—C6—C8	110.3 (4)	C11—C12—C13	122.6 (5)
N5—C6—C7	107.9 (4)	C11—C12—H12D	118.7
C8—C6—C7	110.7 (5)	C13—C12—H12D	118.7
N5—C6—H6B	109.3	C12—C13—C8	119.9 (5)
C8—C6—H6B	109.3	C12—C13—H13D	120.0
C7—C6—H6B	109.3	C8—C13—H13D	120.0
C6—C7—H7B	109.5	C11—C14—H14A	109.5
C6—C7—H7C	109.5	C11—C14—H14B	109.5
H7B—C7—H7C	109.5	H14A—C14—H14B	109.5
C6—C7—H7D	109.5	C11—C14—H14C	109.5
H7B—C7—H7D	109.5	H14A—C14—H14C	109.5
H7C—C7—H7D	109.5	H14B—C14—H14C	109.5
C9—C8—C13	117.8 (5)		

C2^{i}—S1—C2—C3	0.5 (3)	C7—C6—C8—C13	−100.2 (6)
C2^{i}—S1—C2—C4	−177.0 (5)	C13—C8—C9—C10	0.9 (8)
C4—C2—C3—C3^{i}	176.0 (5)	C6—C8—C9—C10	−175.9 (5)
S1—C2—C3—C3^{i}	−1.3 (7)	C8—C9—C10—C11	−0.6 (9)
C3—C2—C4—N5	−171.3 (5)	C9—C10—C11—C12	−0.7 (9)
S1—C2—C4—N5	5.7 (7)	C9—C10—C11—C14	179.6 (6)
C2—C4—N5—C6	179.4 (4)	C10—C11—C12—C13	1.6 (9)
C4—N5—C6—C8	−132.6 (5)	C14—C11—C12—C13	−178.6 (6)
C4—N5—C6—C7	106.3 (6)	C11—C12—C13—C8	−1.4 (9)
N5—C6—C8—C9	−42.7 (7)	C9—C8—C13—C12	0.0 (8)
C7—C6—C8—C9	76.6 (7)	C6—C8—C13—C12	176.9 (5)
N5—C6—C8—C13	140.5 (5)		

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