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1,5-Bis[(2-thienyl)methyleneamino]-naphthalene

Jan Grzegorz Małecki,[a] Rafal Kruszynski[b]* and Grzegorz Jarosz[c]

[a]Department of Crystallography, Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland, [b]Institute of General and Ecological Chemistry, Technical University of Łódź, Zeromskiego 116, 90-924 Łódź, Poland, and [c]Faculty of Chemistry, Silesian University of Technology, B. Krzywoustego 4, 44-100 Gliwice, Poland
Correspondence e-mail: rafal.kruszynski@p.lodz.pl

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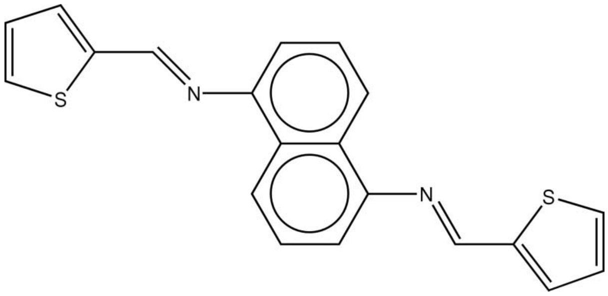
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.094; data-to-parameter ratio = 14.1.

All interatomic distances in the centrosymmetric title compound, $C_{20}H_{14}N_2S_2$, are normal. The dihedral angle between the naphthyl and thienyl rings is 49.38 (6)°. Molecules assemble into chains along the c-axis direction *via* thienyl–naphthyl C—H···π interactions. The thienyl rings stack at an interplanar distance of 3.43 Å [offset with C_4S ring centroids 3.827 (1) Å apart].

Related literature

For examples of related syntheses, see: Calligaris *et al.* (1972); Kruszynski *et al.* (2006); Sawka-Dobrowolska *et al.* (1990); Liu *et al.* (2000); Siswanta *et al.* (1996); Williams (1972); Cohen *et al.* (1964); Moustakali-Mavridis *et al.* (1978); Zotti *et al.* (1995); Zhu & Swager (1996); Prasad & Williams (1991); Marder *et al.* (1991); Chou *et al.* (1996); Wolf & Wrighton (1994); Yamamoto *et al.* (1992); Hirao (2002). See also: Allen (2002); Desiraju & Steiner (1999).



Experimental

Crystal data

$C_{20}H_{14}N_2S_2$
M_r = 346.45
Monoclinic, $C2/c$
a = 18.4421 (6) Å
b = 7.2454 (2) Å
c = 13.1885 (3) Å
β = 102.254 (3)°
V = 1722.10 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 291.0 (3) K
0.34 × 0.33 × 0.32 mm

Data collection

Kuma KM4 CCD diffractometer
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
$T_{\min}$ = 0.896, $T_{\max}$ = 0.899
8325 measured reflections
1537 independent reflections
1304 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.094
S = 1.06
1537 reflections
109 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.17 e Å^{-3}
$\Delta\rho_{\min}$ = −0.28 e Å^{-3}

Table 1
Selected torsion angles (°).

C2—C1—C5—N1	178.01 (17)	C5—N1—C6—C7	−46.7 (2)
C1—C5—N1—C6	177.37 (15)		

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C6-containing naphthyl six-membered ring.

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···N1	0.93	2.51	2.828 (2)	100
C2—H2···*Cg*1$^{\rm i}$	0.93	2.78	3.7015 (18)	173

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

Data collection: *CrysAlis CCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990*b*) and *ORTEP-3* (Version 1.062; Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG3103).

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supplementary materials

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1,5-Bis[(2-thienyl)methyleneamino]naphthalene

J. G. Malecki, R. Kruszynski and G. Jarosz

Comment

A principal area of interest in modern supramolecular chemistry is the synthesis of new ligands, which are able to selectively complex organic or inorganic compounds (Calligaris *et al.*, 1972; Kruszynski *et al.*, 2006). Supramolecular Schiff bases are known to yield stable metal complexes (Sawka-Dobrowolska *et al.*, 1990). On the other hand introduction of thio-substituted pendant arms lower the ability of the ligand in binding alkaline and alkaline earth hard cations and increase the ability to selectively bind transition and heavy metals soft cations such as Ag^+, Pb^{2+}, Hg^{2+} (Liu *et al.*, 2000; Siswanta *et al.*, 1996). Thus we decided to synthesis and determine the structure of the title compound (I) which has the advantage of both being a Schiff base and having sulfur containing pendant arms.

For many years these type of supramolecular compounds have been widely used as antibacterial, anticancer, and antiinflammatory agents (Williams, 1972), as photochromes and thermochromes (Cohen *et al.*, 1964; Moustakali-Mavridis *et al.*, 1978; Zotti *et al.*, 1995; Zhu & Swager, 1996), especially in optical communications, information processing, frequency doubling and integrated optics (Prasad & Williams, 1991; Marder *et al.*, 1991; Chou *et al.*, 1996). These compounds are also important substrates for metal-free and metal-containing organic conducting redox polymers (Wolf & Wrighton, 1994; Yamamoto *et al.*, 1992; Hirao, 2002).

All of the interatomic distances in the title compound, (I), (Fig. 1), are normal. The Schiff base C5═N1 bond length 1.272 (2) Å is almost exactly equal to typical C═N bond length of uncomplexed Schiff bases (1.274 Å from the Cambridge Structural Database, version 5.28 (CSD hereafter); Allen, 2002). The torsion angles of the $\mathrm{C_{(thienyl)}{=}C_{(thienyl)}{-}C{=}}N\mathrm{{-}C_{(naphthyl)}{\cdots}C_{(naphthyl)}}$ bridge (Table 1) lie in ranges typical for similar compounds. For 23 compounds (38 structural fragments) containing the (substitued thienyl)—C═N—(substitued phenyl) moiety on the CSD, all $\mathrm{C_{(thienyl)}{=}C_{(thienyl)}{-}C{=}N}$ torsion angles are close to 180° (range 163–180°) which means that the thienyl sulfur atom and Schiff base N atom is always in a *cis* arrangement. The $\mathrm{C_{(thienyl)}{-}C{=}}N\mathrm{{-}C_{(phenyl)}}$ torsion angle adopts two preferred values 0 and 180° (ranges 0–4 and 171–180°, respectively). For the first value the $N\mathrm{{-}C_{(phenyl)}{\cdots}C_{(phenyl)}}$ torsion angles lie in range 80–100° and for the second value, they are in the range 16–63°. The dihedral angle between weighted least squares planes of the thienyl (the C1 atom deviates 0.0023 (10)Å from the plane) and naphthyl (the C6 atom deviates 0.0214 (10)Å from the plane) rings is 49.38 (6)°. In aforementioned compounds in the CSD, the respective angles have no preferred values and are spread over range 18–90°.

The thienyl rings are parallel in adjacent molecules at an interplanar distance of 3.43 Å (ring centroids distance is 3.827 (1) Å), with an angle between the linking rings centroids vector and normal to one of planes 26.40 (2)°, and perpendicular distance of one ring centroid on second ring 3.427 (3) Å) which can be considered as specific stacking interaction. In (I), a C2—H2···π interaction is present (C2···*Cg* distance of 3.7015 (18) Å (where *Cg* means centroid of aromatic ring obtained by $-x + 1, y, -z + 1/2$ and $x, -y, z + 1/2$ symmetry transformation, C2—H2···*Cg* angle 172° and H2···*Cg* distance 2.78 Å), which links molecules to the chain along crystallographic *c* axis. Except those mentioned, there are no unusual short intermolecular contacts in the structure. In (I) an intramolecular C9—H9···N1 short contact is present (Table 2) which, according to Desiraju & Steiner (1999), can be classified as weak hydrogen bond.

Experimental

1,5-Diaminonaphthalene (19.0 mmol) and 2-thiophenecarboxaldehyde (39.6 mmol) in 2-propanol (15 cm^3) were refluxed for 4 h. Then solvent was removed on a vacuum rotary evaporator. 2-Propanol (20 cm^3) and 2-thiophenecarboxaldehyde (9.6 mmol) were added to the residue. The mixture was refluxed for 5 h, and the solvent was removed on a vacuum evaporator. Crude product (6.44 g, 98% yield) was recrystallized from 2-methoxyethanol giving yellow crystals with 37% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (dd, 2H, J_1 = 7.2 Hz, J_2 = 0.9 Hz, H_{Arom}); 7.18 (dd, 2H, J_1 = 5.4 Hz, J_2 = 3.9 Hz, H_{Arom}); 7.49 (dd, 2H, J_1 = 8.4 Hz, J_2 = 7.5 Hz, H_{Arom}); 7.52–7.59 (m, 4H); 8.23 (s, 1H, H_{Arom}); 8.26 (s, 1H, H_{Arom}); 8.68 (s, 2H, H—C=N). IR: (KBr) 1604 (ν)CN; 1431 (ν)Ph; 927 (γ)CH + (γ)ring; 788 (ν)CS + (δ)ring; 722 (γ)CH.

Refinement

The hydrogen atoms were placed in calculated positions after four cycles of anisotrpic refinement and were refined as riding on adjacent carbon atom with U_{iso}(H) = 1.2U_{eq}(C).

Figures

Fig. 1. Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. The symmetry generated atoms (symmetry code: −*x* + 1, −*y*, −*z* + 1) are indicated by the suffix A.

1,5-Bis[(2-thienyl)methyleneamino]naphthalene

Crystal data

$C_{20}H_{14}N_2S_2$	F_{000} = 720
M_r = 346.45	D_x = 1.336 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 4878 reflections
a = 18.4421 (6) Å	θ = 3–20º
b = 7.2454 (2) Å	μ = 0.31 mm^{-1}
c = 13.1885 (3) Å	*T* = 291.0 (3) K
β = 102.254 (3)º	Prism, yellow
V = 1722.10 (9) Å^3	0.34 × 0.33 × 0.32 mm
Z = 4	

Data collection

Kuma KM-4-CCD diffractometer	1537 independent reflections
Radiation source: fine-focus sealed tube	1304 reflections with *I* > 2σ(*I*)

Monochromator: graphite

Detector resolution: 1048576 pixels mm^{-1}

$T = 291.0(3)$ K

ω scans

Absorption correction: numerical (X-RED; Stoe & Cie, 1999)

$T_{\min} = 0.896$, $T_{\max} = 0.899$

8325 measured reflections

$R_{\text{int}} = 0.013$

$\theta_{\max} = 25.1°$

$\theta_{\min} = 2.3°$

$h = -19 \rightarrow 22$

$k = -8 \rightarrow 8$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.094$

$S = 1.06$

1537 reflections

109 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.6069P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.17$ e Å^{-3}

$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Extinction correction: none

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 > 2sigma(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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.27930 (3)	0.44070 (7)	0.19522 (3)	0.0629 (2)
C1	0.34513 (8)	0.3110 (2)	0.15305 (12)	0.0483 (4)
C2	0.34462 (9)	0.3484 (2)	0.05140 (13)	0.0560 (4)
H2	0.3761	0.2914	0.0145	0.067*
C3	0.29214 (10)	0.4806 (3)	0.00872 (14)	0.0606 (5)
H3	0.2849	0.5215	−0.0595	0.073*
C4	0.25304 (10)	0.5426 (3)	0.07699 (15)	0.0630 (5)
H4	0.2159	0.6312	0.0613	0.076*
C5	0.39129 (8)	0.1807 (2)	0.21898 (12)	0.0516 (4)
H5	0.4241	0.1093	0.1909	0.062*

N1	0.38947 (7)	0.15816 (19)	0.31405 (10)	0.0516 (4)
C6	0.43546 (8)	0.0198 (2)	0.36997 (12)	0.0476 (4)
C7	0.44006 (9)	−0.1546 (2)	0.33209 (13)	0.0548 (4)
H7	0.4114	−0.1865	0.2676	0.066*
C8	0.47596 (8)	0.0675 (2)	0.47118 (12)	0.0449 (4)
C9	0.47121 (9)	0.2439 (2)	0.51517 (13)	0.0528 (4)
H9	0.4395	0.3322	0.4785	0.063*
C10	0.51237 (10)	0.2856 (2)	0.61031 (13)	0.0573 (4)
H10	0.5090	0.4028	0.6377	0.069*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0704 (3)	0.0683 (3)	0.0565 (3)	0.0213 (2)	0.0283 (2)	0.0115 (2)
C1	0.0441 (8)	0.0543 (9)	0.0492 (8)	0.0033 (7)	0.0157 (7)	0.0071 (7)
C2	0.0550 (9)	0.0648 (10)	0.0534 (9)	0.0045 (8)	0.0233 (7)	0.0080 (8)
C3	0.0646 (11)	0.0676 (11)	0.0503 (9)	0.0001 (9)	0.0136 (8)	0.0178 (8)
C4	0.0594 (11)	0.0608 (11)	0.0702 (11)	0.0145 (8)	0.0172 (9)	0.0201 (9)
C5	0.0423 (8)	0.0597 (10)	0.0566 (9)	0.0066 (7)	0.0190 (7)	0.0103 (8)
N1	0.0456 (7)	0.0581 (8)	0.0535 (8)	0.0080 (6)	0.0161 (6)	0.0126 (6)
C6	0.0407 (8)	0.0543 (9)	0.0529 (9)	0.0057 (7)	0.0211 (7)	0.0139 (7)
C7	0.0567 (9)	0.0591 (10)	0.0527 (9)	0.0018 (8)	0.0207 (7)	0.0068 (8)
C8	0.0417 (8)	0.0468 (8)	0.0520 (8)	0.0050 (6)	0.0228 (6)	0.0135 (7)
C9	0.0559 (9)	0.0477 (9)	0.0606 (10)	0.0122 (7)	0.0255 (8)	0.0150 (7)
C10	0.0693 (11)	0.0476 (9)	0.0604 (10)	0.0060 (8)	0.0259 (8)	0.0053 (8)

Geometric parameters (Å, °)

S1—C4	1.7003 (18)	N1—C6	1.4151 (19)
S1—C1	1.7186 (16)	C6—C7	1.368 (2)
C1—C2	1.366 (2)	C6—C8	1.427 (2)
C1—C5	1.434 (2)	C7—C10$^{\mathrm{i}}$	1.402 (2)
C2—C3	1.393 (2)	C7—H7	0.9300
C2—H2	0.9300	C8—C9	1.414 (2)
C3—C4	1.344 (3)	C8—C8$^{\mathrm{i}}$	1.427 (3)
C3—H3	0.9300	C9—C10	1.356 (2)
C4—H4	0.9300	C9—H9	0.9300
C5—N1	1.272 (2)	C10—C7$^{\mathrm{i}}$	1.402 (2)
C5—H5	0.9300	C10—H10	0.9300
C4—S1—C1	91.38 (8)	C5—N1—C6	117.80 (14)
C2—C1—C5	127.25 (15)	C7—C6—N1	122.73 (15)
C2—C1—S1	110.54 (12)	C7—C6—C8	120.31 (14)
C5—C1—S1	122.19 (11)	N1—C6—C8	116.93 (14)
C1—C2—C3	113.12 (15)	C6—C7—C10$^{\mathrm{i}}$	120.52 (16)
C1—C2—H2	123.4	C6—C7—H7	119.7
C3—C2—H2	123.4	C10$^{\mathrm{i}}$—C7—H7	119.7
C4—C3—C2	112.62 (15)	C9—C8—C8$^{\mathrm{i}}$	119.12 (19)

C4—C3—H3	123.7	C9—C8—C6	122.48 (14)
C2—C3—H3	123.7	C8^{i}—C8—C6	118.38 (18)
C3—C4—S1	112.34 (13)	C10—C9—C8	120.67 (15)
C3—C4—H4	123.8	C10—C9—H9	119.7
S1—C4—H4	123.8	C8—C9—H9	119.7
N1—C5—C1	123.07 (14)	C9—C10—C7^{i}	120.90 (16)
N1—C5—H5	118.5	C9—C10—H10	119.6
C1—C5—H5	118.5	C7^{i}—C10—H10	119.6
C2—C1—C5—N1	178.01 (17)	C5—N1—C6—C7	−46.7 (2)
C1—C5—N1—C6	177.37 (15)		

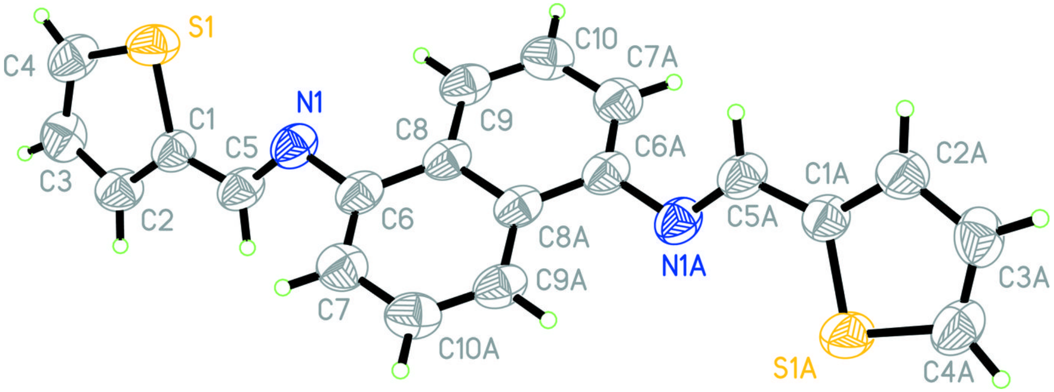
Symmetry codes: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···N1	0.93	2.51	2.828 (2)	100
C2—H2···Cg1^{ii}	0.93	2.78	3.7015 (18)	173

Symmetry codes: (ii) −*x*+1/2, *y*+1/2, −*z*−1/2.

Fig. 1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C1A
C2A
C3A
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