Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Naphthylmethyl *N*-(3-pyridylmethylene)hydrazinecarbodithioate

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Received 21 May 2007; accepted 25 May 2007

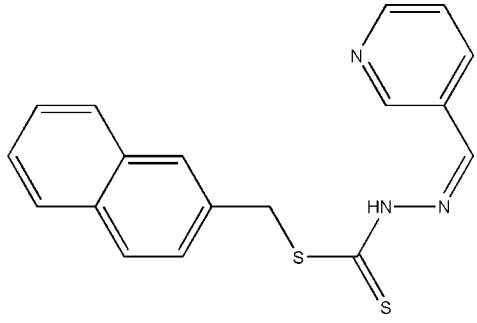
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.005 Å; R factor = 0.056; wR factor = 0.198; data-to-parameter ratio = 21.2.

The title molecule, $C_{18}H_{15}N_3S_2$, is a *trans–cis* conformer. The thione S atom is in a *trans* configuration with respect to the pyridine ring but adopts a *cis* configuration with respect to the napthylmethyl substituent. In the crystal structure, molecules are linked by intermolecular N—H···N hydrogen bonds *via* α-N donor atoms and pyridyl N acceptor atoms into one-dimensional chains along the *a* axis. In addition, pairs of inversion-related dithiocarbazate groups and the attached pyridine groups are arranged with an interplanar distance 3.30 Å, leading to π–π stacking interactions. The crystal used for the structure determination was twinned.

Related literature

S-Naphthalen-2-ylmethyldithiocarbazate was used as a starting material (How *et al.*, 2007*a*). Interatomic parameters for the crystal structure are comparable to those reported by Chan *et al.* (2003), Ali *et al.* (2005) and How *et al.* (2007*a*,*b*).

For related literature, see: Crouse *et al.* (2004); Parsons & Gould (2001).



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Experimental

Crystal data

$C_{18}H_{15}N_3S_2$
M_r = 337.47
Monoclinic, $P2_1/a$
a = 13.0527 (3) Å
b = 7.8222 (2) Å
c = 16.4471 (4) Å
β = 104.2903 (12)°
V = 1627.30 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 150 K
0.48 × 0.28 × 0.14 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.91, T_{max} = 0.95
8557 measured reflections
4436 independent reflections
3138 reflections with $I > 2\sigma(I)$
R_{int} = 0.089

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.198
S = 0.82
4435 reflections
209 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H61···N11^{i}	0.87	1.96	2.825 (2)	170

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

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*.

FNFH gratefully acknowledges MOSTI, Malaysia, for an attachment grant under an NSF scholarship and the Chemical Crystallography Laboratory, Oxford University, for instrumental facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2397).

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supplementary materials

Acta Cryst. (2007). E**63**, o3133-o3134 [**doi:10.1107/S1600536807025676**]

2-Naphthylmethyl *N*-(3-pyridylmethylene)hydrazinecarbodithioate

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Comment

It is well established that Schiff bases derived from substituted dithiocarbazic acids and their metal complexes are biologically active [Ali *et al.*, 2005 & Crouse *et al.*, 2004]. As part of our continuing efforts to prepare new dithiocarbazate derivatives, we have introduced a new substituted dithiocarbazate ligand, *S*-napthalen-2-ylmethyldithiocarbazate. The title compound (the molecular structure is shown in Fig. 1) is one of the new Schiff base compounds synthesized, which was derived from *S*-napthalen-2-ylmethyldithiocarbazate.

The C5—N6 bond [1.352 (4) Å] is comparable with Schiff bases derived from *S*-benzyl- and -quinolin-2-ylmethyldithiocarbazate. [1.342 (2) Å; Chan *et al.*, 2003] and [1.352 (2) Å; How *et al.*, 2007*b*].

The C5—S15 bond [1.659 (4) Å] displays double bond character. It is comparable with Schiff bases derived from *S*-benzyl- and -quinolin-2-ylmethyl-dithiocarbazate. [1.6503 (17) Å; Chan *et al.*, 2003 and 1.6593 (17) Å; How *et al.*, 2007*b*].

The N7—N6—C5 bond angle [116.9 (3)°] is comparable with schiff base derived from *S*-quinolin-2-yldithiocarbazate [117.61 (13)°; How *et al.*, 2007*b*] but slightly shorter than schiff bases derived from *S*-benzyldithiocarbazate [119.20 (14)°; Chan *et al.*, 2003].

The bond angle S15—C5—S4 [125.7 (2)°] is comparable with literature values [125.60 (10)°; Chan *et al.*, 2003 and 125.7 (3)°; Ali *et al.*, 2005].

The dihedral angle between the C1/C2/C3/C16/C17/C18/C19/C20/C21/C22/C23 fragment and the S4/C5/N6/N7/C8/C9/C10/N11/C12/C13/C14/S15 fragment is 79.4 (1)°. Molecules in the crystal structure are packed in diagonal layers of napthalene residues lying parallel to *bc* plane. The dithiocarbazate moiety together with the pyridine fragments are arranged above and below this plane [Fig. 2].

In the crystal structure, molecules display π-π interaction forming pairs of overlapping S4/C5/N6/N7/C8/C9/C10/N11/C12/C13/C14/S15 fragments related by inversion symmetry with a mean distance of 3.43 Å. Similarly pairs of inversion related N6/N7/C8/C9/C10/N11/C12/C13/C14 fragments with a mean separation of 3.30Å [Fig. 4]. The pyridine fragment C8/C9/C10/N11/C12/C13/C14 undergoes substantial libration with mean square displacement of 16.8 $Å^2$.

There is an intermolecular N—H—N hydrogen bond formed *via* the pyridyl N atom and the α-nitrogen atom linking molecules together [Fig. 3] and this is also present in the Schiff base derived from 4-acetylpyridine [2.839 (2)°; 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 reported for S-substituted dithiocarbazates (How *et al.*, 2007*a*) 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 pyridine-3-carboxyaldehyde. 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: 65.8%) 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 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_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

The unusual scattering of reflection in the F_o *versus* Fc plot with a high *R*-factor (9.9%) were indicators of potential twinning. Twining was confirmed using ROTAX (Parsons & Gould, 2001) to analyze the structure factor residuals. Refinement were done using twinning matrix [1 0 0, 0 − 1 0, −0.622 0 − 1], which gave a twin ratio of 0.837:0.163 (2).

Figures

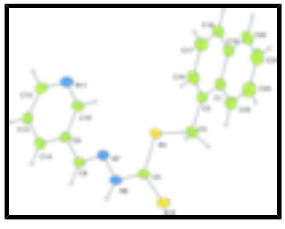

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

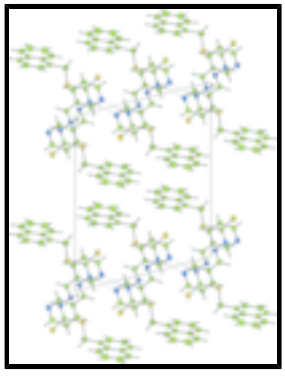

Fig. 2. The packing of the molecule viewed along the *b* axis.

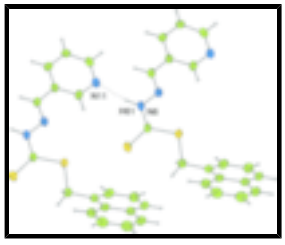

Fig. 3. The molecules are stabilized by intermolecular N—H—N hydrogen bond. Dotted line denotes the N—H—N hydrogen bond.

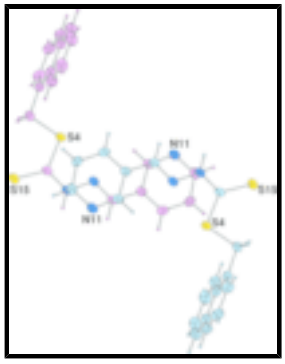

Fig. 4. View of the π···π stacking of N6/N7/C8/C9/C10/N11/C12/C13/C14 fragments realted by inversion symmetry.

2-Naphthylmethyl *N*-(3-pyridylmethylene)hydrazinecarbodithioate

Crystal data

$C_{18}H_{15}N_3S_2$	F_{000} = 704
M_r = 337.47	D_x = 1.377 Mg m^{-3}
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yab	Cell parameters from 4600 reflections
a = 13.0527 (3) Å	θ = 5–30º
b = 7.8222 (2) Å	μ = 0.33 mm^{-1}
c = 16.4471 (4) Å	T = 150 K
β = 104.2903 (12)º	Plate, yellow
V = 1627.30 (7) Å^3	0.48 × 0.28 × 0.14 mm
Z = 4	

Data collection

Bruker–Nonius KappaCCD diffractometer	3138 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.000
T = 150 K	θ_{max} = 29.5º
ω scans	θ_{min} = 5.1º
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	h = −17→18
T_{min} = 0.91, T_{max} = 0.95	k = −10→10
8557 measured reflections	l = −22→22
4436 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.057$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.12P)^2 + 5.11P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$wR(F^2) = 0.198$	$(\Delta/\sigma)_{max} = 0.0001$
$S = 0.82$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
4435 reflections	$\Delta\rho_{min} = -0.62$ e Å^{-3}
209 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	0.2346 (3)	0.8628 (5)	0.3705 (2)	0.0263
C2	0.1883 (3)	1.0170 (5)	0.3308 (2)	0.0255
C3	0.0720 (3)	1.0276 (5)	0.2894 (2)	0.0273
S4	0.05644 (6)	0.92864 (11)	0.18668 (5)	0.0247
C5	−0.0791 (2)	0.9565 (4)	0.1406 (2)	0.0226
N6	−0.1078 (2)	0.8992 (4)	0.06063 (18)	0.0243
N7	−0.0311 (2)	0.8166 (4)	0.03065 (17)	0.0238
C8	−0.0624 (2)	0.7433 (4)	−0.0410 (2)	0.0230
C9	0.0152 (2)	0.6506 (4)	−0.0743 (2)	0.0225
C10	0.1205 (3)	0.6408 (5)	−0.0295 (2)	0.0266
N11	0.1951 (2)	0.5563 (4)	−0.05595 (19)	0.0277
C12	0.1665 (3)	0.4786 (5)	−0.1315 (2)	0.0278
C13	0.0639 (3)	0.4804 (5)	−0.1802 (2)	0.0265
C14	−0.0133 (3)	0.5658 (4)	−0.1511 (2)	0.0257
S15	−0.16657 (7)	1.03963 (13)	0.18748 (6)	0.0317
C16	0.2517 (3)	1.1548 (5)	0.3274 (2)	0.0315
C17	0.3622 (3)	1.1501 (5)	0.3616 (2)	0.0354
C18	0.4075 (3)	1.0046 (6)	0.3989 (2)	0.0336
C19	0.3472 (3)	0.8590 (5)	0.4056 (2)	0.0289
C20	0.3926 (3)	0.7082 (6)	0.4469 (2)	0.0384
C21	0.3316 (4)	0.5685 (5)	0.4530 (3)	0.0414
C22	0.2230 (4)	0.5725 (5)	0.4182 (3)	0.0388
C23	0.1755 (3)	0.7142 (5)	0.3777 (2)	0.0310
H31	0.0505	1.1468	0.2822	0.0361*
H32	0.0291	0.9684	0.3223	0.0361*
H81	−0.1340	0.7475	−0.0711	0.0298*
H101	0.1404	0.6977	0.0223	0.0338*
H121	0.2188	0.4234	−0.1516	0.0370*
H131	0.0466	0.4237	−0.2298	0.0323*

H141	−0.0835	0.5658	−0.1812	0.0320*
H161	0.2215	1.2561	0.3022	0.0392*
H171	0.4034	1.2469	0.3577	0.0460*
H181	0.4793	0.9987	0.4218	0.0430*
H201	0.4654	0.7053	0.4698	0.0481*
H211	0.3637	0.4701	0.4807	0.0471*
H221	0.1825	0.4757	0.4223	0.0500*
H231	0.1028	0.7148	0.3554	0.0411*
H61	−0.1720	0.9124	0.0296	0.0316*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0286 (17)	0.0293 (17)	0.0205 (14)	0.0020 (14)	0.0052 (12)	−0.0015 (13)
C2	0.0247 (15)	0.0304 (17)	0.0213 (14)	0.0017 (13)	0.0057 (12)	0.0002 (13)
C3	0.0241 (16)	0.0308 (18)	0.0263 (15)	0.0057 (13)	0.0051 (12)	−0.0010 (13)
S4	0.0185 (4)	0.0297 (4)	0.0249 (4)	0.0029 (3)	0.0033 (3)	−0.0009 (3)
C5	0.0173 (14)	0.0227 (16)	0.0272 (15)	0.0009 (12)	0.0039 (12)	0.0027 (12)
N6	0.0162 (12)	0.0277 (14)	0.0290 (14)	0.0013 (11)	0.0055 (10)	0.0005 (11)
N7	0.0199 (12)	0.0242 (13)	0.0273 (13)	0.0026 (11)	0.0059 (11)	0.0029 (11)
C8	0.0193 (14)	0.0228 (15)	0.0259 (15)	−0.0002 (12)	0.0038 (12)	0.0023 (12)
C9	0.0193 (14)	0.0227 (16)	0.0255 (15)	−0.0026 (12)	0.0055 (12)	0.0017 (12)
C10	0.0192 (14)	0.0306 (18)	0.0283 (16)	−0.0008 (13)	0.0027 (12)	0.0004 (14)
N11	0.0217 (13)	0.0289 (15)	0.0328 (15)	−0.0001 (11)	0.0073 (11)	0.0010 (12)
C12	0.0248 (16)	0.0282 (17)	0.0327 (17)	−0.0010 (13)	0.0118 (13)	0.0003 (14)
C13	0.0276 (16)	0.0312 (17)	0.0212 (14)	−0.0053 (13)	0.0068 (13)	−0.0015 (13)
C14	0.0246 (15)	0.0277 (17)	0.0226 (15)	−0.0027 (13)	0.0016 (12)	0.0022 (13)
S15	0.0218 (4)	0.0409 (5)	0.0335 (4)	0.0047 (3)	0.0087 (3)	−0.0037 (4)
C16	0.0347 (18)	0.0294 (19)	0.0276 (16)	−0.0033 (15)	0.0026 (14)	0.0003 (14)
C17	0.0344 (19)	0.040 (2)	0.0311 (18)	−0.0106 (16)	0.0062 (15)	−0.0034 (16)
C18	0.0243 (16)	0.052 (2)	0.0226 (16)	−0.0042 (16)	0.0025 (13)	−0.0059 (16)
C19	0.0279 (16)	0.037 (2)	0.0215 (15)	0.0076 (15)	0.0057 (13)	−0.0004 (14)
C20	0.0335 (19)	0.053 (3)	0.0270 (17)	0.0150 (18)	0.0045 (15)	0.0035 (17)
C21	0.051 (2)	0.037 (2)	0.038 (2)	0.0177 (19)	0.0148 (19)	0.0105 (17)
C22	0.047 (2)	0.032 (2)	0.040 (2)	0.0056 (17)	0.0156 (18)	0.0044 (16)
C23	0.0320 (18)	0.0329 (19)	0.0287 (16)	−0.0020 (15)	0.0085 (14)	0.0007 (14)

Geometric parameters (Å, °)

C1—C2	1.433 (5)	N11—C12	1.350 (5)
C1—C19	1.441 (5)	C12—C13	1.380 (5)
C1—C23	1.416 (5)	C12—H121	0.935
C2—C3	1.504 (5)	C13—C14	1.390 (5)
C2—C16	1.368 (5)	C13—H131	0.905
C3—S4	1.824 (4)	C14—H141	0.928
C3—H31	0.973	C16—C17	1.414 (5)
C3—H32	0.985	C16—H161	0.935
S4—C5	1.758 (3)	C17—C18	1.357 (6)
C5—N6	1.352 (4)	C17—H171	0.940

C5—S15	1.659 (3)	C18—C19	1.404 (6)
N6—N7	1.381 (4)	C18—H181	0.921
N6—H61	0.873	C19—C20	1.416 (5)
N7—C8	1.283 (4)	C20—C21	1.369 (6)
C8—C9	1.458 (5)	C20—H201	0.933
C8—H81	0.944	C21—C22	1.393 (7)
C9—C10	1.392 (4)	C21—H211	0.939
C9—C14	1.393 (5)	C22—C23	1.362 (6)
C10—N11	1.336 (4)	C22—H221	0.935
C10—H101	0.939	C23—H231	0.929
C2—C1—C19	118.3 (3)	C13—C12—H121	119.1
C2—C1—C23	123.5 (3)	C12—C13—C14	119.1 (3)
C19—C1—C23	118.2 (3)	C12—C13—H131	120.6
C1—C2—C3	121.1 (3)	C14—C13—H131	120.3
C1—C2—C16	119.4 (3)	C9—C14—C13	119.2 (3)
C3—C2—C16	119.4 (3)	C9—C14—H141	119.4
C2—C3—S4	105.3 (2)	C13—C14—H141	121.4
C2—C3—H31	109.7	C2—C16—C17	122.1 (4)
S4—C3—H31	109.2	C2—C16—H161	119.5
C2—C3—H32	111.9	C17—C16—H161	118.4
S4—C3—H32	111.2	C16—C17—C18	119.4 (4)
H31—C3—H32	109.4	C16—C17—H171	119.7
C3—S4—C5	102.53 (16)	C18—C17—H171	120.9
S4—C5—N6	112.7 (2)	C17—C18—C19	121.7 (3)
S4—C5—S15	125.7 (2)	C17—C18—H181	120.9
N6—C5—S15	121.7 (2)	C19—C18—H181	117.4
C5—N6—N7	116.9 (3)	C1—C19—C18	119.2 (3)
C5—N6—H61	121.7	C1—C19—C20	118.3 (4)
N7—N6—H61	121.4	C18—C19—C20	122.5 (3)
N6—N7—C8	116.2 (3)	C19—C20—C21	121.2 (4)
N7—C8—C9	118.3 (3)	C19—C20—H201	118.5
N7—C8—H81	121.0	C21—C20—H201	120.3
C9—C8—H81	120.7	C20—C21—C22	120.2 (4)
C8—C9—C10	121.0 (3)	C20—C21—H211	119.5
C8—C9—C14	121.5 (3)	C22—C21—H211	120.3
C10—C9—C14	117.5 (3)	C21—C22—C23	120.9 (4)
C9—C10—N11	123.9 (3)	C21—C22—H221	119.3
C9—C10—H101	118.1	C23—C22—H221	119.8
N11—C10—H101	118.0	C1—C23—C22	121.2 (4)
C10—N11—C12	117.7 (3)	C1—C23—H231	119.2
N11—C12—C13	122.6 (3)	C22—C23—H231	119.7
N11—C12—H121	118.3		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H61···N11^{i}	0.87	1.96	2.825 (2)	170

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

Fig. 1

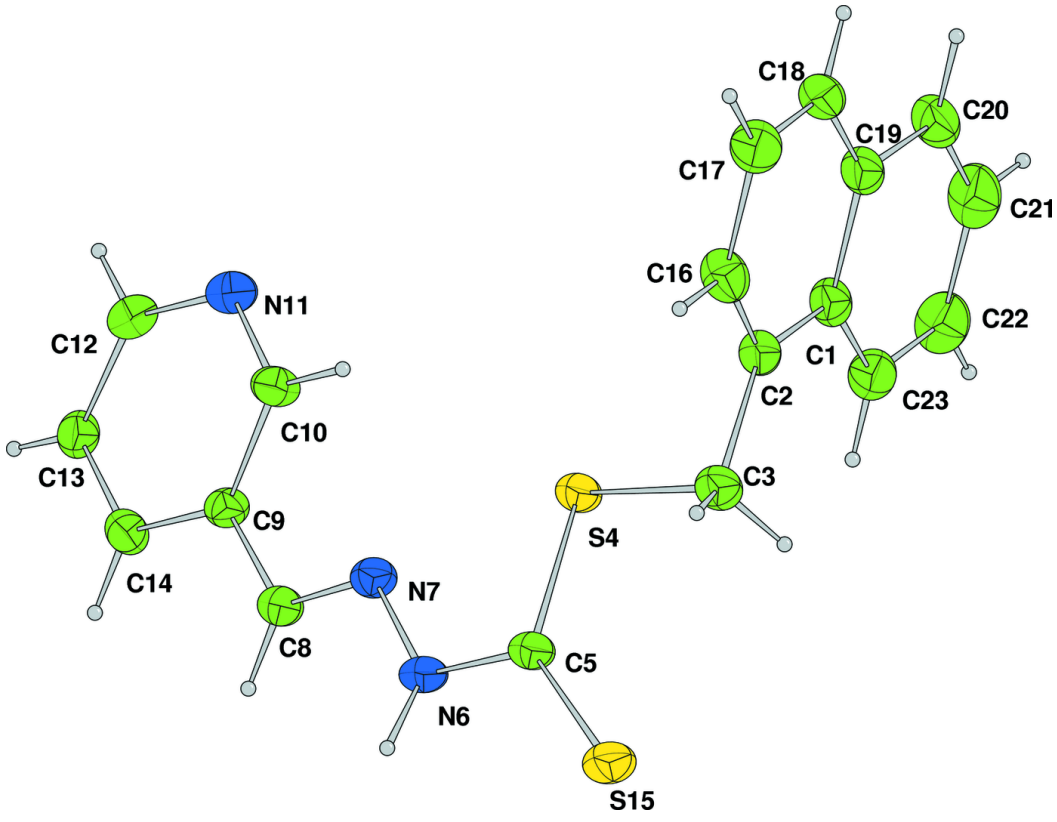
C18
C20
C19
C17
C21
C16
N11
C22
C12
C1
C10
C2
C23
C13
C3
S4
C9
C14
N7
C8
C5
N6
S15

Fig. 2

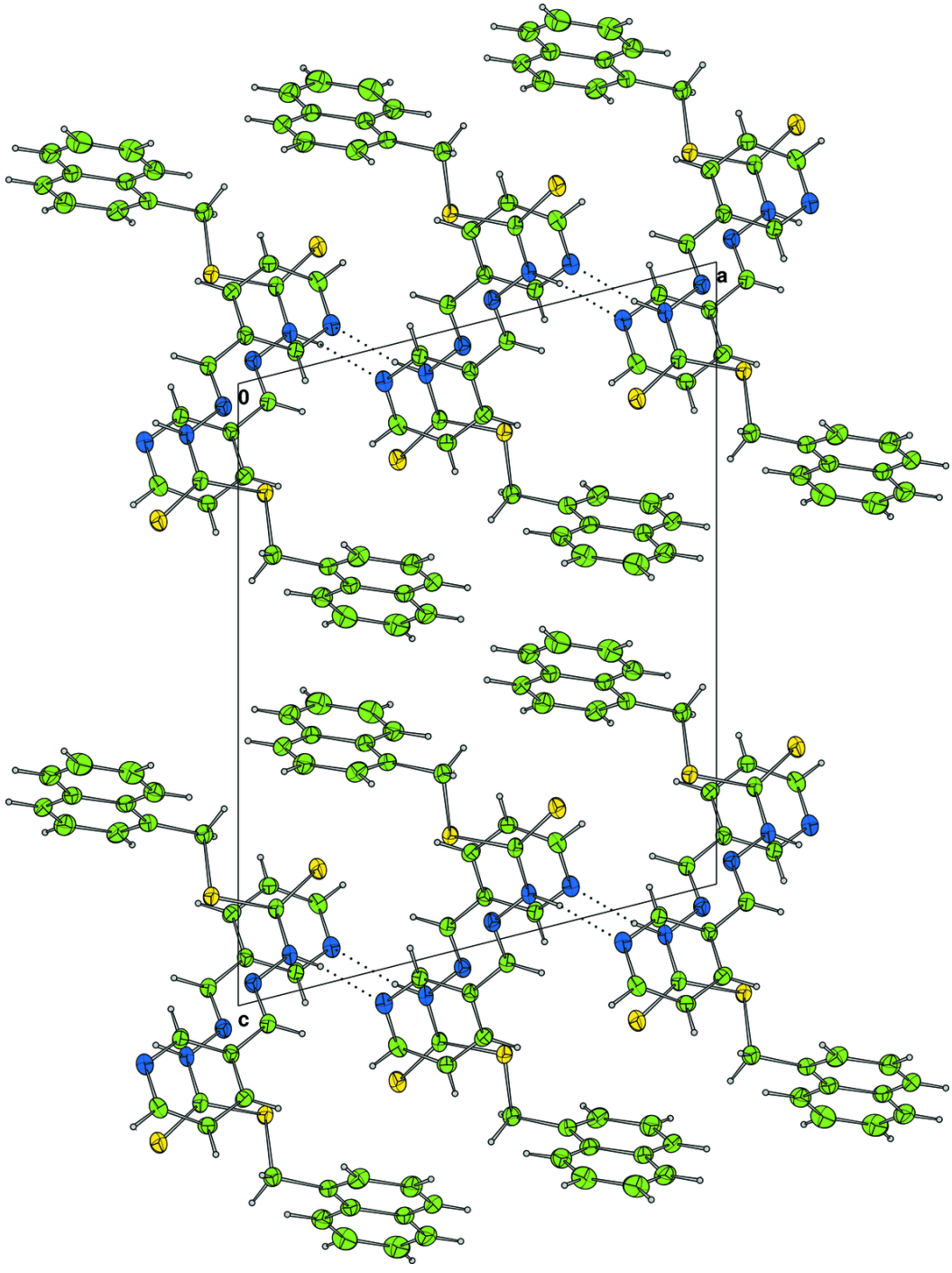

Fig. 3

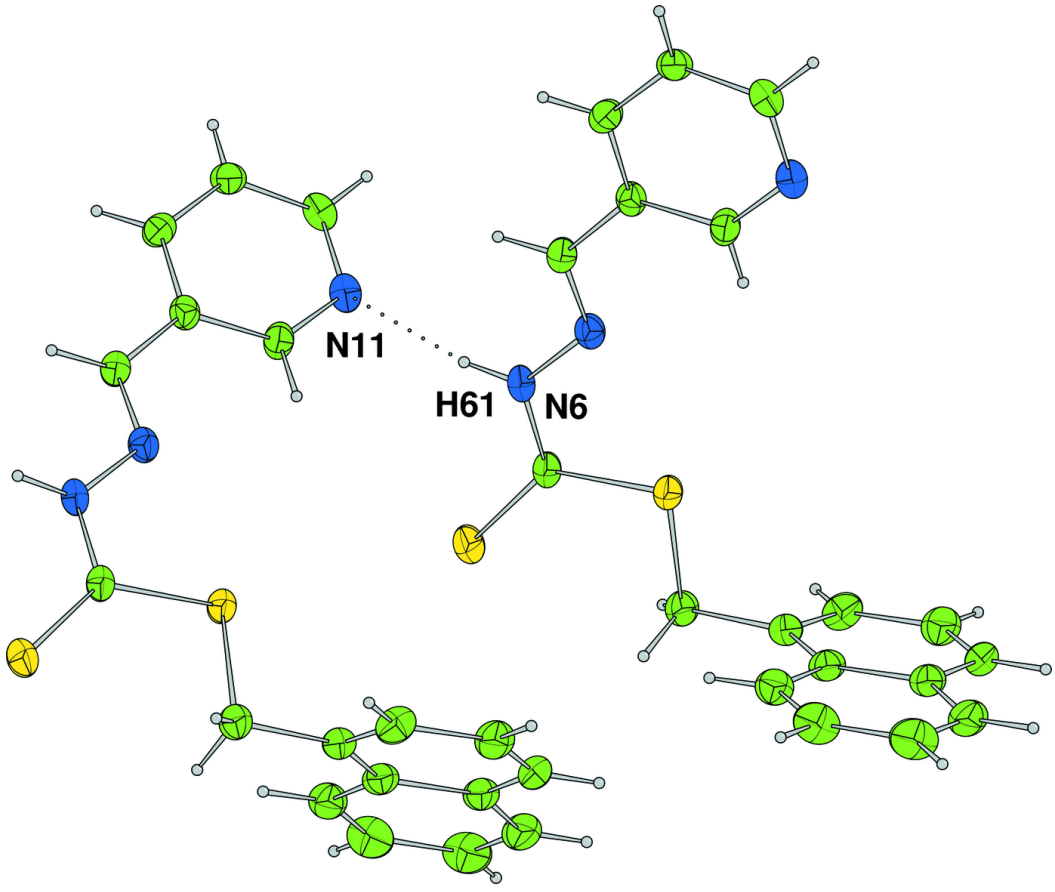

Fig. 4