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Key indicators

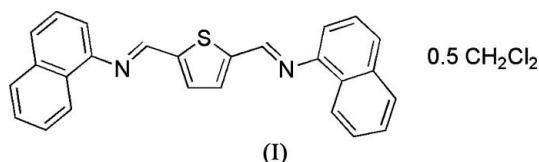
Single-crystal X-ray study
 $T = 220$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
Disorder in solvent or counterion
 R factor = 0.065
 wR factor = 0.166
Data-to-parameter ratio = 14.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A naphthalene–thiophene–naphthalene
diazomethine triad solvated with
dichloromethane

The highly conjugated title compound, (*E*)-*N*-{5-[(*E*)-1-naphthyliminomethyl]-2-thienylmethylene}naphthalen-1-amine dichloromethane hemisolvate, $\text{C}_{26}\text{H}_{18}\text{N}_2\text{S}\cdot 0.5\text{CH}_2\text{Cl}_2$, exhibits a non-planar yet extended configuration. The naphthyl ring systems are twisted 33.8 (4) and 32.6 (5)° out of the mean plane that passes through the thiophene ring. The nitrogen-containing double bonds are *ca* 0.05 Å shorter than their carbon analogues and both adopt the thermodynamically favourable *E* configuration.

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Comment

New approaches to light-harvesting materials are currently being pursued in the hope of developing inexpensive and easily produced photo-active devices. We recently developed an efficient and easy synthesis using a snap-together approach incorporating thiophene units. This involves the complementary aldehyde and amine condensation that gives rise to a robust azomethine ($-\text{C}=\text{N}-$) bond (Skene & Dufresne, 2004). The azomethine approach is favourable over other means because of its synthetic ease. Its formation does not require expensive catalysts or drastic reaction conditions such as anhydrous solvent or inert atmospheres. The azomethine has the added advantage of being isoelectronic with its $\text{C}=\text{C}$ analogue (Yang & Jenekhe, 1991; Kuder *et al.*, 1975). During our studies, we have isolated the title conjugated azomethine, (I), as a deep-orange solid, which crystallized easily from dichloromethane. The crystallographic data illustrate the unique azomethine crystal properties that arise with the use of a thiophene unit.



Homoaryl aromatic rings are generally twisted from the mean planes of azomethines to which they are directly bound. For example, the planes described by two conjugated aromatic units are twisted by 65° (Bürgi & Dunitz, 1969; Manecke *et al.*, 1972). Linking the azomethine substituents to a thiophene ring, as in (I), reduces this angle, with the naphthalene mean planes inclined at 33.8 (4) and 32.6 (5)° with respect to the thiophene plane. NMR data confirm that only one isomer is formed for (I), but cannot differentiate between the *E* and *Z* configurations. However, structural data (Fig. 1) show clearly that both azomethines adopt the thermodynamically favourable *E* configuration. Furthermore, the $\text{N}=\text{C}$ bond distances

[1.275 (6) and 1.281 (6) Å; Table 1] are shorter than the C=C analogues, reported to be 1.316 (8) Å (Zobel & Ruban, 1978).

Experimental

The title compound was synthesized according to the method of Skene & Dufresne (2004). Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution in dichloromethane.

Crystal data

C₂₆H₁₈N₂S·0.5CH₂Cl₂

M_r = 432.97

Monoclinic, *P*2₁

a = 11.2320 (8) Å

b = 5.8762 (2) Å

c = 16.7657 (9) Å

β = 94.872 (4)°

V = 1102.56 (11) Å³

Z = 2

D_x = 1.304 Mg m⁻³

Cu Kα radiation

Cell parameters from 3232

reflections

θ = 2.7–72.1°

μ = 2.53 mm⁻¹

T = 220 (2) K

Needle, yellow–orange

0.76 × 0.09 × 0.05 mm

Data collection

Bruker SMART 2K/PLATFORM diffractometer

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)

T_{min} = 0.417, *T_{max}* = 0.883

9046 measured reflections

4127 independent reflections

2223 reflections with *I* > 2σ(*I*)

R_{int} = 0.030

θ_{max} = 72.9°

h = −13 → 10

k = −7 → 7

l = −20 → 20

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.065

wR(*F*²) = 0.166

S = 0.87

4127 reflections

290 parameters

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0811*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δσ)_{max} < 0.001

Δρ_{max} = 0.27 e Å⁻³

Δρ_{min} = −0.25 e Å⁻³

Extinction correction: SHELXL97

Extinction coefficient: 0.0022 (5)

Absolute structure: Flack (1983),

1741 Friedel pairs

Flack parameter: 0.00 (3)

Table 1

Selected geometric parameters (Å, °).

N1–C1	1.274 (6)	N2–C17	1.413 (6)
N1–C7	1.409 (6)	C1–C2	1.436 (6)
N2–C6	1.281 (6)	C5–C6	1.414 (7)
C7–N1–C1–C2	−179.0 (4)	S1–C5–C6–N2	1.0 (8)
N1–C1–C2–S1	−0.9 (8)	C1–N1–C7–C8	36.1 (7)
C17–N2–C6–C5	177.1 (4)	C6–N2–C17–C18	−33.6 (7)

All H atoms were refined using a riding model, with C–H = 0.94 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms, and C–H = 0.98 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for dichloromethane H atoms. Restraints were applied to the anisotropic displacement parameters to obtain a converging refinement. The dichloromethane molecule was located in proximity of a symmetry element. The symmetry application to generate the model over itself was required to reduce the occupancy factors to no more than 0.5 for all the atoms in the model. SIMU and ISOR restraints were applied to convergence in the last refinement cycles. A harder isotropic restraint was applied to the central C atom by applying a reduced s.u. value of 0.01 instead of the default 0.1

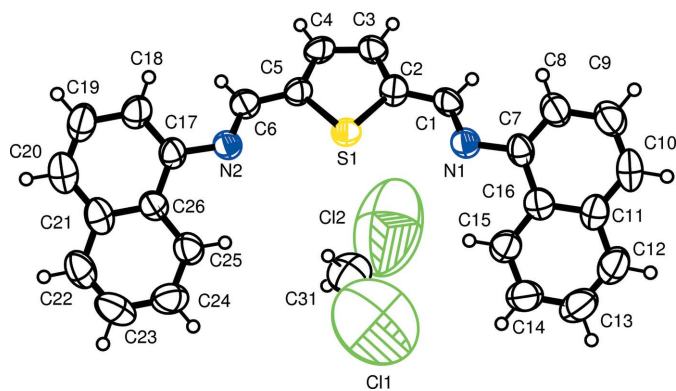


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. The diagram includes a cocrystallized molecule of dichloromethane.

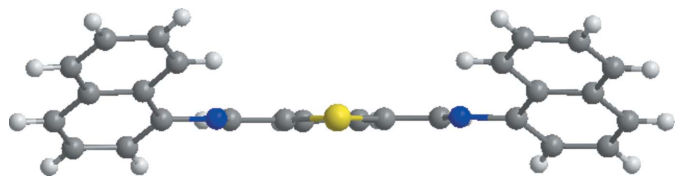


Figure 2

Schematic representation of compound (I), viewed parallel to the plane of the thiophene ring. The dichloromethane solvent molecule has been omitted for clarity.

value. The latter was used for all other ISOR restraints. The SIMU restraint was applied to the model by using the default 0.04 (central C atom) and 0.08 (terminal Cl atom) s.u. values.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and SHELXTL (Bruker, 1997); software used to prepare material for publication: UDMX (local program).

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