# organic compounds

# 2,5-Bis{[(−)-(S)-1-(4-bromophenyl)-ethyl]iminomethyl}thiophene

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The title compound, $C_{22}H_{20}Br_2N_2S$, was synthesized under solvent-free conditions. The molecule shows crystallographic $C_2$ symmetry, with the S atom of the central thiophene ring lying on a twofold rotation axis. Furthermore, as a consequence of the (S,S) stereochemistry, the molecule has a twisted conformation. The dihedral angle between the thiophene and benzene rings is 72.7 (2)° and that between the two benzene rings is 55.9 (2)°. In the crystal, molecules are arranged in a chevron-like pattern, without any significant intermolecular interactions.

## Related literature

For the solvent-free 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: Bernès et al. (2013); Kudyakova et al. (2012).
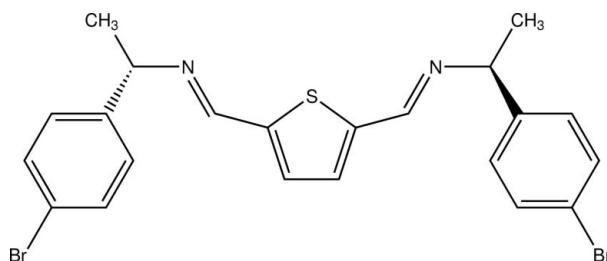


## Experimental

### Crystal data

| | |
|---|---|
| $C_{22}H_{20}Br_2N_2S$ | $V$ = 1101.11 (14) Å$^3$ |
| $M_r$ = 504.27 | $Z$ = 2 |
| Monoclinic, $C2$ | Mo $K\alpha$ radiation |
| $a$ = 24.5329 (15) Å | $\mu$ = 3.79 mm$^{-1}$ |
| $b$ = 5.9762 (5) Å | $T$ = 298 K |
| $c$ = 7.5944 (5) Å | 0.52 × 0.15 × 0.06 mm |
| $\beta$ = 98.536 (6)° | |

### Data collection

| | |
|---|---|
| Agilent Xcalibur (Atlas, Gemini) diffractometer | 6101 measured reflections |
| Absorption correction: numerical (*CrysAlis PRO*; Agilent, 2013) | 2107 independent reflections |
| $T_{min}$ = 0.400, $T_{max}$ = 0.815 | 1630 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.035 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.036 | $\Delta\rho_{max}$ = 0.20 e Å$^{-3}$ |
| $wR(F^2)$ = 0.072 | $\Delta\rho_{min}$ = −0.35 e Å$^{-3}$ |
| $S$ = 1.03 | Absolute structure: Flack (1983), |
| 2107 reflections | 914 Friedel pairs |
| 124 parameters | Absolute structure parameter: |
| 1 restraint | 0.011 (8) |
| H-atom parameters constrained | |

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2013); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5340).

## References

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# supplementary materials

## 2,5-Bis{[(−)-(*S*)-1-(4-bromophenyl)ethyl]iminomethyl}thiophene

**Angel Mendoza, Sylvain Bernès, Guadalupe Hernández-Téllez, Oscar Portillo-Moreno and René Gutiérrez**

### 1. Comment

In continuation of our work focused on chiral bisimines (Espinosa Leija *et al.*, 2009; Bernès *et al.*, 2013), we have now synthesized the title compound under the solvent-free approach because of the cleaner, safer, and easier aspects to perform in the synthetic work. So, solvent-free conditions are becoming more popular and it is often claimed that the best solvent is no solvent. (Tanaka & Toda, 2000).

The bis-aldimine compound shows an *E* configuration over every imine bond (Fig. 1). The molecule is an (*S*,*S*) diastereoisomer as expected by synthetic procedure. The asymmetric unit contains a half-molecule. The S atom of the molecule is located on a twofold rotation axis of the space group *C*2. and as a consequence the Br-aldimines groups are placed opposite to the central thiophene ring. Only some previous reports of 2,5-thiophene compounds with achiral or chiral substituents have showed $C_2$ crystallographic symmetry like title compound (Kudyakova *et al.*, 2012, space group *C*2/*c*; Bernès *et al.*, 2013, space group *P*22₁2₁). The crystal packing does not feature any particular interactions (intra or intermolecular) and the supramolecular arrangement in the solid state shows a chevron-like pattern viewed along the *b* axis (Fig. 2).

### 2. Experimental

Under solvent-free conditions, a mixture of 2,5-thiophenedicarboxaldehyde (100 mg, 0.71 mmol) and (*S*)-(−)-1-(4-bromophenyl)ethylamine (285 mg, 1.42 mmol) in a 1:2 molar ratio were mixed at room temperature, giving a white solid. The crude was recrystallized from CH₂Cl₂, affording colorless crystals of the title compound.

Yield 96%; m.p. 147–149 °C. Spectroscopic data: $[a]_D^{25}$ = +59.6 (c 1, CHCl₃). IR (KBr): 1623 cm⁻¹ (C=N). ¹H NMR (400 MHz, CDCl₃/TMS): $\delta$ = 1.51, 1.53 (d, 6H, CHC*H₃*,), 4.44, 4.45, 4.47, 4.49(q, 2H, C*H*), 7.29–7.45 (m, 10 H, Ar), 8.36 (s, 2 H, *H*C=N). ¹³C NMR (100 MHz, CDCl₃/TMS) $\delta$ = 25.1 (C*C*H₃), 68.7 (*C*HCH₃), 120.6 (Ar), 128.3 (Ar), 130.1 (Ar), 131.4 (Ar), 144.0 (Ar), 145.1 (Ar), 152. 7 (H*C*=N). MS—EI: *m/z*= 504 (*M*⁺).

### 3. Refinement

The absolute configuration was determined using the anomalous dispersion of the Br atom, and was that expected from the synthesis, carried-out with an enantiomerically pure amine. All H atoms were placed in calculated positions, with C—H bond lengths fixed to 0.96 Å for the methyl group and 0.93 Å for aromatic CH groups. Isotropic displacement parameters were calculated as $U_{iso}(H) = 1.5U_{eq}$(carrier atom) for the methyl group and $U_{iso}(H) = 1.2U_{eq}$(carrier atom) otherwise.

## Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis RED* (Agilent, 2013); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).
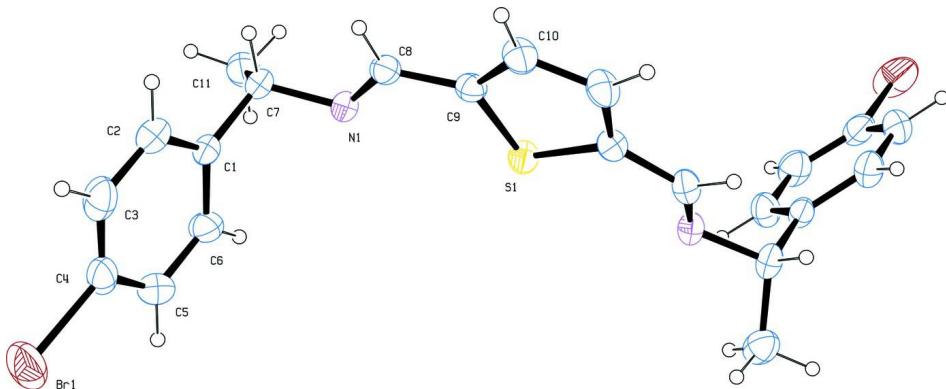


**Figure 1**

The molecular structure of title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.
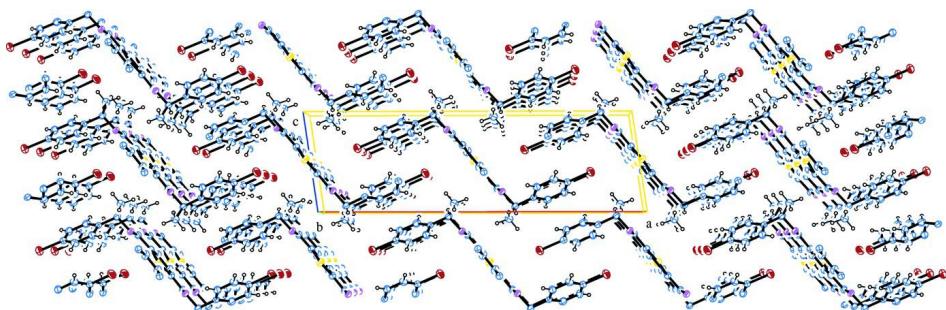


**Figure 2**

A packing diagram of the title compound, viewed along the *b* axis.

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

*Crystal data*

| | |
|---|---|
| $C_{22}H_{20}Br_2N_2S$ | $F(000) = 504$ |
| $M_r = 504.27$ | $D_x = 1.521$ Mg m$^{-3}$ |
| Monoclinic, $C2$ | Melting point: 420 K |
| Hall symbol: C 2y | Mo *Kα* radiation, $\lambda = 0.71073$ Å |
| $a = 24.5329$ (15) Å | Cell parameters from 1609 reflections |
| $b = 5.9762$ (5) Å | $\theta = 4.4–25.2°$ |
| $c = 7.5944$ (5) Å | $\mu = 3.79$ mm$^{-1}$ |
| $\beta = 98.536$ (6)° | $T = 298$ K |
| $V = 1101.11$ (14) Å$^3$ | Prism, colourless |
| $Z = 2$ | $0.52 \times 0.15 \times 0.06$ mm |

*Data collection*

| | |
|---|---|
| Agilent Xcalibur (Atlas, Gemini) diffractometer | 6101 measured reflections |
| Radiation source: Enhance (Mo) X-ray Source | 2107 independent reflections |
| Graphite monochromator | 1630 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 10.5564 pixels mm$^{-1}$ | $R_{int} = 0.035$ |
| $\omega$ scans | $\theta_{max} = 26.1°$, $\theta_{min} = 3.0°$ |
| Absorption correction: numerical (*CrysAlis PRO*; Agilent, 2013) | $h = -30 \rightarrow 30$ |
| $T_{min} = 0.400$, $T_{max} = 0.815$ | $k = -7 \rightarrow 7$ |
| | $l = -9 \rightarrow 9$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | H-atom parameters constrained |
| $wR(F^2) = 0.072$ | $w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.0296P]$ |
| $S = 1.03$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2107 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 124 parameters | $\Delta\rho_{max} = 0.20$ e Å$^{-3}$ |
| 1 restraint | $\Delta\rho_{min} = -0.35$ e Å$^{-3}$ |
| 0 constraints | Absolute structure: Flack (1983), 914 Friedel pairs |
| | Absolute structure parameter: 0.011 (8) |

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.15628 (2) | 0.49000 (18) | 0.61658 (7) | 0.1112 (4) |
| S1 | 0.5 | 0.2196 (2) | 0.5 | 0.0472 (4) |
| C9 | 0.47486 (16) | 0.0181 (7) | 0.6292 (5) | 0.0427 (10) |
| C11 | 0.4216 (2) | 0.4840 (10) | 1.0744 (5) | 0.0657 (13) |
| H11A | 0.4194 | 0.6248 | 1.0129 | 0.099* |
| H11B | 0.4595 | 0.4499 | 1.1175 | 0.099* |
| H11C | 0.4013 | 0.4929 | 1.173 | 0.099* |
| C4 | 0.2306 (2) | 0.4327 (11) | 0.7169 (6) | 0.0639 (15) |
| C1 | 0.33894 (18) | 0.3489 (7) | 0.8651 (5) | 0.0441 (11) |
| C6 | 0.3243 (2) | 0.5418 (9) | 0.7670 (6) | 0.0569 (13) |
| H6 | 0.3514 | 0.6457 | 0.7513 | 0.068* |
| N1 | 0.43094 (15) | 0.2748 (6) | 0.8052 (5) | 0.0452 (9) |
| C5 | 0.2703 (2) | 0.5823 (9) | 0.6921 (7) | 0.0674 (16) |
| H5 | 0.2613 | 0.711 | 0.6253 | 0.081* |
| C2 | 0.2971 (2) | 0.1997 (9) | 0.8837 (6) | 0.0603 (13) |
| H2 | 0.3056 | 0.0688 | 0.9482 | 0.072* |
| C3 | 0.2431 (2) | 0.2389 (11) | 0.8092 (7) | 0.0690 (14) |
| H3 | 0.2157 | 0.135 | 0.8218 | 0.083* |
| C7 | 0.3974 (2) | 0.3024 (8) | 0.9485 (5) | 0.0501 (12) |

| | | | |
|---|---|---|---|
| H7 | 0.398 | 0.1616 | 1.0149 | 0.06* |
| C8 | 0.44434 (18) | 0.0769 (7) | 0.7709 (6) | 0.0469 (12) |
| H8 | 0.4339 | −0.038 | 0.8414 | 0.056* |
| C10 | 0.4853 (2) | −0.1907 (8) | 0.5728 (7) | 0.0540 (13) |
| H10 | 0.4743 | −0.3205 | 0.625 | 0.065* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0529 (4) | 0.2036 (8) | 0.0729 (4) | 0.0279 (5) | −0.0044 (3) | −0.0229 (5) |
| S1 | 0.0553 (11) | 0.0347 (8) | 0.0547 (10) | 0 | 0.0179 (8) | 0 |
| C9 | 0.043 (2) | 0.038 (2) | 0.047 (2) | 0.001 (2) | 0.0052 (18) | 0.005 (2) |
| C11 | 0.058 (3) | 0.085 (3) | 0.053 (2) | 0.009 (3) | 0.005 (2) | −0.003 (3) |
| C4 | 0.044 (3) | 0.106 (5) | 0.042 (2) | 0.005 (3) | 0.006 (2) | −0.009 (3) |
| C1 | 0.044 (3) | 0.053 (3) | 0.037 (2) | 0.001 (2) | 0.012 (2) | 0.002 (2) |
| C6 | 0.052 (3) | 0.062 (3) | 0.056 (3) | −0.002 (3) | 0.007 (2) | 0.016 (3) |
| N1 | 0.042 (2) | 0.052 (2) | 0.0439 (19) | 0.0014 (17) | 0.0134 (17) | 0.0053 (16) |
| C5 | 0.063 (4) | 0.084 (4) | 0.053 (3) | 0.010 (3) | 0.003 (3) | 0.014 (3) |
| C2 | 0.064 (4) | 0.067 (3) | 0.053 (3) | −0.002 (3) | 0.017 (2) | 0.011 (3) |
| C3 | 0.051 (3) | 0.094 (4) | 0.065 (3) | −0.019 (3) | 0.017 (3) | −0.005 (3) |
| C7 | 0.051 (3) | 0.060 (3) | 0.043 (2) | 0.006 (2) | 0.017 (2) | 0.011 (2) |
| C8 | 0.039 (3) | 0.051 (3) | 0.051 (3) | 0.000 (2) | 0.008 (2) | 0.013 (2) |
| C10 | 0.057 (3) | 0.035 (2) | 0.073 (3) | −0.001 (2) | 0.017 (3) | 0.005 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C4 | 1.899 (5) | C1—C7 | 1.505 (6) |
| S1—C9$^i$ | 1.724 (4) | C6—H6 | 0.93 |
| S1—C9 | 1.724 (4) | C6—C5 | 1.383 (7) |
| C9—C8 | 1.442 (6) | N1—C7 | 1.468 (5) |
| C9—C10 | 1.356 (6) | N1—C8 | 1.265 (5) |
| C11—H11A | 0.96 | C5—H5 | 0.93 |
| C11—H11B | 0.96 | C2—H2 | 0.93 |
| C11—H11C | 0.96 | C2—C3 | 1.382 (7) |
| C11—C7 | 1.509 (7) | C3—H3 | 0.93 |
| C4—C5 | 1.356 (7) | C7—H7 | 0.98 |
| C4—C3 | 1.365 (7) | C8—H8 | 0.93 |
| C1—C6 | 1.391 (6) | C10—C10$^i$ | 1.405 (10) |
| C1—C2 | 1.383 (7) | C10—H10 | 0.93 |
| | | | |
| C9—S1—C9$^i$ | 91.4 (3) | C4—C5—H5 | 120.3 |
| C8—C9—S1 | 121.6 (3) | C6—C5—H5 | 120.3 |
| C10—C9—S1 | 111.2 (3) | C1—C2—H2 | 119 |
| C10—C9—C8 | 127.1 (4) | C3—C2—C1 | 122.0 (5) |
| H11A—C11—H11B | 109.5 | C3—C2—H2 | 119 |
| H11A—C11—H11C | 109.5 | C4—C3—C2 | 118.9 (5) |
| H11B—C11—H11C | 109.5 | C4—C3—H3 | 120.6 |
| C7—C11—H11A | 109.5 | C2—C3—H3 | 120.6 |
| C7—C11—H11B | 109.5 | C11—C7—H7 | 108.5 |
| C7—C11—H11C | 109.5 | C1—C7—C11 | 113.2 (4) |

| C5—C4—Br1 | 119.5 (4) | C1—C7—H7 | 108.5 |
| C5—C4—C3 | 121.3 (5) | N1—C7—C11 | 109.9 (4) |
| C3—C4—Br1 | 119.2 (4) | N1—C7—C1 | 108.2 (3) |
| C6—C1—C7 | 122.2 (4) | N1—C7—H7 | 108.5 |
| C2—C1—C6 | 116.9 (4) | C9—C8—H8 | 117.9 |
| C2—C1—C7 | 120.9 (4) | N1—C8—C9 | 124.1 (4) |
| C1—C6—H6 | 119.3 | N1—C8—H8 | 117.9 |
| C5—C6—C1 | 121.3 (5) | C9—C10—C10<sup>i</sup> | 113.1 (3) |
| C5—C6—H6 | 119.3 | C9—C10—H10 | 123.5 |
| C8—N1—C7 | 116.7 (3) | C10<sup>i</sup>—C10—H10 | 123.5 |
| C4—C5—C6 | 119.5 (5) | | |
| | | | |
| Br1—C4—C5—C6 | 179.2 (4) | C2—C1—C6—C5 | 0.2 (7) |
| Br1—C4—C3—C2 | −179.2 (4) | C2—C1—C7—C11 | −122.6 (5) |
| S1—C9—C8—N1 | 4.2 (6) | C2—C1—C7—N1 | 115.3 (4) |
| S1—C9—C10—C10<sup>i</sup> | 1.2 (7) | C3—C4—C5—C6 | −2.3 (8) |
| C9<sup>i</sup>—S1—C9—C8 | −177.3 (4) | C7—C1—C6—C5 | −179.6 (4) |
| C9<sup>i</sup>—S1—C9—C10 | −0.4 (3) | C7—C1—C2—C3 | 179.7 (4) |
| C1—C6—C5—C4 | 1.0 (7) | C7—N1—C8—C9 | 176.9 (4) |
| C1—C2—C3—C4 | −1.0 (7) | C8—C9—C10—C10<sup>i</sup> | 177.9 (5) |
| C6—C1—C2—C3 | −0.2 (7) | C8—N1—C7—C11 | 131.9 (4) |
| C6—C1—C7—C11 | 57.3 (5) | C8—N1—C7—C1 | −104.0 (4) |
| C6—C1—C7—N1 | −64.8 (5) | C10—C9—C8—N1 | −172.2 (5) |
| C5—C4—C3—C2 | 2.3 (7) | | |

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