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2-(Thiophen-2-yl)-N-(4-[(E)-[2-(thiophen-2-yl)ethyl]iminomethyl]benzylidene)-ethanamine

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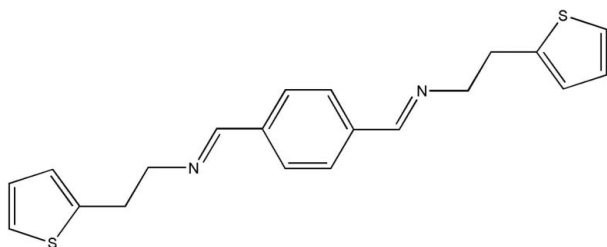
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.057; wR factor = 0.181; data-to-parameter ratio = 20.5.

In the crystal of the centrosymmetric title compound, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{S}_2$, molecules are linked by head-to-tail $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds, resulting in chains extending along the a axis. Three additional $\text{C}-\text{H}\cdots\pi$ intermolecular interactions give rise to a herringbone packing motif which extends along the c axis. The $\text{C}-\text{H}\cdots\text{N}$ interactions provide links between the sheets.

Related literature

For related literature on bidentate Schiff base ligands, see: Chakraborty *et al.* (1999); Haga & Koizumi (1985).



Experimental

Crystal data

$\text{C}_{20}\text{H}_{20}\text{N}_2\text{S}_2$
 $M_r = 352.52$
 Monoclinic, $C2/c$
 $a = 9.8592$ (10) Å

$b = 7.1533$ (6) Å
 $c = 25.678$ (2) Å
 $\beta = 96.646$ (5)°
 $V = 1798.8$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹

$T = 173$ K
 $0.22 \times 0.2 \times 0.04$ mm

Data collection

Nonius Kappa CCD diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2007)
 $T_{\min} = 0.925$, $T_{\max} = 0.988$

16248 measured reflections
 2230 independent reflections
 1679 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.181$
 $S = 1.08$
 2230 reflections
 109 parameters

14 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.80$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the thiophene and benzene rings, respectively.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C4}-\text{H4}\cdots\text{N8}^i$	0.95	2.61	3.514 (3)	159
$\text{C2}-\text{H2}\cdots\text{Cg1}^{ii}$	0.95	2.79	3.702 (3)	161
$\text{C6}-\text{H6A}\cdots\text{Cg2}^{iii}$	0.99	2.72	3.515 (3)	137
$\text{C6}-\text{H6A}\cdots\text{Cg2}^{iv}$	0.99	2.72	3.515 (3)	137

Symmetry codes: (i) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, y - 1, z$; (iv) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2005) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

We gratefully acknowledge Mintek and Project AuTEK for funding this project.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GO2007).

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supporting information

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2-(Thiophen-2-yl)-N-(4-{(E)-[2-(thiophen-2-yl)ethyl]iminomethyl}benzylidene)ethanamine

Haleden Chiririwa, Reinout Meijboom and Bernard Omondi

S1. Comment

The title compound belongs to a class of tetradentate ligands. To the best of our knowledge, this is the first example of a neutral thiophenyldimine-based bridging ligand. This compound is a potential tetra-coordinate ligand but on complexation the compound will probably behave as a bidentate ligand as the sulfur, on the thiophene, has weak donor capacity towards co-ordination for majority of metal ions. Besides its use as a ligand, it is interesting from the crystal engineering point of view for the analysis of the packing mode of (I).

Compound (I) crystallizes with half a molecule in the asymmetric unit, with the other half generated through symmetry located in the center of the phenyl ring (Fig. 1). The phenyl ring together with the atoms C7—N8—C9 and the thiophene ring together with the atom C6 are planar with N8 and C5 deviating the most from the planes by 0.018 (2) Å and 0.010 (2) Å respectively. The two planes are close to parallel, the angle between them being 9.3 (1)°. Bond distances and angles in (I) are as expected from the chemical bonding.

The crystal structure of (I) is composed of head-to-tail C—H...N hydrogen bonded chains (Table 1) that extend in the crystallographic *a* axis (Fig. 2). Additionally, the phenyl and thiophen rings are involved in C—H... π intermolecular interactions that result in a herringbone motif that spreads along the crystallographic *c* axis (Fig. 3). The C—H...N interactions are found to connect these herringbone sheets along the *a* axis.,

S2. Experimental

A solution of benzene 1,4-dicarboxaldehyde (0.50 g, 3.73 mmol) in methanol (10 ml) was added dropwise to a stirred solution of 2-thiophenylethylamine (0.95 g, 7.42 mmol) in methanol (10 ml). The mixture was stirred at room temperature for *ca* 16 h. The precipitate was filtered off and washed with diethylether and dried under vacuum for 4 h affording a fine shiny white powder in 80% yield. *M.p.*: 240–242 °C. Recrystallization was done by slow diffusion of Et₂O into a concentrated CH₂Cl₂ solution of the white powder to give colorless crystals fo (I).

S3. Refinement

The methine and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, C—H = 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂, C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH.

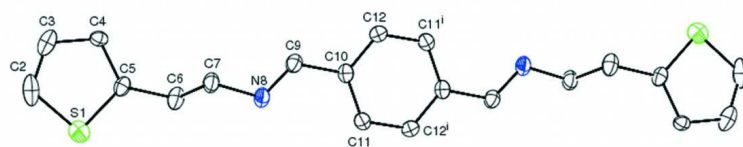


Figure 1

View of (I) (50% probability displacement ellipsoids) with H atoms presented as small spheres of arbitrary radii.

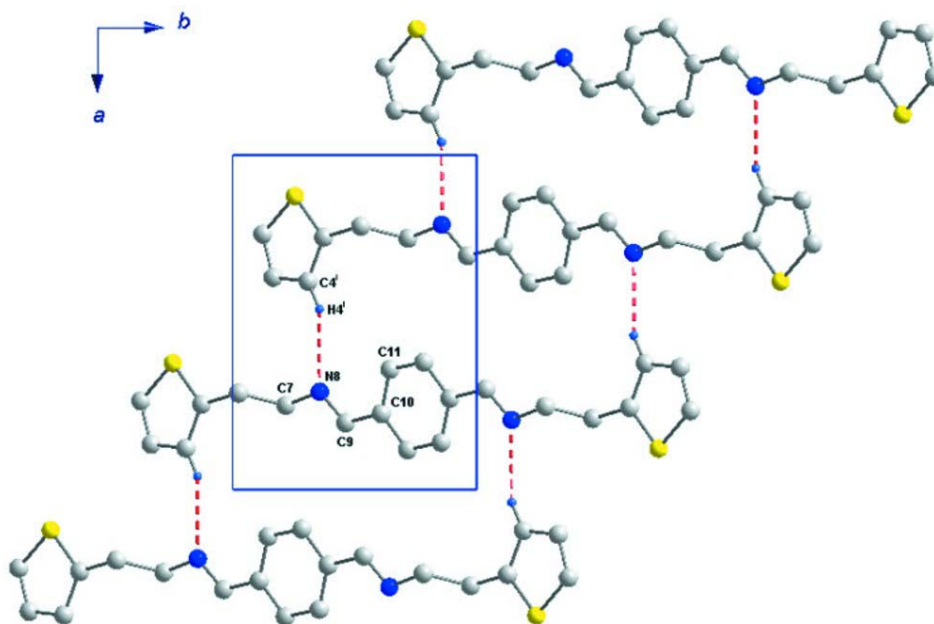


Figure 2

C—H...N hydrogen bond interactions in the crystal structure of (I). [Symmetry operators: (i) = $-1/2 + x, 1/2 + y, z$]

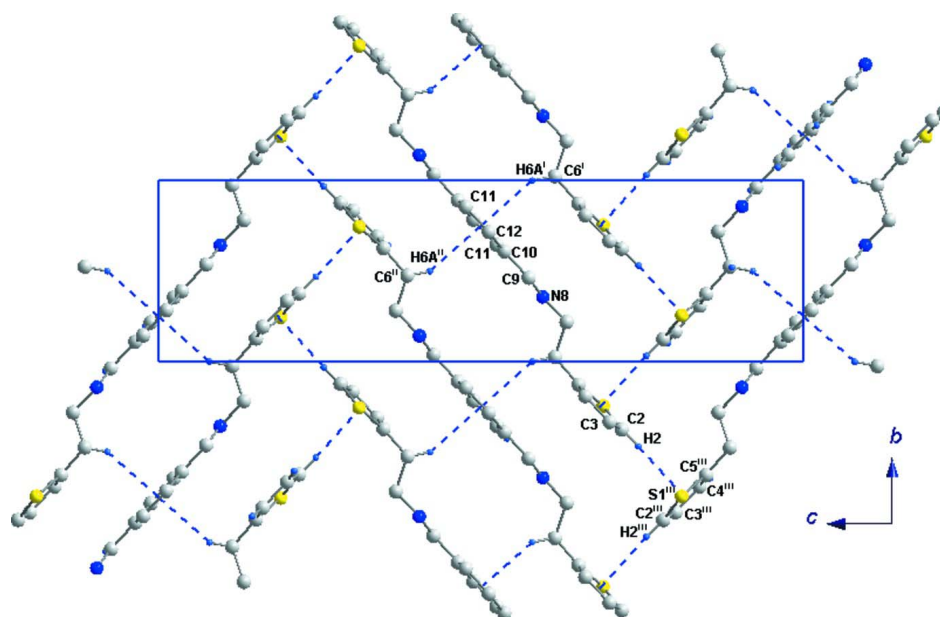


Figure 3

Sheets of C—H... π intermolecular interactions between molecules aligned along the *bc* face.

2-(Thiophen-2-yl)-N-(4-((*E*)-[2-(thiophen-2-yl)ethyl]iminomethyl)benzylidene)ethanamine

Crystal data

$C_{20}H_{20}N_2S_2$

$M_r = 352.52$

Monoclinic, *C2/c*

Hall symbol: $-C\ 2yc$

$a = 9.8592\ (10)\ \text{\AA}$

$b = 7.1533\ (6)\ \text{\AA}$

$c = 25.678\ (2)\ \text{\AA}$

$\beta = 96.646\ (5)^\circ$

$V = 1798.8\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 744$

$D_x = 1.302\ \text{Mg m}^{-3}$

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

Cell parameters from 34223 reflections

$\theta = 3.2\text{--}28.3^\circ$

$\mu = 0.30\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Plate, colourless

$0.22 \times 0.2 \times 0.04\ \text{mm}$

Data collection

Nonius Kappa CCD

diffractometer

Graphite monochromator

$1.0^\circ\ \omega$ scans, 60s

16248 measured reflections

2230 independent reflections

1679 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 3.2^\circ$

$h = -13 \rightarrow 13$

$k = -9 \rightarrow 9$

$l = -34 \rightarrow 34$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.181$

$S = 1.08$

2230 reflections

109 parameters

14 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

$$w = 1/[\sigma^2(F_o^2) + (0.0971P)^2 + 3.1807P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The intensity data was collected on a Nonius Kappa CCD diffractometer using an exposure time of 60 sec/per frame. Analytical data: IR (KBr): 1613[?]cm⁻¹ (C=N, imine); 1H NMR: (CDCl₃) δ H 8.23 (d, 2H) 7.76 (s, 2H) 7.13 (dd, 2H) 6.92 (dd, 2H) 6.84 (dd, 4H) 3.91 (dt, 4H) 3.25 (t, 4H); Anal. calcd. for C₂₀H₂₀N₂S₂: C, 68.14%; H, 5.72%; N, 7.95%; S, 18.19; Found: C, 68.19%; H, 5.52%; N, 7.72%; S, 18.44; EI—MS: m/z 351.76 [M]⁺;

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 $F^2 > \sigma(F^2)$ 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	0.62222 (7)	-0.24504 (10)	0.31079 (3)	0.0357 (3)
C2	0.7356 (3)	-0.3763 (4)	0.28220 (10)	0.0400 (7)
H2	0.711	-0.4684	0.2562	0.048*
C3	0.8651 (3)	-0.3341 (4)	0.30095 (10)	0.0355 (6)
H3	0.9419	-0.3955	0.2896	0.043*
C4	0.8766 (2)	-0.1915 (3)	0.33866 (8)	0.0194 (4)
H4	0.9607	-0.1441	0.3552	0.023*
C5	0.7453 (2)	-0.1270 (3)	0.34886 (9)	0.0230 (5)
C6	0.7117 (3)	0.0246 (3)	0.38573 (10)	0.0286 (5)
H6A	0.7616	0.0005	0.4208	0.034*
H6B	0.6128	0.0204	0.3891	0.034*
C7	0.7483 (3)	0.2186 (3)	0.36770 (10)	0.0266 (5)
H7A	0.8479	0.2266	0.366	0.032*
H7B	0.701	0.2431	0.3322	0.032*
N8	0.7077 (2)	0.3574 (3)	0.40432 (8)	0.0257 (5)
C9	0.8002 (2)	0.4632 (3)	0.42630 (9)	0.0232 (5)
H9	0.891	0.4474	0.4181	0.028*
C10	0.7729 (2)	0.6096 (3)	0.46404 (9)	0.0220 (5)
C11	0.6408 (2)	0.6450 (3)	0.47609 (9)	0.0235 (5)
H11	0.5661	0.5741	0.4598	0.028*
C12	0.8813 (2)	0.7162 (3)	0.48807 (9)	0.0234 (5)
H12	0.9713	0.6935	0.4798	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0339 (4)	0.0352 (4)	0.0373 (4)	-0.0022 (3)	0.0007 (3)	-0.0044 (3)
C2	0.073 (2)	0.0227 (13)	0.0245 (12)	-0.0002 (13)	0.0045 (13)	-0.0058 (10)
C3	0.0487 (16)	0.0284 (13)	0.0314 (13)	0.0127 (12)	0.0133 (12)	-0.0009 (9)

C4	0.0167 (9)	0.0190 (10)	0.0217 (10)	0.0007 (8)	-0.0012 (8)	0.0046 (7)
C5	0.0288 (11)	0.0183 (11)	0.0230 (11)	0.0037 (9)	0.0073 (9)	0.0019 (9)
C6	0.0396 (14)	0.0218 (12)	0.0262 (12)	0.0020 (10)	0.0118 (10)	-0.0013 (9)
C7	0.0309 (13)	0.0223 (12)	0.0282 (12)	-0.0010 (9)	0.0096 (10)	-0.0063 (9)
N8	0.0293 (11)	0.0214 (10)	0.0269 (10)	0.0010 (8)	0.0055 (8)	-0.0061 (8)
C9	0.0260 (11)	0.0207 (11)	0.0238 (11)	0.0007 (9)	0.0073 (9)	-0.0010 (9)
C10	0.0269 (12)	0.0181 (11)	0.0211 (10)	-0.0002 (9)	0.0028 (8)	-0.0003 (9)
C11	0.0236 (11)	0.0220 (11)	0.0248 (11)	-0.0024 (9)	0.0026 (9)	-0.0030 (9)
C12	0.0200 (11)	0.0245 (12)	0.0263 (11)	0.0009 (9)	0.0048 (9)	-0.0015 (9)

Geometric parameters (Å, °)

S1—C2	1.691 (3)	C7—N8	1.455 (3)
S1—C5	1.693 (2)	C7—H7A	0.99
C2—C3	1.345 (4)	C7—H7B	0.99
C2—H2	0.95	N8—C9	1.266 (3)
C3—C4	1.402 (4)	C9—C10	1.472 (3)
C3—H3	0.95	C9—H9	0.95
C4—C5	1.427 (3)	C10—C11	1.397 (3)
C4—H4	0.95	C10—C12	1.397 (3)
C5—C6	1.501 (3)	C11—C12 ⁱ	1.388 (3)
C6—C7	1.520 (3)	C11—H11	0.95
C6—H6A	0.99	C12—C11 ⁱ	1.388 (3)
C6—H6B	0.99	C12—H12	0.95
C2—S1—C5	93.55 (13)	N8—C7—C6	109.48 (19)
C3—C2—S1	111.6 (2)	N8—C7—H7A	109.8
C3—C2—H2	124.2	C6—C7—H7A	109.8
S1—C2—H2	124.2	N8—C7—H7B	109.8
C2—C3—C4	114.1 (2)	C6—C7—H7B	109.8
C2—C3—H3	122.9	H7A—C7—H7B	108.2
C4—C3—H3	122.9	C9—N8—C7	117.3 (2)
C3—C4—C5	111.0 (2)	N8—C9—C10	122.8 (2)
C3—C4—H4	124.5	N8—C9—H9	118.6
C5—C4—H4	124.5	C10—C9—H9	118.6
C4—C5—C6	128.3 (2)	C11—C10—C12	119.2 (2)
C4—C5—S1	109.73 (17)	C11—C10—C9	121.4 (2)
C6—C5—S1	121.93 (18)	C12—C10—C9	119.4 (2)
C5—C6—C7	113.0 (2)	C12 ⁱ —C11—C10	119.9 (2)
C5—C6—H6A	109	C12 ⁱ —C11—H11	120
C7—C6—H6A	109	C10—C11—H11	120
C5—C6—H6B	109	C11 ⁱ —C12—C10	120.8 (2)
C7—C6—H6B	109	C11 ⁱ —C12—H12	119.6
H6A—C6—H6B	107.8	C10—C12—H12	119.6
C5—S1—C2—C3	0.4 (2)	C5—C6—C7—N8	177.7 (2)
S1—C2—C3—C4	-0.9 (3)	C6—C7—N8—C9	121.8 (2)
C2—C3—C4—C5	1.1 (3)	C7—N8—C9—C10	179.9 (2)

C3—C4—C5—C6	-179.2 (2)	N8—C9—C10—C11	-2.7 (4)
C3—C4—C5—S1	-0.8 (2)	N8—C9—C10—C12	177.7 (2)
C2—S1—C5—C4	0.25 (18)	C12—C10—C11—C12 ⁱ	-0.5 (4)
C2—S1—C5—C6	178.7 (2)	C9—C10—C11—C12 ⁱ	179.9 (2)
C4—C5—C6—C7	69.3 (3)	C11—C10—C12—C11 ⁱ	0.6 (4)
S1—C5—C6—C7	-108.9 (2)	C9—C10—C12—C11 ⁱ	-179.9 (2)

Symmetry code: (i) $-x+3/2, -y+3/2, -z+1$.

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the thiophene and benzene rings, respectively.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C4—H4 \cdots N8 ⁱⁱ	0.95	2.61	3.514 (3)	159
C2—H2 \cdots Cg1 ⁱⁱⁱ	0.95	2.79	3.702 (3)	161
C6—H6A \cdots Cg2 ^{iv}	0.99	2.72	3.515 (3)	137
C6—H6A \cdots Cg2 ^v	0.99	2.72	3.515 (3)	137

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