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2-Naphthylmethyl *N*-[1-(4-pyridyl)ethylidene]hydrazinecarbodithioate

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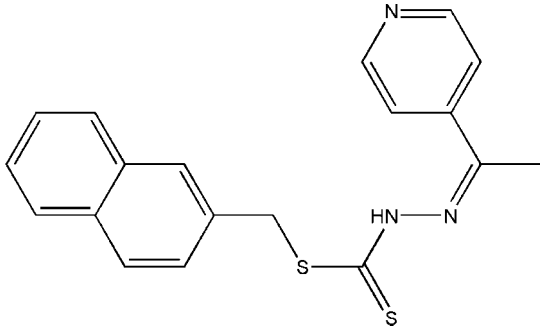
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.006 Å; R factor = 0.073; wR factor = 0.211; data-to-parameter ratio = 17.6.

The molecules in the crystal structure of the title compound, $C_{19}H_{17}N_3S_2$, are linked by an intermolecular N—H···N [2.839 (5) Å] hydrogen bond *via* the α-N and the pyridyl N atoms. The thione S atom is in a *trans* position with respect to the methylpyridine fragment across the C—N bond but adopts a *cis* position with respect to the naphthalene ring across the C—S bond. There is a π–π stacking interaction between the naphthalene rings, with a centroid–centroid distance of 3.397 (2) Å.

Related literature

The title compound was prepared from *S*-naphthalen-2-ylmethyldithiocarbazate. Interatomic parameters of the crystal structure are comparable with previous literature values (How *et al.*, 2007*a*,*b*). For other relevant literature, see: Crouse *et al.* (2004); Shanmuga Sundara Raj *et al.* (2000); Tarafder *et al.* (2002); Wang *et al.* (2002); Zhou *et al.* (2007).



Experimental

Crystal data

$C_{19}H_{17}N_3S_2$
M_r = 351.50
Orthorhombic, *Pbca*
a = 16.0781 (7) Å
b = 9.8406 (4) Å
c = 22.2201 (8) Å
V = 3515.6 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 150 K
0.40 × 0.06 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.76, T_{max} = 0.99
14358 measured reflections
3811 independent reflections
2209 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.133

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.073
$wR(F^2)$ = 0.211
S = 0.92
3811 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N6—H1···N12^{i}	0.88	1.98	2.839 (5)	166

Symmetry code: (i) $x-\frac{1}{2}, y, -z+\frac{3}{2}$.

Data collection: *COLLECT* (Nonius, 2001).; cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LW2018).

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supplementary materials

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2-Naphthylmethyl *N*-[1-(4-pyridyl)ethylidene]hydrazinecarbodithioate

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Comment

Dithiocarbazate and its substituted compounds are of interest for researchers because these compound have various chemical properties [Wang *et al.*, 2002 and Zhou *et al.*, 2007] and they are biologically active [Crouse *et al.*, 2004 and Tarafder *et al.*, 2002].

The C5—N6 bond [1.351 (5) Å] has a partial double bond character. It is comparable with Schiff bases derived from S-napthalen-2-yl- and -quinolin-2-yl-methyldithiocarbazate. [1.352 (4) Å; How *et al.*, 2007*a* and 1.352 (2) Å; How *et al.*, 2007*b*].

The C5—S16 bond [1.660 (4) Å] displays a double bond character. It is comparable with previous literature [1.659 (4) Å; How *et al.*, 2007*a* and 1.6593 (17) Å; How *et al.*, 2007*b*]

The bond angle N7—N6—C5 [117.0 (3)°] and S16—C5—S4 [126.3 (2)°] are comparable with schiff base derived from *S*-quinolin-2-yldithiocarbazate. and *S*-napthalen-2-ylmethyldithiocarbazate [117.61 (13)° and 125.7 (2)°; How *et al.*, 2007*b*] and [116.9 (3)° and 125.7 (2)°; How *et al.*, 2007*a*] respectively.

There are two planar fragment in the molecule of the crystal structure. The C1/C2/C3/C17/C18/C19/C20/C21/C22/C23/C24 fragment inclines with the S4/C5/N6/N7/C8/C9/C10/C11/N12/C13/C14/C15/C16 fragment in an angle of 79.2 (1)°.

The single molecule formed *L*-shaped but packed as W-shaped as the naphthalene fragments formed stacked as rows parallel to each other [Fig 2.]

The naphthalene ring defined by the atoms C1/C2/C3/C17/C18/C19/C20 at (*x*,*y*,*z*) and (1 − *x*,-*y*, 1 − *z*) are stacked parallel to each other with a separation of 3.589 (2)Å between the centres-of-gravity, an interplanar spacing of 3.407Å and an offset of 1.130Å giving a π—π stacking interaction, [Fig. 5].

The whole pyridine fragment C8/C9/C10/N11/C12/C13/C14 behaves as a rigid body (*R*-factor= 6.73) and undergoes substantial libration with mean square displacement of 121.73°^2^.

The intermolecular N—H—N hydrogen bond [2.839 (5) Å] *via* the pyridyl nitrogen atom and the \a-nitrogen atom linking the molecules [Fig. 3] is comparable with Schiff base derived from pyridine-3-carboxaldehyde [2.825 (2) Å; How *et al.*, 2007*a*].

Experimental

S-Napthalen-2-ylmethyldithiocarbazate (SNMDTC) was used as a starting ligand for the synthesis of Schiff base. *S*-napthalen-2-ylmethyldithiocarbazate (SNMDTC) was prepared as previously reported for S-substituted dithiocarbazates [Shanmuga Sundara Raj *et al.*, 2000] except the addition of benzyl chloride being replaced with 1-(chloromethyl) naphthalene (29.9 ml, 0.2 mol).

SNMDTC (0.02 mol) was dissolved in hot acetonitrile (30 ml) with dropwise addition of equimolar amount of 4-acetylpyridine. The mixture was left heated with stirring to reduce half the volume. The mixture was allowed to stand for 1 day. Precipitates formed were filtered and recrystallized from ethanol. The recrystallized product was then dried over silica gel. (yield: 62.7%, m.p.= 460.15 K) Yellow needle like crystals were formed upon slow evaporation in a ethanol solution.

Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 Å) and *U*ĩso~(H) (in the range 1.2–1.5 times *U*~eq~ of the parent atom), after which the positions were refined with riding constraints.

Figures

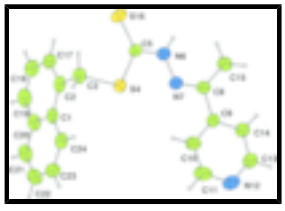

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

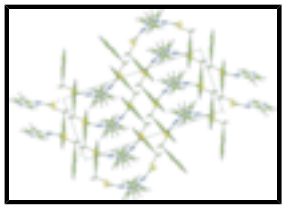

Fig. 2. The packing of the molecule viewed along the *a* axis.

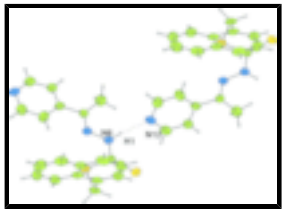

Fig. 3. The molecules are stabilized by intermolecular N—H—N hydrogen bond. Dotted line denotes the N—H—N hydrogen bond.

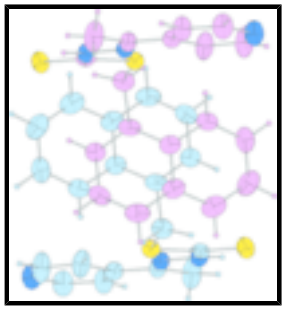

Fig. 4. The \⟨i⟩*p*-π interaction of pairs of the naphthalene rings at (*x*,*y*,*z*) and (*x*,*y* + 1,*z*)

2-Naphthylmethyl *N*-[1-(4-pyridyl)ethylidene]hydrazinecarbodithioate

Crystal data

$C_{19}H_{17}N_3S_2$	$D_x = 1.328$ Mg m^{-3}
$M_r = 351.50$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 3836 reflections
$a = 16.0781$ (7) Å	$\theta = 5$–27º
$b = 9.8406$ (4) Å	$\mu = 0.31$ mm^{-1}
$c = 22.2201$ (8) Å	$T = 150$ K
$V = 3515.6$ (2) Å^3	Plate, yellow
$Z = 8$	0.40 × 0.06 × 0.04 mm
$F_{000} = 1472$	

Data collection

Nonius KappaCCD diffractometer	2209 reflections with $I > 2.0\sigma(I)$
Monochromator: graphite	$R_{int} = 0.133$
$T = 150$ K	$\theta_{max} = 27.1$º
ω scans	$\theta_{min} = 5.1$º
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	$h = -20\rightarrow20$
$T_{min} = 0.76$, $T_{max} = 0.99$	$k = -12\rightarrow12$
14358 measured reflections	$l = -28\rightarrow28$
3811 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.073$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.12P)^2 + 0.6P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$wR(F^2) = 0.211$	$(\Delta/\sigma)_{max} = 0.0004$
$S = 0.92$	$\Delta\rho_{max} = 0.79$ e Å^{-3}
3811 reflections	$\Delta\rho_{min} = -0.82$ e Å^{-3}
217 parameters	Extinction correction: None
Primary atom site location: structure-invariant direct methods	

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

	x	*y*	*z*	U_{iso}*/U_{eq}

C1	0.5625 (3)	0.0827 (4)	0.56610 (15)	0.0356
C2	0.4905 (3)	0.1605 (4)	0.55211 (15)	0.0362
C3	0.4983 (3)	0.3005 (4)	0.52538 (15)	0.0392
S4	0.53368 (6)	0.42180 (11)	0.58251 (4)	0.0331
C5	0.4391 (2)	0.4928 (4)	0.60772 (16)	0.0298
N6	0.4480 (2)	0.5648 (4)	0.65904 (13)	0.0342
N7	0.52675 (18)	0.5734 (3)	0.68279 (12)	0.0319
C8	0.5395 (2)	0.6455 (4)	0.73024 (15)	0.0340
C9	0.6280 (2)	0.6436 (4)	0.74997 (16)	0.0336
C10	0.6864 (3)	0.5634 (5)	0.7215 (2)	0.0533
C11	0.7675 (3)	0.5652 (6)	0.7404 (2)	0.0615
N12	0.7939 (2)	0.6385 (4)	0.78781 (14)	0.0486
C13	0.7375 (3)	0.7141 (5)	0.81497 (17)	0.0492
C14	0.6561 (3)	0.7204 (5)	0.79824 (17)	0.0440
C15	0.4774 (3)	0.7254 (6)	0.76459 (19)	0.0588
S16	0.34742 (6)	0.48061 (12)	0.57372 (4)	0.0409
C17	0.4128 (3)	0.1115 (4)	0.56429 (16)	0.0394
C18	0.4028 (3)	−0.0166 (5)	0.59089 (19)	0.0463
C19	0.4696 (3)	−0.0934 (5)	0.60457 (18)	0.0474
C20	0.5509 (3)	−0.0485 (4)	0.59193 (16)	0.0411
C21	0.6216 (3)	−0.1300 (5)	0.60357 (18)	0.0502
C22	0.6993 (3)	−0.0859 (6)	0.5917 (2)	0.0558
C23	0.7113 (3)	0.0428 (5)	0.56598 (18)	0.0484
C24	0.6448 (3)	0.1243 (5)	0.55388 (17)	0.0402
H31	0.4438	0.3303	0.5109	0.0467*
H32	0.5392	0.3019	0.4931	0.0474*
H101	0.6699	0.5071	0.6898	0.0702*
H111	0.8071	0.5134	0.7194	0.0772*
H131	0.7550	0.7670	0.8477	0.0624*
H141	0.6190	0.7759	0.8186	0.0572*
H151	0.4968	0.8167	0.7708	0.0862*
H152	0.4690	0.6835	0.8031	0.0863*
H153	0.4253	0.7278	0.7441	0.0864*
H171	0.3662	0.1626	0.5538	0.0465*
H181	0.3496	−0.0493	0.5995	0.0578*
H191	0.4627	−0.1795	0.6211	0.0558*
H211	0.6135	−0.2165	0.6198	0.0598*
H221	0.7446	−0.1411	0.6011	0.0669*
H231	0.7649	0.0735	0.5567	0.0587*
H241	0.6534	0.2097	0.5380	0.0485*
H1	0.4046	0.6011	0.6767	0.0425*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.051 (2)	0.036 (2)	0.0197 (16)	0.000 (2)	0.0003 (15)	−0.0063 (15)
C2	0.055 (3)	0.035 (2)	0.0184 (14)	−0.007 (2)	0.0034 (17)	−0.0016 (15)
C3	0.051 (2)	0.047 (3)	0.0197 (15)	−0.002 (2)	0.0037 (16)	−0.0026 (16)

S4	0.0363 (5)	0.0370 (6)	0.0259 (4)	−0.0008 (4)	0.0010 (4)	−0.0016 (4)
C5	0.032 (2)	0.031 (2)	0.0266 (16)	−0.0041 (16)	−0.0003 (14)	0.0044 (15)
N6	0.0356 (17)	0.045 (2)	0.0215 (13)	0.0033 (15)	−0.0006 (12)	0.0001 (13)
N7	0.0349 (17)	0.0388 (19)	0.0220 (13)	0.0007 (15)	0.0002 (12)	0.0015 (13)
C8	0.032 (2)	0.045 (2)	0.0248 (16)	0.0051 (18)	0.0025 (15)	0.0012 (16)
C9	0.038 (2)	0.039 (2)	0.0234 (16)	0.0002 (18)	−0.0030 (15)	−0.0019 (16)
C10	0.041 (2)	0.072 (3)	0.047 (2)	0.015 (2)	−0.0072 (19)	−0.020 (2)
C11	0.043 (3)	0.095 (4)	0.046 (2)	0.020 (3)	0.002 (2)	−0.019 (3)
N12	0.042 (2)	0.078 (3)	0.0261 (15)	0.0045 (19)	−0.0056 (14)	−0.0014 (17)
C13	0.047 (3)	0.067 (3)	0.0331 (18)	0.004 (2)	−0.0052 (19)	−0.014 (2)
C14	0.039 (2)	0.062 (3)	0.0308 (18)	0.006 (2)	0.0000 (16)	−0.0132 (19)
C15	0.047 (3)	0.085 (4)	0.044 (2)	0.020 (3)	−0.004 (2)	−0.033 (3)
S16	0.0342 (6)	0.0581 (7)	0.0305 (5)	−0.0036 (5)	−0.0045 (4)	0.0014 (5)
C17	0.045 (2)	0.040 (2)	0.0337 (19)	−0.002 (2)	−0.0008 (17)	−0.0024 (17)
C18	0.048 (3)	0.046 (3)	0.044 (2)	−0.010 (2)	0.008 (2)	−0.003 (2)
C19	0.071 (3)	0.041 (3)	0.0301 (18)	−0.004 (2)	0.008 (2)	−0.0004 (18)
C20	0.059 (3)	0.043 (3)	0.0210 (16)	0.004 (2)	0.0002 (17)	−0.0028 (16)
C21	0.072 (3)	0.047 (3)	0.0322 (19)	0.007 (2)	−0.001 (2)	−0.0055 (19)
C22	0.064 (3)	0.056 (3)	0.047 (2)	0.018 (3)	−0.008 (2)	−0.010 (2)
C23	0.039 (2)	0.066 (3)	0.041 (2)	0.004 (2)	0.0003 (18)	−0.015 (2)
C24	0.049 (2)	0.038 (2)	0.0331 (19)	−0.006 (2)	0.0030 (18)	−0.0029 (17)

Geometric parameters (Å, °)

C1—C2	1.423 (6)	N12—C13	1.319 (5)
C1—C20	1.425 (6)	C13—C14	1.361 (6)
C1—C24	1.412 (6)	C13—H131	0.937
C2—C3	1.505 (6)	C14—H141	0.927
C2—C17	1.366 (6)	C15—H151	0.962
C3—S4	1.833 (4)	C15—H152	0.960
C3—H31	0.979	C15—H153	0.953
C3—H32	0.973	C17—C18	1.401 (6)
S4—C5	1.765 (4)	C17—H171	0.932
C5—N6	1.351 (5)	C18—C19	1.347 (7)
C5—S16	1.660 (4)	C18—H181	0.934
N6—N7	1.374 (4)	C19—C20	1.408 (6)
N6—H1	0.876	C19—H191	0.930
N7—C8	1.287 (5)	C20—C21	1.416 (6)
C8—C9	1.488 (5)	C21—C22	1.348 (7)
C8—C15	1.483 (5)	C21—H211	0.933
C9—C10	1.381 (6)	C22—C23	1.403 (7)
C9—C14	1.388 (5)	C22—H221	0.933
C10—C11	1.369 (7)	C23—C24	1.363 (6)
C10—H101	0.934	C23—H231	0.936
C11—N12	1.346 (6)	C24—H241	0.922
C11—H111	0.941		
C2—C1—C20	118.0 (4)	C14—C13—H131	118.4
C2—C1—C24	124.4 (4)	C9—C14—C13	120.0 (4)
C20—C1—C24	117.6 (4)	C9—C14—H141	119.3

C1—C2—C3	120.7 (4)	C13—C14—H141	120.8
C1—C2—C17	120.7 (4)	C8—C15—H151	110.5
C3—C2—C17	118.6 (4)	C8—C15—H152	109.0
C2—C3—S4	110.4 (2)	H151—C15—H152	108.5
C2—C3—H31	109.2	C8—C15—H153	111.1
S4—C3—H31	108.1	H151—C15—H153	109.3
C2—C3—H32	111.1	H152—C15—H153	108.3
S4—C3—H32	107.1	C2—C17—C18	120.4 (4)
H31—C3—H32	110.9	C2—C17—H171	119.7
C3—S4—C5	102.14 (19)	C18—C17—H171	119.9
S4—C5—N6	112.6 (3)	C17—C18—C19	120.6 (4)
S4—C5—S16	126.3 (2)	C17—C18—H181	120.1
N6—C5—S16	121.1 (3)	C19—C18—H181	119.4
C5—N6—N7	117.0 (3)	C18—C19—C20	121.2 (4)
C5—N6—H1	120.5	C18—C19—H191	120.3
N7—N6—H1	122.4	C20—C19—H191	118.4
N6—N7—C8	119.7 (3)	C1—C20—C19	119.1 (4)
N7—C8—C9	112.7 (3)	C1—C20—C21	118.8 (4)
N7—C8—C15	127.3 (3)	C19—C20—C21	122.1 (4)
C9—C8—C15	120.0 (3)	C20—C21—C22	121.7 (5)
C8—C9—C10	121.5 (4)	C20—C21—H211	118.4
C8—C9—C14	122.1 (4)	C22—C21—H211	119.9
C10—C9—C14	116.4 (4)	C21—C22—C23	119.9 (5)
C9—C10—C11	120.0 (4)	C21—C22—H221	119.5
C9—C10—H101	119.4	C23—C22—H221	120.6
C11—C10—H101	120.6	C22—C23—C24	120.2 (4)
C10—C11—N12	123.2 (4)	C22—C23—H231	120.6
C10—C11—H111	119.1	C24—C23—H231	119.2
N12—C11—H111	117.7	C1—C24—C23	121.8 (4)
C11—N12—C13	116.4 (4)	C1—C24—H241	118.5
N12—C13—C14	124.1 (4)	C23—C24—H241	119.7
N12—C13—H131	117.4		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H1···N12^{i}	0.88	1.98	2.839 (5)	166

Symmetry codes: (i) *x*−1/2, *y*, −*z*+3/2.

Fig. 1

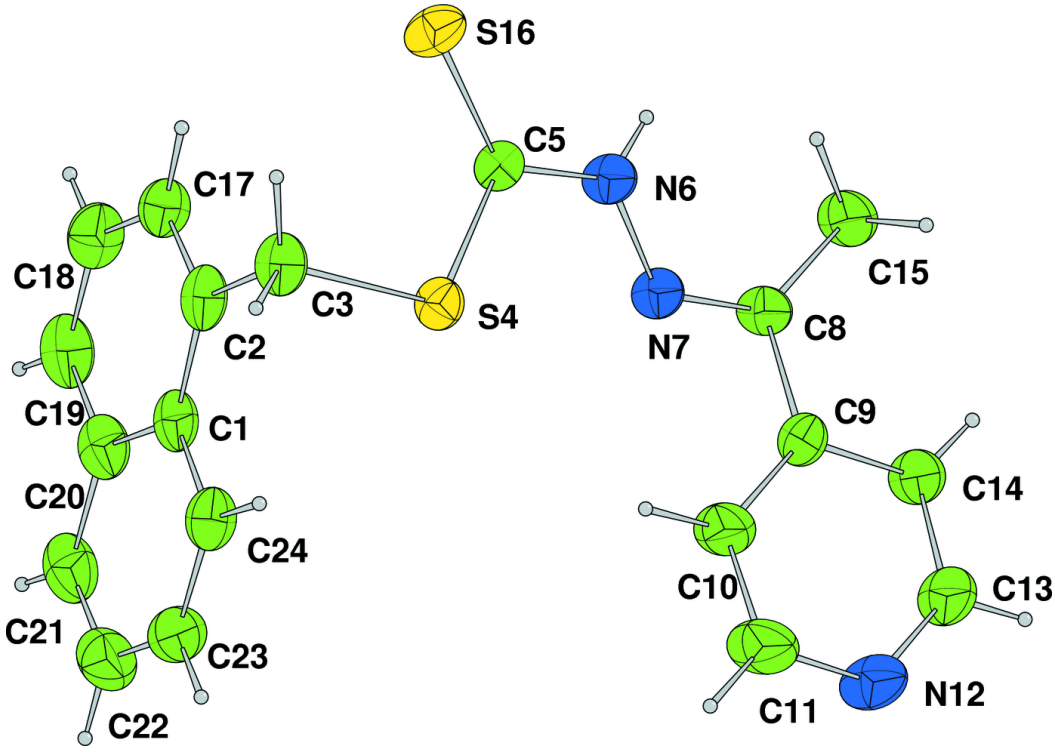
S16
C5
N6
C17
C18
C3
S4
C15
C2
N7
C8
C19
C1
C9
C20
C14
C24
C10
C13
C21
C23
C11
N12
C22

Fig. 2

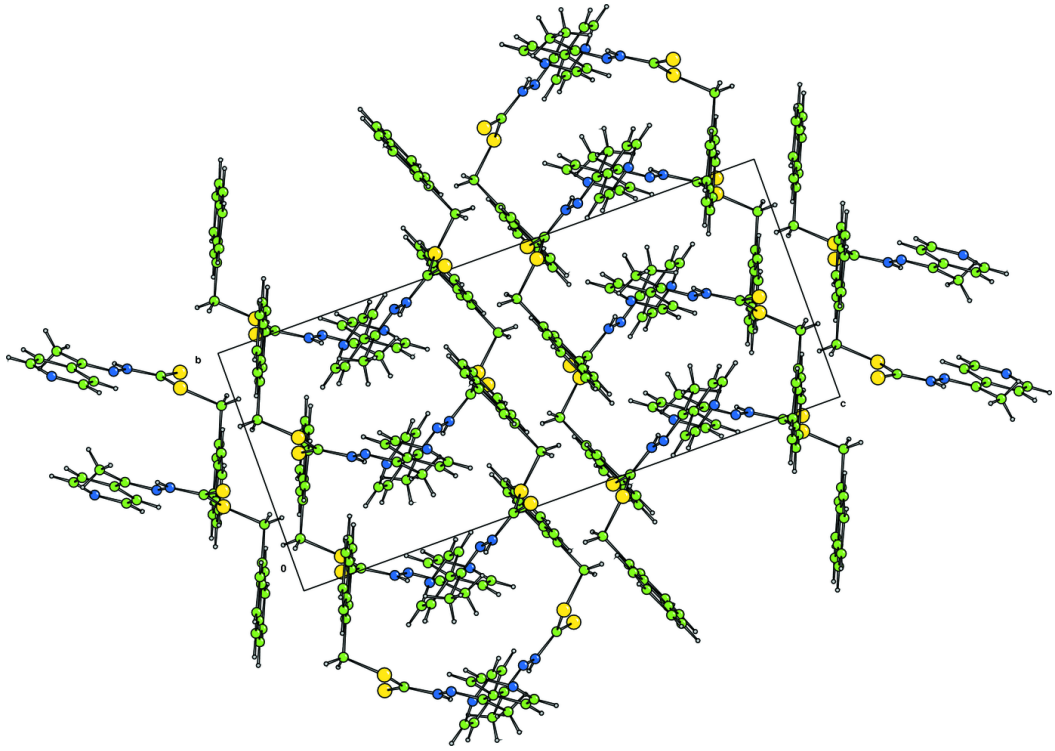

Fig. 3

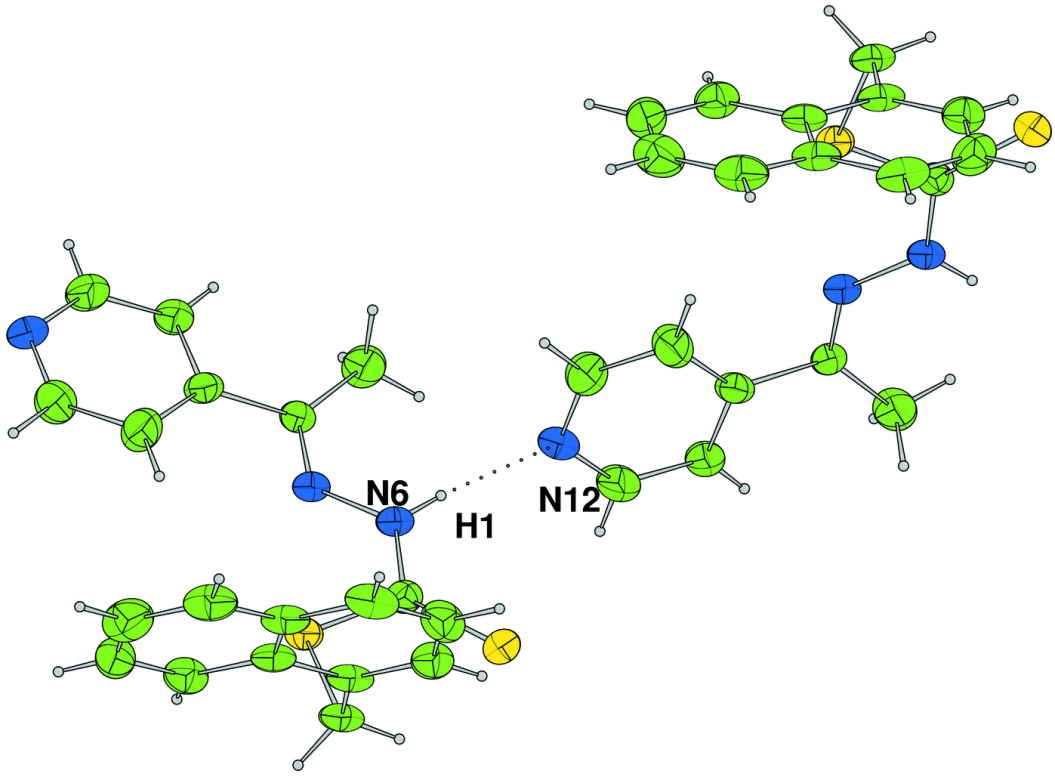

Fig. 4