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N,N'-Bis[(*E*)-(5-chloro-2-thienyl)methylene]ethane-1,2-diamine

 R. Prasath,^a P. Bhavana,^{a‡} Seik Weng Ng^b and Edward R. T. Tiekink^{b*}
^aChemistry Group, BITS, Pilani – K. K. Birla Goa Campus, Goa, India 403 726, and

^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: Edward.Tiekink@gmail.com

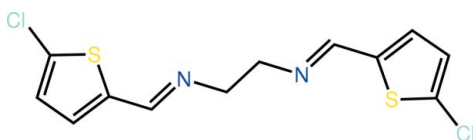
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.038; wR factor = 0.117; data-to-parameter ratio = 19.2.

The full molecule of the title compound, $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}_2$, is generated by the application of a centre of inversion. The thiophene and imine residues are co-planar [the $\text{N}-\text{C}-\text{C}-\text{S}$ torsion angle is $-2.5(4)^\circ$] and the conformation about the imine bond [1.268 (4) Å] is *E*. Supramolecular arrays are formed in the *bc* plane via $\text{C}-\text{Cl}\cdots\pi$ interactions and these stack along the *a* axis.

Related literature

For background to 2-substituted thiophenes, see: Campaigne (1984); Kleemann *et al.* (2006). For related structures, see: Wang *et al.* (2007); Wardell *et al.* (2010); Prasath *et al.* (2010).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}_2$
 $M_r = 317.24$

 Monoclinic, $P2_1/c$
 $a = 14.682(2)$ Å

 $b = 4.7016(7)$ Å

 $c = 10.6607(15)$ Å

 $\beta = 109.439(2)^\circ$
 $V = 693.92(17)$ Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 0.75$ mm⁻¹
 $T = 100$ K

 $0.25 \times 0.15 \times 0.05$ mm

Data collection

Bruker SMART APEX

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.835$, $T_{\max} = 0.963$

5721 measured reflections

1576 independent reflections

 1270 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.117$
 $S = 1.01$

1576 reflections

82 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.36$ e Å⁻³
 $\Delta\rho_{\min} = -0.48$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

 Cg1 is the centroid of the $\text{S3}, \text{C3}-\text{C6}$ ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C6}-\text{Cl1}\cdots\text{Cg1}^1$	1.71 (1)	3.52 (1)	3.994 (3)	93 (1)

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2729).

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[‡] Additional correspondence author, e-mail: juliebhavana@gmail.com.

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S1. Comment

Interest in their putative biological activity (Wardell *et al.*, 2010) motivates studies of 2-substituted thiophene rings (Campaigne, 1984; Kleemann *et al.*, 2006), including on-going crystallographic investigations (Wardell *et al.* 2010; Prasath *et al.*, 2010).

The asymmetric unit of (I), Fig. 1, comprises half a molecule with the full molecule generated by a crystallographic centre of inversion. The thiophene residue is co-planar with the imine group as seen in the value of the N1—C2—C3—S1 torsion angle of $-2.5(4)^\circ$. The conformation about the imine N1—C2 [1.268(4) Å] bond is *E*. The observed conformation matches closely those found for related compounds (Wang *et al.*, 2007; Prasath *et al.*, 2010).

The most prominent contacts in the crystal packing are of the type C—Cl \cdots π , Table 1. These serve to connect molecules into a 2-D array in the *bc* plane, Fig. 2, which stack along the *a* axis, Fig. 3, with the chlorido atoms facing each other. Concerning the latter, the closest interlayer Cl \cdots Cl contact is 3.3831(11) Å [symmetry operation: $2 - x, -1/2 + y, 3/2 - z$].

S2. Experimental

A mixture of 5-chloro-2-thiophenecarboxaldehyde (0.43 ml, 0.004 *M*) and ethylenediamine (0.13 ml, 0.002 *M*) was stirred in dichloromethane for 3 h at room temperature. The solvent from the reaction mixture was removed under reduced pressure. The resulting solid was dried and purified by column chromatography using a 1:3 mixture of ethyl acetate and hexane. Recrystallization was by slow evaporation of a dichloromethane solution of (I) which yielded colourless needles (yield: 73%). *M.* pt. 353–355 K.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{equiv}}(\text{C})$. In the final refinement a low angle reflection evidently effected by the beam stop was omitted, *i.e.* (100).

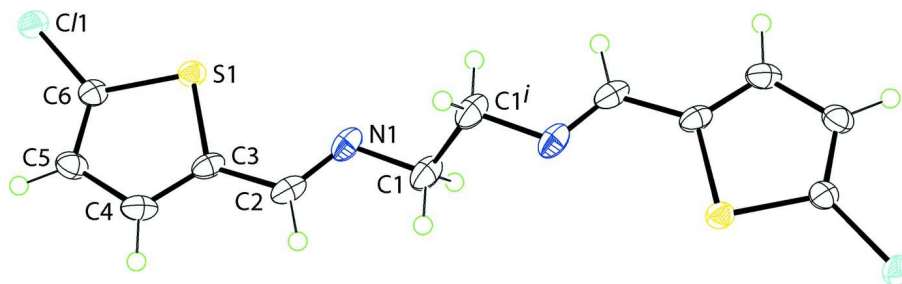


Figure 1

Molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. Symmetry operation *i*: $1 - x, 1 - y, 1 - z$.

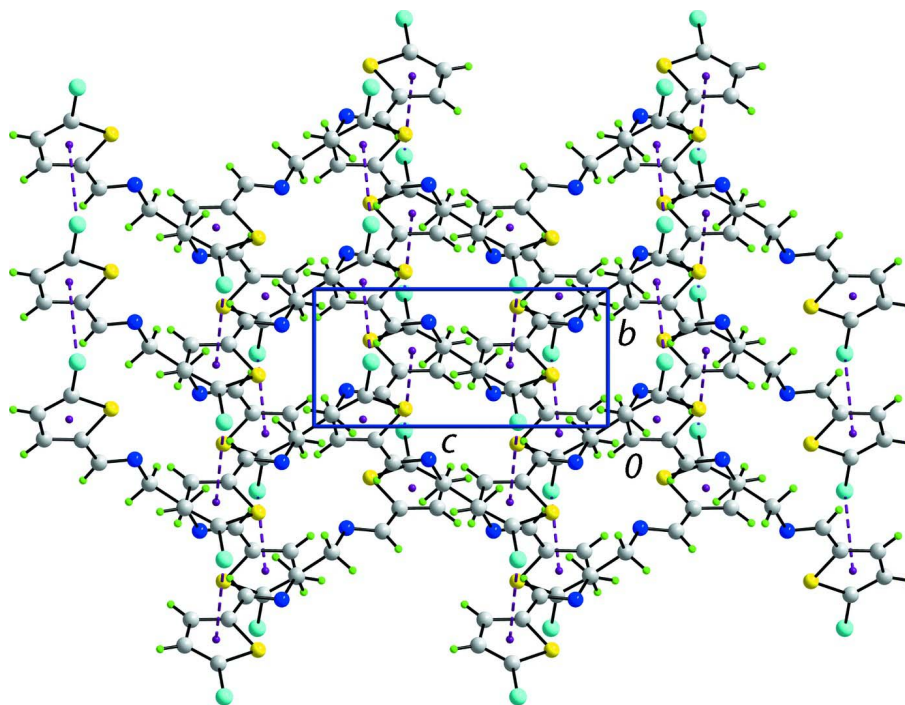


Figure 2

A view of the supramolecular 2-D array in the *bc* plane mediated by C—Cl \cdots π interactions (purple dashed lines).

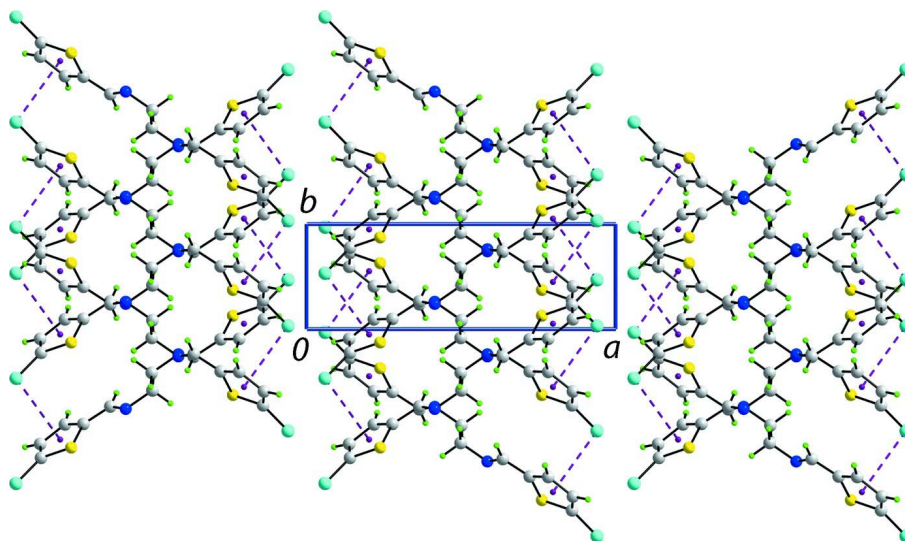


Figure 3

Stacking of layers along the *a* axis in the crystal structure of (I). The C—Cl \cdots π interactions are shown as purple dashed lines.

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Crystal data

$C_{12}H_{10}Cl_2N_2S_2$

$M_r = 317.24$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 14.682 (2) \text{ \AA}$

$b = 4.7016 (7) \text{ \AA}$

$c = 10.6607 (15) \text{ \AA}$
 $\beta = 109.439 (2)^\circ$
 $V = 693.92 (17) \text{ \AA}^3$
 $Z = 2$
 $F(000) = 324$
 $D_x = 1.518 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2363 reflections
 $\theta = 3.0\text{--}28.0^\circ$
 $\mu = 0.75 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Prism, colourless
 $0.25 \times 0.15 \times 0.05 \text{ mm}$

Data collection

Bruker SMART APEX
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.835$, $T_{\max} = 0.963$

5721 measured reflections
 1576 independent reflections
 1270 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.9^\circ$
 $h = -18 \rightarrow 18$
 $k = -6 \rightarrow 6$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.117$
 $S = 1.01$
 1576 reflections
 82 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
 $w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.3727P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e \AA}^{-3}$

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 $F^2 > \sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.94014 (5)	1.46904 (14)	0.80609 (6)	0.0258 (2)
S1	0.76180 (5)	1.12742 (14)	0.69149 (6)	0.0220 (2)
N1	0.58522 (16)	0.7601 (5)	0.6104 (2)	0.0286 (5)
C1	0.4988 (2)	0.5840 (6)	0.5603 (3)	0.0333 (7)
H1A	0.4406	0.7062	0.5355	0.040*
H1B	0.4955	0.4514	0.6308	0.040*
C2	0.63515 (19)	0.7367 (6)	0.7325 (3)	0.0267 (6)
H2	0.6151	0.6077	0.7868	0.032*
C3	0.72211 (19)	0.9026 (5)	0.7907 (3)	0.0238 (6)
C4	0.7822 (2)	0.9074 (6)	0.9193 (3)	0.0282 (6)

H4	0.7716	0.7970	0.9879	0.034*
C5	0.8620 (2)	1.0934 (6)	0.9411 (3)	0.0271 (6)
H5	0.9109	1.1220	1.0247	0.033*
C6	0.85924 (19)	1.2254 (6)	0.8263 (2)	0.0220 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0284 (4)	0.0242 (4)	0.0285 (3)	-0.0067 (2)	0.0141 (3)	-0.0066 (2)
S1	0.0249 (4)	0.0199 (4)	0.0230 (3)	-0.0031 (2)	0.0104 (3)	-0.0007 (2)
N1	0.0241 (12)	0.0212 (12)	0.0432 (14)	-0.0047 (9)	0.0149 (10)	-0.0032 (10)
C1	0.0288 (15)	0.0285 (15)	0.0463 (18)	-0.0089 (12)	0.0173 (13)	-0.0043 (13)
C2	0.0302 (14)	0.0184 (13)	0.0402 (16)	-0.0028 (11)	0.0232 (12)	-0.0029 (11)
C3	0.0287 (14)	0.0169 (13)	0.0323 (14)	-0.0025 (10)	0.0187 (12)	-0.0013 (10)
C4	0.0416 (17)	0.0220 (14)	0.0274 (13)	-0.0028 (12)	0.0202 (12)	0.0001 (10)
C5	0.0353 (15)	0.0261 (15)	0.0219 (12)	-0.0025 (11)	0.0122 (11)	-0.0033 (10)
C6	0.0259 (13)	0.0188 (13)	0.0241 (12)	-0.0002 (10)	0.0122 (10)	-0.0050 (9)

Geometric parameters (Å, °)

Cl1—C6	1.714 (3)	C2—C3	1.448 (4)
S1—C6	1.719 (3)	C2—H2	0.9500
S1—C3	1.728 (3)	C3—C4	1.362 (4)
N1—C2	1.268 (4)	C4—C5	1.419 (4)
N1—C1	1.459 (3)	C4—H4	0.9500
C1—C1 ⁱ	1.519 (6)	C5—C6	1.361 (4)
C1—H1A	0.9900	C5—H5	0.9500
C1—H1B	0.9900		
C6—S1—C3	90.50 (13)	C4—C3—S1	111.7 (2)
C2—N1—C1	117.5 (2)	C2—C3—S1	119.7 (2)
N1—C1—C1 ⁱ	110.1 (3)	C3—C4—C5	113.4 (2)
N1—C1—H1A	109.6	C3—C4—H4	123.3
C1 ⁱ —C1—H1A	109.6	C5—C4—H4	123.3
N1—C1—H1B	109.6	C6—C5—C4	111.0 (3)
C1 ⁱ —C1—H1B	109.6	C6—C5—H5	124.5
H1A—C1—H1B	108.2	C4—C5—H5	124.5
N1—C2—C3	121.3 (2)	C5—C6—Cl1	127.1 (2)
N1—C2—H2	119.4	C5—C6—S1	113.4 (2)
C3—C2—H2	119.4	Cl1—C6—S1	119.53 (15)
C4—C3—C2	128.6 (2)		
C2—N1—C1—C1 ⁱ	-126.6 (3)	S1—C3—C4—C5	0.0 (3)
C1—N1—C2—C3	179.9 (2)	C3—C4—C5—C6	0.2 (4)
N1—C2—C3—C4	178.4 (3)	C4—C5—C6—Cl1	179.4 (2)
N1—C2—C3—S1	-2.5 (4)	C4—C5—C6—S1	-0.3 (3)
C6—S1—C3—C4	-0.1 (2)	C3—S1—C6—C5	0.3 (2)

C6—S1—C3—C2	-179.4 (2)	C3—S1—C6—C11	-179.49 (17)
C2—C3—C4—C5	179.1 (3)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of the S3,C3-C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—C11 \cdots Cg1 ⁱⁱ	1.71 (1)	3.52 (1)	3.994 (3)	93 (1)

Symmetry code: (ii) $x, y+1, z$.