Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

S-Quinolin-2-ylmethyldithiocarbazate

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Received 1 May 2007; accepted 18 May 2007

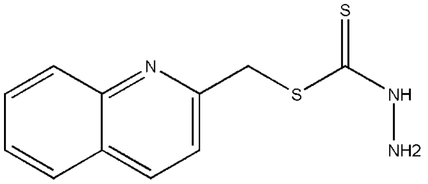
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.079; data-to-parameter ratio = 18.7.

In the title compound, $C_{11}H_{11}N_2S_2$, there is an intramolecular N—H···N [2.778 (2) Å] hydrogen bond linking the quinoline N atom and the imino N atom. The planar quinoline ring system forms an angle of 67.7 (1)° with the dithiocarbazate group. Bond angles for both S—C—S [115.66 (8)°] and N—C—S [119.05 (11)°] are comparable with *cis–trans S*-methyldithiocarbazate but differ from those found in *trans–cis S*-methyldithiocarbazate and *trans–cis S*-benzyldithiocarbazate. This is due to the N—H···N hydrogen bond that exists only in the *cis–trans* conformation found for the title compound.

Related literature

For chemical properties, see: Wang *et al.* (2002); Zhou *et al.* (2007). For biological activity, see: Crouse *et al.* (2004); Ali *et al.* (2004); Tarafder *et al.* (2002); Neelam *et al.* (2000). For similar structures, see: Das & Livingstone (1976); Crouse *et al.* (2004); Sutton (1965); Shanmuga Sundara Raj *et al.* (2000).

For related literature, see: Crouse *et al.* (2003); Lanfredi *et al.* (1977); Mattes & Weber (1980).



Experimental

Crystal data

$C_{11}H_{11}N_3S_2$
M_r = 249.36
Monoclinic, $P2_1/c$
a = 11.0514 (2) Å
b = 10.0620 (2) Å
c = 11.2780 (2) Å
α = 90°
β = 113.2607 (11)°
γ = 90°
V = 1152.17 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 150 K
0.36 × 0.26 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.78, $T_{\max}$ = 0.92
11993 measured reflections
2717 independent reflections
2717 reflections with $I > -3\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.079
S = 0.97
2717 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N10—H1···N6	0.86	1.96	2.778 (2)	157

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *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: FL2133).

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o3138 How *et al.* • $C_{11}H_{11}N_3S_2$ *Acta Cryst.* (2007). E**63**, o3137–o3138

supplementary materials

Acta Cryst. (2007). E**63**, o3137-o3138   [**doi:10.1107/S1600536807024609**]

***S*-Quinolin-2-ylmethyldithiocarbazate**

F. N.-F. How, D. J. Watkin, K. A. Crouse and **M. I. M. Tahir**

Comment

There has been considerable work done on the synthesis and characterization of new compounds derived from *S*-methyl and *S*-benzyldithiocarbazate due to the fact that these compounds have donor atoms that chelate with metal ions to form metal complexes with various coordination modes or they can react with carbonyl compounds to yield Schiff bases which may also be multidentate ligands. Most importantly, they and/or their metal complexes are often biologically active. [Crouse *et al.*, 2004; Neelam *et al.*, 2000 & Tarafder *et al.*, 2002]. Our attempt to synthesize a novel dithiocarbazate ligand was very successful, and eventually led us to the title compound. [Fig. 1.]

The C—N bond [1.3142 (17) Å] has some double-bond character. [1.296 (2)Å for *S*-2-picolyldithiocarbazate; Crouse *et al.*, 2003] and [1.320 (3)Å for *S*-benzyldithiocarbazate; Shanmuga Sundara Raj *et al.*, 2000]. The N10—N11 [1.4056 (17) Å] is slightly shorter than in *cis-trans* *S*-methyldithiocarbazate [1.415 (3) Å; Lanfredi *et al.*, 1977] and *S*-2-picolyldithiocarbazate [1.437 (2) Å; Crouse *et al.*, 2003] but comparable with *trans-cis* Sbenzyldithiocarbazate. [1.406 (3) Å; Shanmuga Sundara Raj *et al.*, 2000]

The C=S bond length [1.6804 (14) Å] agrees well with both literature values of 1.679 (4)Å (Lanfredi *et al.*, 1977) and 1.678 (3)Å (Shanmuga Sundara Raj *et al.*, 2000) proposed as an intermediate between a single [1.82 Å] and a double bond [1.56 Å] character [Sutton, 1965]. This was attributed to delocalization of negative charge over the C–N–N–C–S chain, which was generated upon deprotonation of the ligands during coordination.

The conformations of the structures were assigned based on significant differences in the bond angles and not the bond lengths. Bond angles of S—C—S and N—C—S differ significantly for both *cis-trans* and *trans-cis* conformations. [Mattes & Weber, 1980]

The bond angles, S8—C9—S12 [115.66 (8)°] and N10—C9—S8 [119.05 (11)°] are agreeable with *cis-trans* *S*-methyldithiocarbazate [116.2 (1)° and 119.3 (1)°; Lanfredi *et al.*, 1977] but was significantly different from *trans-cis* *S*-methyldithiocarbazate [125.5 (3)° and 113.6 (3)°; Mattes & Weber, 1980] and *trans-cis* *S*-benzyldithiocarbazate [125.5 (2)° and 113.5 (2)°; Shanmuga Sundara Raj *et al.*, 2000]

The significance of the bond angles is related to the existence of intramolecular hydrogen bonds in both *cis-trans* and *trans-cis* conformers. N—H···N hydrogen bonds only exists in *cis-trans* conformer while the *trans-cis* conformer have N—H···S hydrogen bonds. [Lanfredi *et al.*, 1977, Mattes & Weber, 1980 & Shanmuga Sundara Raj *et al.*, 2000]. The type of hydrogen bonding and the bond angles help differentiate between the types of conformation. Therefore, the title compound is confirmed as *cis-trans* *S*-quinolin-2ylmethyldithiocarbazate.

The crystal structure consists of layers of aromatic residues lying parallel to the *bc* plane at a=0.5. [Fig. 2.] The dithiocarbazate moieties protrude above and below this plane. Pairs of quinoline rings lie parallel and overlapping with each other (mean separation of 3.4 Å). This exhibits the characteristic of a π-π interaction between the rings. [Fig. 3.]

There is an intramolecular hydrogen bond N10—H1···N6 [2.778 (2)°] is slightly shorter than in *cis*-*trans* *S*-methyldithiocarbazate. [2.968 (4)°; Lanfredi *et al.*, 1977], which stabillizes the conformation of the molecule. [Fig. 1.]

The N11—H3···S8 contacts could be considered as a weak intermolecular hydrogen bond because the distance of H3···S8 is 2.832 (1)°, is smaller than the total radii of H(1.20) and S(1.80), which is 3.0° [Fig. 2].

Experimental

Potassium hydroxide (0.2 mol) was dissolved in 90% ethanol (70 ml) and mixed with hydrazine hydrate (0.2 mol). The mixture was placed in an ice salt bath to cool to 273 K. Carbon disulfide (0.2 mol) was added dropwise below 265 K with constant stirring over a period of 1 h. Upon addition of carbon disulfide, two layers were formed. 40% ethanol (60 ml) was added to the brown oil (lower layer) and the mixture was kept in an ice bath. 2-chloromethylquinoline hydrochloride (0.2 mol) dissolved in 80% ethanol (80 ml) was added dropwise with vigorous stirring. The product, cream coloured SQ2MDTC, (I) formed was filtered, recrystallized from ethanol and dried *in vacuo* over silica gel. (yield 75%, m.p 414.2–415.7 K). Cystals of SQ2MDTC suitable for X-ray analysis were grown in ethanol through slow evaporation.

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_{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 other atoms were refined with anisotropic atomic displacement parameters.

Figures

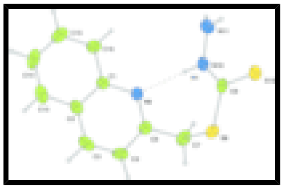

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius. The molecule is stabilized by intramolecular N—H—N hydrogen bond. Dotted line denotes the N—H—N hydrogen bond.

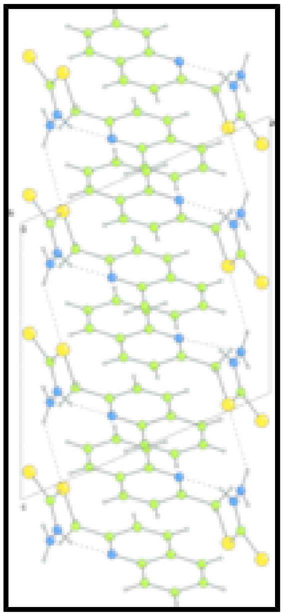

Fig. 2. The packing of the molecule viewed along the *b* axis showing the aromatic layer lying parallel to the *bc* plane at a=0.5.

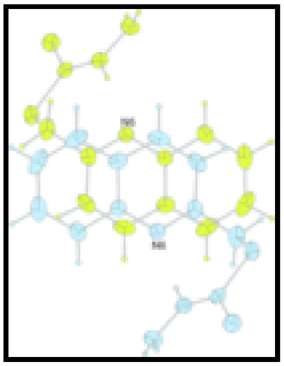

Fig. 3. The stacking π-π interaction of pairs of the quinoline rings.

S-quinolin-2-ylmethyldithiocarbazate

Crystal data

$C_{11}H_{11}N_3S_2$

M_r = 249.36

Monoclinic, $P2_1/c$

a = 11.0514 (2) Å

b = 10.0620 (2) Å

c = 11.2780 (2) Å

β = 113.2607 (11)°

V = 1152.17 (4) Å^3

Z = 4

F_{000} = 520

D_x = 1.437 Mg m^{-3}

Melting point: 415.7 K

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 2735 reflections

θ = 5–28°

μ = 0.44 mm^{-1}

T = 150 K

Plate, yellow

0.36 × 0.26 × 0.20 mm

Data collection

Nonius KappaCCD area-detector

2717 reflections with $I > -3\sigma(I)$

diffractometer	
Monochromator: graphite	$R_{\text{int}} = 0.025$
$T = 150$ K	$\theta_{\max} = 27.9°$
ω scans	$\theta_{\min} = 5.2°$
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	$h = -14 \rightarrow 14$
$T_{\min} = 0.78$, $T_{\max} = 0.92$	$k = -11 \rightarrow 13$
11993 measured reflections	$l = -14 \rightarrow 14$
2717 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	Method = modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.02P)^2 + 0.66P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 0.97$	$\Delta\rho_{\max} = 0.37$ e Å^{-3}
2717 reflections	$\Delta\rho_{\min} = -0.41$ e Å^{-3}
145 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	0.48620 (13)	0.67545 (14)	0.41804 (12)	0.0223
C2	0.60247 (14)	0.60714 (15)	0.42925 (14)	0.0260
C3	0.58815 (16)	0.48964 (16)	0.35641 (15)	0.0328
C4	0.46609 (16)	0.44675 (15)	0.27809 (14)	0.0311
C5	0.35528 (14)	0.52185 (14)	0.26985 (13)	0.0252
N6	0.36434 (11)	0.63152 (12)	0.33708 (11)	0.0233
C7	0.21899 (16)	0.48171 (16)	0.17912 (14)	0.0326
S8	0.16795 (4)	0.56396 (4)	0.02240 (3)	0.0284
C9	0.11613 (13)	0.72301 (15)	0.04637 (13)	0.0235
N10	0.14555 (12)	0.76515 (13)	0.16482 (11)	0.0250
N11	0.11690 (13)	0.89477 (13)	0.19239 (12)	0.0307
S12	0.03297 (4)	0.81044 (4)	−0.08834 (3)	0.0302
C13	0.72616 (16)	0.65867 (18)	0.51324 (16)	0.0369
C14	0.73288 (17)	0.77111 (19)	0.58239 (16)	0.0413
C15	0.61735 (18)	0.83803 (17)	0.57193 (15)	0.0372
C16	0.49628 (16)	0.79170 (15)	0.49167 (14)	0.0291
H31	0.6658	0.4422	0.3632	0.0419*
H41	0.4521	0.3684	0.2293	0.0390*
H71	0.1548	0.5028	0.2159	0.0368*

H72	0.2190	0.3877	0.1611	0.0368*
H131	0.8015	0.6126	0.5194	0.0431*
H141	0.8138	0.8033	0.6377	0.0442*
H151	0.6249	0.9149	0.6204	0.0422*
H161	0.4192	0.8344	0.4858	0.0353*
H1	0.1992	0.7206	0.2298	0.0303*
H2	0.0887	0.9460	0.1277	0.0390*
H3	0.0912	0.8983	0.2537	0.0395*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0250 (7)	0.0228 (7)	0.0189 (6)	0.0008 (5)	0.0085 (5)	0.0039 (5)
C2	0.0258 (7)	0.0294 (7)	0.0237 (7)	0.0042 (6)	0.0105 (6)	0.0084 (6)
C3	0.0370 (8)	0.0352 (8)	0.0309 (8)	0.0145 (7)	0.0183 (7)	0.0072 (7)
C4	0.0459 (9)	0.0252 (7)	0.0233 (7)	0.0072 (6)	0.0148 (7)	0.0006 (6)
C5	0.0327 (8)	0.0231 (7)	0.0182 (6)	−0.0009 (6)	0.0083 (6)	0.0040 (5)
N6	0.0239 (6)	0.0243 (6)	0.0203 (5)	0.0014 (5)	0.0072 (5)	0.0026 (5)
C7	0.0394 (9)	0.0266 (7)	0.0257 (7)	−0.0068 (6)	0.0063 (6)	0.0029 (6)
S8	0.0326 (2)	0.02827 (19)	0.01951 (18)	−0.00116 (15)	0.00525 (15)	−0.00155 (14)
C9	0.0186 (6)	0.0308 (7)	0.0206 (6)	−0.0027 (5)	0.0074 (5)	−0.0001 (6)
N10	0.0236 (6)	0.0315 (6)	0.0182 (5)	0.0040 (5)	0.0063 (5)	0.0022 (5)
N11	0.0331 (7)	0.0355 (7)	0.0216 (6)	0.0093 (6)	0.0089 (5)	0.0004 (5)
S12	0.0314 (2)	0.0362 (2)	0.01872 (18)	0.00486 (15)	0.00525 (15)	0.00255 (15)
C13	0.0243 (7)	0.0456 (9)	0.0362 (8)	0.0023 (7)	0.0071 (6)	0.0147 (8)
C14	0.0340 (9)	0.0454 (10)	0.0301 (8)	−0.0136 (7)	−0.0028 (7)	0.0114 (7)
C15	0.0518 (10)	0.0280 (8)	0.0250 (7)	−0.0102 (7)	0.0079 (7)	0.0002 (6)
C16	0.0369 (8)	0.0249 (7)	0.0248 (7)	0.0016 (6)	0.0114 (6)	0.0005 (6)

Geometric parameters (Å, °)

C1—C2	1.4181 (19)	S8—C9	1.7563 (15)
C1—N6	1.3680 (18)	C9—N10	1.3142 (17)
C1—C16	1.413 (2)	C9—S12	1.6804 (14)
C2—C3	1.413 (2)	N10—N11	1.4056 (17)
C2—C13	1.418 (2)	N10—H1	0.864
C3—C4	1.358 (2)	N11—H2	0.846
C3—H31	0.958	N11—H3	0.845
C4—C5	1.410 (2)	C13—C14	1.359 (3)
C4—H41	0.938	C13—H131	0.931
C5—N6	1.3201 (18)	C14—C15	1.407 (3)
C5—C7	1.504 (2)	C14—H141	0.924
C7—S8	1.8275 (15)	C15—C16	1.368 (2)
C7—H71	0.976	C15—H151	0.932
C7—H72	0.967	C16—H161	0.933
C2—C1—N6	121.42 (13)	C7—S8—C9	104.99 (7)
C2—C1—C16	119.36 (13)	S8—C9—N10	119.05 (11)
N6—C1—C16	119.21 (13)	S8—C9—S12	115.66 (8)

C1—C2—C3	117.67 (14)	N10—C9—S12	125.28 (11)
C1—C2—C13	118.86 (14)	C9—N10—N11	122.50 (12)
C3—C2—C13	123.47 (14)	C9—N10—H1	120.4
C2—C3—C4	119.90 (14)	N11—N10—H1	115.7
C2—C3—H31	118.6	N10—N11—H2	114.4
C4—C3—H31	121.5	N10—N11—H3	113.4
C3—C4—C5	119.09 (14)	H2—N11—H3	123.4
C3—C4—H41	122.6	C2—C13—C14	120.48 (16)
C5—C4—H41	118.3	C2—C13—H131	117.7
C4—C5—N6	122.89 (14)	C14—C13—H131	121.8
C4—C5—C7	120.75 (14)	C13—C14—C15	120.54 (15)
N6—C5—C7	116.34 (13)	C13—C14—H141	119.9
C1—N6—C5	119.01 (12)	C15—C14—H141	119.6
C5—C7—S8	112.34 (10)	C14—C15—C16	120.71 (16)
C5—C7—H71	110.7	C14—C15—H151	118.7
S8—C7—H71	108.3	C16—C15—H151	120.6
C5—C7—H72	108.8	C1—C16—C15	120.04 (15)
S8—C7—H72	105.4	C1—C16—H161	118.8
H71—C7—H72	111.2	C15—C16—H161	121.2

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H1···N6	0.86	1.96	2.778 (2)	157

Fig. 1

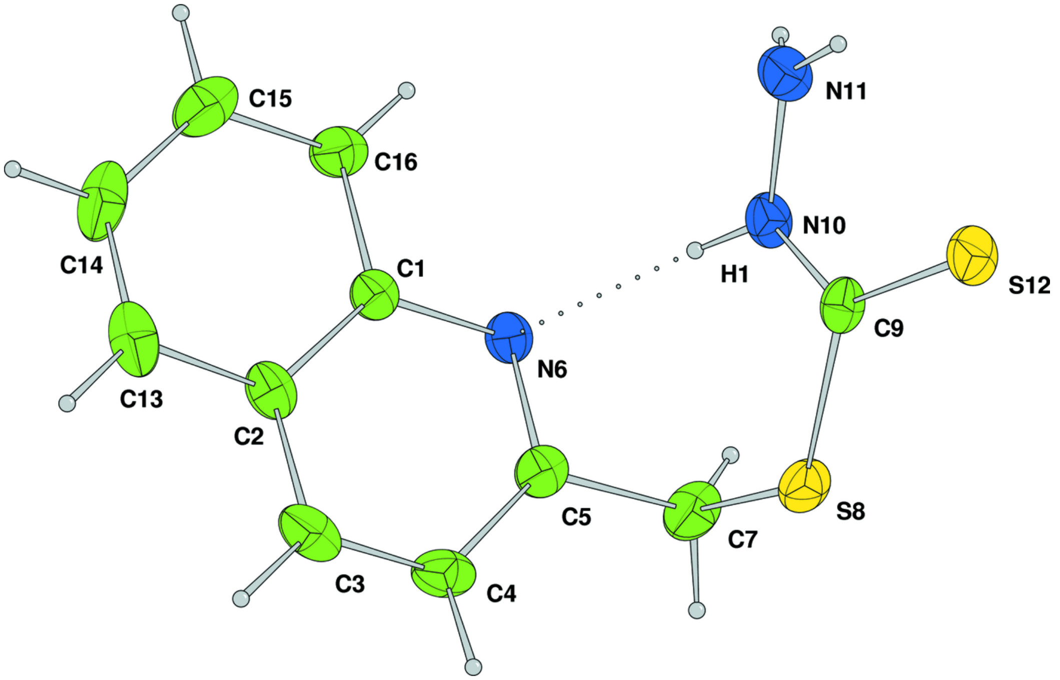

Fig. 2

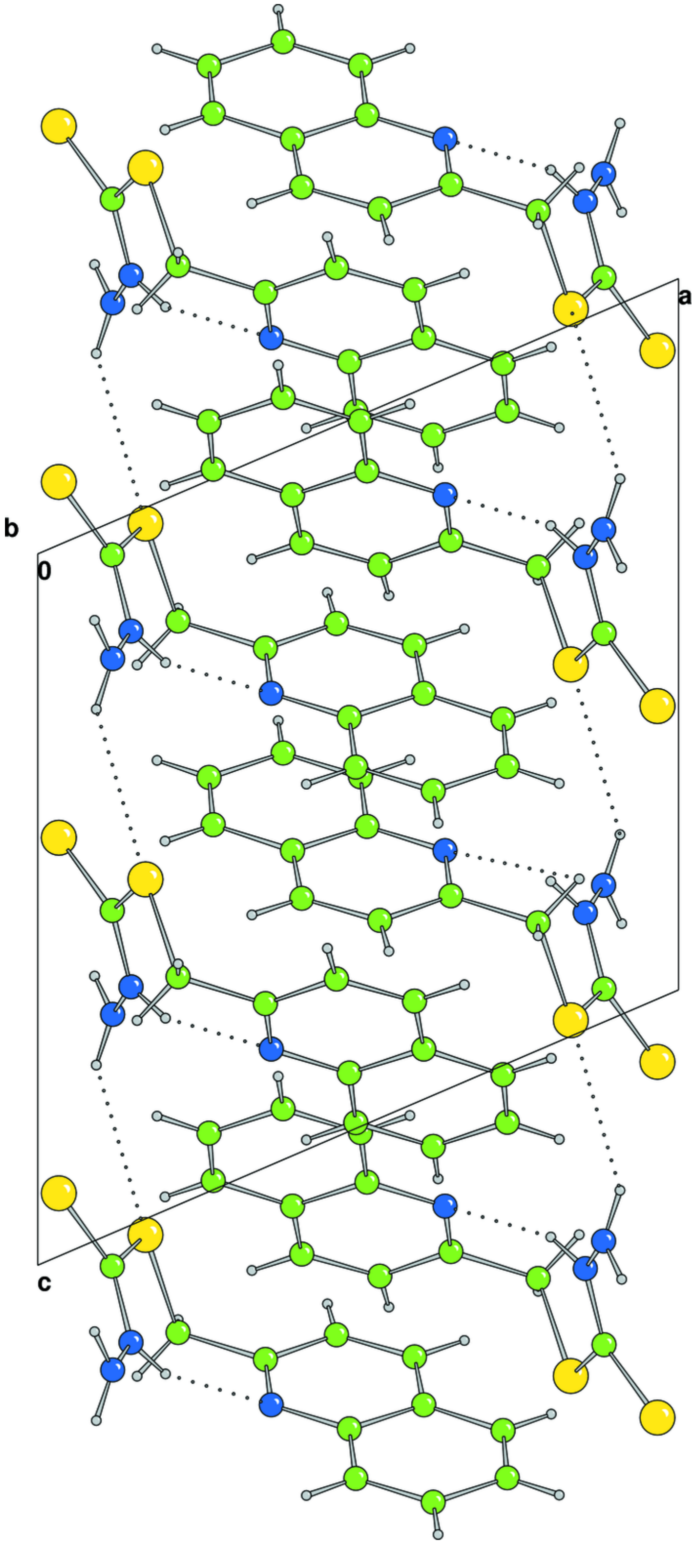

Fig. 3