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Benzyl *N*′-[1-(3-pyridyl)ethylidene]-hydrazinecarbodithioate

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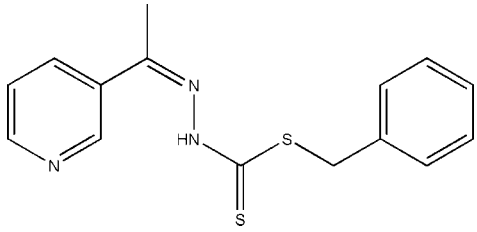
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.074; data-to-parameter ratio = 19.4.

The title compound, $C_{15}H_5N_2S_2$, crystallizes as a *trans–cis* conformer. The thione sulfur is in a *trans* position with the methyl pyridyl fragment with respect to the C—N bond but adopts a *cis* position with the benzyl ring across the C—S bond. The dihedral angle between the planar quinoline ring and the dithiocarbazate unit is 103.70 (1)°. The inclination of the dithiocarbazate unit with the benzyl group is 17.20 (1)°. There are strong π–π stacking interactions between pairs of dithiocarbazate units and also pairs of pyridine rings [3.27 (5) and 3.28 (5) Å, respectively]. A long-distance intermolecular N—H···N hydrogen bond [3.171 (2) Å] also stabilizes the structure.

Related literature

The dithiocarbazate ligand, *S*-benzyldithiocarbazate (SBDTC), was prepared as described by Shanmuga Sundara Raj *et al.* (2000). Interatomic parameters for the crystal structure are comparable with those reported by Chan *et al.* (2003), Khoo *et al.* (2005) and How *et al.* (2007). For related literature, see: Ali *et al.* (2002, 2005); Görbitz (1999); Tarafder *et al.* (2002).



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Experimental

Crystal data

$C_{15}H_{15}N_3S_2$
M_r = 301.44
Monoclinic, $P2_1/c$
a = 11.7234 (2) Å
b = 13.5577 (2) Å
c = 9.3637 (1) Å
β = 93.2187 (7)°
V = 1485.94 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 150 K
0.50 × 0.48 × 0.42 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.58, T_{max} = 0.86
18346 measured reflections
3512 independent reflections
3512 reflections with $I > -3\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.074
S = 0.98
3512 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N10—H1···N15^{i}	0.87	2.32	3.171 (2)	165

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

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: PK2024).

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supplementary materials

Acta Cryst. (2007). E**63**, o3023-o3024 [**doi:10.1107/S1600536807025056**]

Benzyl *N*'-[1-(3-pyridyl)ethylidene]hydrazinecarbodithioate

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

Comment

Many Schiff bases and metal complexes have been derived from *S*-benzyldithiocarbazate (SBDTC) because these compounds are often biologically active. [Ali *et al.*, 2005, Tarafder *et al.*, 2002 and Ali *et al.*, 2002]. Our attempt to synthesize Schiff bases with different pyridyl isomers led to the title compound [Fig. 1].

The C1—N10 bond [1.3549 (15) Å] is comparable with the literature value and shows some double-bond character [1.342 (2) Å; Chan *et al.*, 2003] and [1.343 (3) Å; Khoo *et al.*, 2005]. The C=S bond is 1.6526 (12) Å, comparable with Schiff bases derived from *S*-benzyldithiocarbazate. [1.6503 (17) Å; Chan *et al.*, 2003] and [1.664 (2) Å; Khoo *et al.*, 2005]

The bond angle N11—N10—C1 [116.92 (10)°] is slightly smaller than in Schiff bases derived from *S*-benzyldithiocarbazate [119.20 (14)°; Chan *et al.*, 2003] and [119.35 (17)°; Khoo *et al.*, 2005], but comparable with Schiff base derived from *S*-quinolin-2-ylmethyldithiocarbazate [117.61 (13)°; How *et al.*, 2007]. Bond angle of S20—C1—S2 [124.99 (7)°] is comparable with other literature values. [125.60 (10)°; Chan *et al.*, 2003] and [125.22 (12)°; Khoo *et al.*, 2005].

Viewed along the *b* axis [Fig. 2], the molecules form columnar stacks with overlapping benzyl fragments and overlapping π-π stacked pyridine [mean separation of 3.28 (5) Å] and dithiocarabazate [mean separation of 3.27 (5) Å] groups. There is also a long N—H···N [3.171 (2) Å] hydrogen bond [Fig 3.]

Experimental

S-benzyldithiocarbazate(SBDTC) (1.98 g, 0.01 mol), prepared as previously described (Shanmuga Sundara Raj *et al.*, 2000), was dissolved in hot absolute ethanol (35 ml). Equimolar amount of 3-acetylpyridine was added dropwise into the dissolved SBDTC (in ethanol). The mixture was left heated with stirring to reduce to half the volume and allowed to stand until precipitates formed. Products were filtered, washed with ethanol and dried *in vacuo* over P_2O_5. Crystals suitable for X-ray analysis were obtained by upon slow evaporation of ethanol. Yield: 72.6%

Refinement

The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.48) reflect effects in addition to absorption, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO*/*SCALEPACK*, Otwinowski & Minor, 1997).

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 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.

Figures

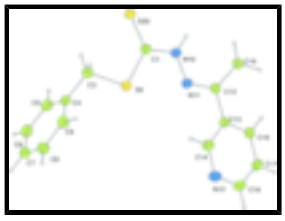


Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

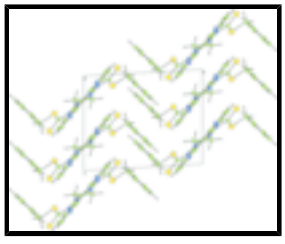


Fig. 2. A packing diagram of the molecules viewed along the *b* axis.

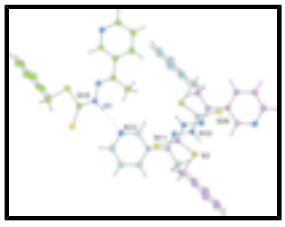


Fig. 3. Weak intermolecular N10—H1···N15 hydrogen bond stabilize the molecules, while pairs of dithiocarbazate moieties overlap each other.

Benzyl *N*'-[1-(3-pyridyl)ethylidene]hydrazinecarbodithioate

Crystal data

$C_{15}H_{15}N_3S_2$	F_{000} = 632
M_r = 301.44	D_x = 1.347 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 3554 reflections
a = 11.7234 (2) Å	θ = 5–28º
b = 13.5577 (2) Å	μ = 0.35 mm^{-1}
c = 9.3637 (1) Å	T = 150 K
β = 93.2187 (7)º	Block, yellow
V = 1485.94 (4) Å^3	0.50 × 0.48 × 0.42 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	3512 reflections with $I > -3\sigma(I)$
Monochromator: graphite	R_{int} = 0.023
T = 150 K	θ_{max} = 27.9º
ω scans	θ_{min} = 5.3º
Absorption correction: multi-scan	h = −15→15

(DENZO/SCALEPACK; Otwinowski & Minor, 1997)

T_{min} = 0.58, T_{max} = 0.86

18346 measured reflections

3512 independent reflections

$k = -17 \rightarrow 16$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.074$

$S = 0.98$

3512 reflections

181 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.02P)^2 + 0.86P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.30$ e Å^{-3}

$\Delta\rho_{min} = -0.26$ e Å^{-3}

Extinction correction: None

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.78782 (10)	0.50631 (9)	0.44621 (12)	0.0204
S2	0.75601 (3)	0.62579 (2)	0.38062 (3)	0.0260
C3	0.63081 (12)	0.65609 (10)	0.47897 (15)	0.0299
C4	0.57579 (10)	0.74496 (9)	0.40744 (13)	0.0245
C5	0.49029 (11)	0.73279 (10)	0.29964 (14)	0.0279
C6	0.43974 (11)	0.81421 (11)	0.23204 (14)	0.0303
C7	0.47496 (11)	0.90850 (10)	0.27085 (15)	0.0302
C8	0.56030 (12)	0.92152 (10)	0.37744 (15)	0.0309
C9	0.60965 (11)	0.83996 (10)	0.44638 (15)	0.0288
N10	0.88055 (9)	0.46646 (7)	0.38812 (11)	0.0219
N11	0.93938 (9)	0.52578 (7)	0.29861 (11)	0.0215
C12	1.02748 (10)	0.49194 (8)	0.23857 (12)	0.0197
C13	1.08339 (10)	0.56350 (8)	0.14515 (12)	0.0192
C14	1.06341 (11)	0.66496 (9)	0.15753 (13)	0.0248
N15	1.11066 (10)	0.73385 (8)	0.07742 (12)	0.0277
C16	1.18224 (11)	0.70228 (9)	−0.02079 (14)	0.0263
C17	1.20734 (11)	0.60399 (10)	−0.04110 (14)	0.0267
C18	1.15730 (10)	0.53334 (9)	0.04278 (14)	0.0238
C19	1.07337 (11)	0.38876 (9)	0.25203 (14)	0.0247
S20	0.71415 (3)	0.44675 (2)	0.56445 (3)	0.0232
H31	0.6542	0.6703	0.5772	0.0370*
H32	0.5808	0.5988	0.4735	0.0362*
H51	0.4672	0.6679	0.2716	0.0337*
H61	0.3812	0.8048	0.1577	0.0372*

H71	0.4403	0.9651	0.2234	0.0369*
H81	0.5850	0.9864	0.4052	0.0372*
H91	0.6661	0.8487	0.5191	0.0358*
H141	1.0131	0.6874	0.2285	0.0300*
H161	1.2152	0.7523	−0.0771	0.0315*
H171	1.2586	0.5850	−0.1096	0.0330*
H181	1.1733	0.4650	0.0300	0.0286*
H191	1.1552	0.3882	0.2461	0.0373*
H192	1.0426	0.3489	0.1756	0.0393*
H193	1.0549	0.3586	0.3418	0.0371*
H1	0.8966	0.4043	0.4024	0.0281*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0209 (5)	0.0197 (5)	0.0207 (5)	−0.0008 (4)	0.0013 (4)	−0.0012 (4)
S2	0.02711 (16)	0.02204 (16)	0.02971 (17)	0.00520 (11)	0.01023 (12)	0.00635 (11)
C3	0.0302 (6)	0.0279 (6)	0.0329 (7)	0.0080 (5)	0.0126 (5)	0.0075 (5)
C4	0.0229 (6)	0.0236 (6)	0.0278 (6)	0.0039 (5)	0.0103 (5)	0.0036 (5)
C5	0.0277 (6)	0.0248 (6)	0.0320 (6)	−0.0023 (5)	0.0085 (5)	−0.0010 (5)
C6	0.0239 (6)	0.0373 (7)	0.0299 (6)	0.0010 (5)	0.0036 (5)	0.0034 (6)
C7	0.0273 (6)	0.0287 (7)	0.0357 (7)	0.0076 (5)	0.0105 (5)	0.0076 (5)
C8	0.0333 (7)	0.0213 (6)	0.0390 (7)	0.0005 (5)	0.0089 (6)	−0.0007 (5)
C9	0.0264 (6)	0.0293 (7)	0.0309 (6)	0.0003 (5)	0.0023 (5)	0.0002 (5)
N10	0.0242 (5)	0.0179 (5)	0.0242 (5)	0.0007 (4)	0.0064 (4)	0.0018 (4)
N11	0.0229 (5)	0.0198 (5)	0.0221 (5)	−0.0012 (4)	0.0047 (4)	0.0011 (4)
C12	0.0206 (5)	0.0171 (5)	0.0213 (5)	−0.0004 (4)	0.0014 (4)	−0.0014 (4)
C13	0.0186 (5)	0.0180 (5)	0.0211 (5)	−0.0004 (4)	0.0005 (4)	−0.0010 (4)
C14	0.0300 (6)	0.0183 (5)	0.0268 (6)	0.0008 (5)	0.0085 (5)	−0.0018 (4)
N15	0.0345 (6)	0.0190 (5)	0.0302 (6)	−0.0018 (4)	0.0081 (5)	−0.0001 (4)
C16	0.0283 (6)	0.0240 (6)	0.0268 (6)	−0.0050 (5)	0.0051 (5)	0.0017 (5)
C17	0.0246 (6)	0.0275 (6)	0.0289 (6)	−0.0006 (5)	0.0093 (5)	−0.0011 (5)
C18	0.0230 (6)	0.0196 (5)	0.0291 (6)	0.0018 (4)	0.0052 (5)	−0.0013 (5)
C19	0.0251 (6)	0.0173 (5)	0.0322 (6)	0.0012 (4)	0.0052 (5)	0.0008 (5)
S20	0.02532 (16)	0.02044 (15)	0.02438 (15)	−0.00051 (11)	0.00682 (11)	0.00225 (11)

Geometric parameters (Å, °)

C1—S2	1.7647 (12)	N10—N11	1.3747 (13)
C1—N10	1.3550 (15)	N10—H1	0.872
C1—S20	1.6526 (12)	N11—C12	1.2879 (15)
S2—C3	1.8229 (13)	C12—C13	1.4834 (16)
C3—C4	1.5059 (17)	C12—C19	1.5014 (16)
C3—H31	0.965	C13—C14	1.4013 (16)
C3—H32	0.973	C13—C18	1.3892 (16)
C4—C5	1.3919 (19)	C14—N15	1.3374 (16)
C4—C9	1.3904 (18)	C14—H141	0.962
C5—C6	1.3886 (19)	N15—C16	1.3490 (16)
C5—H51	0.953	C16—C17	1.3802 (18)

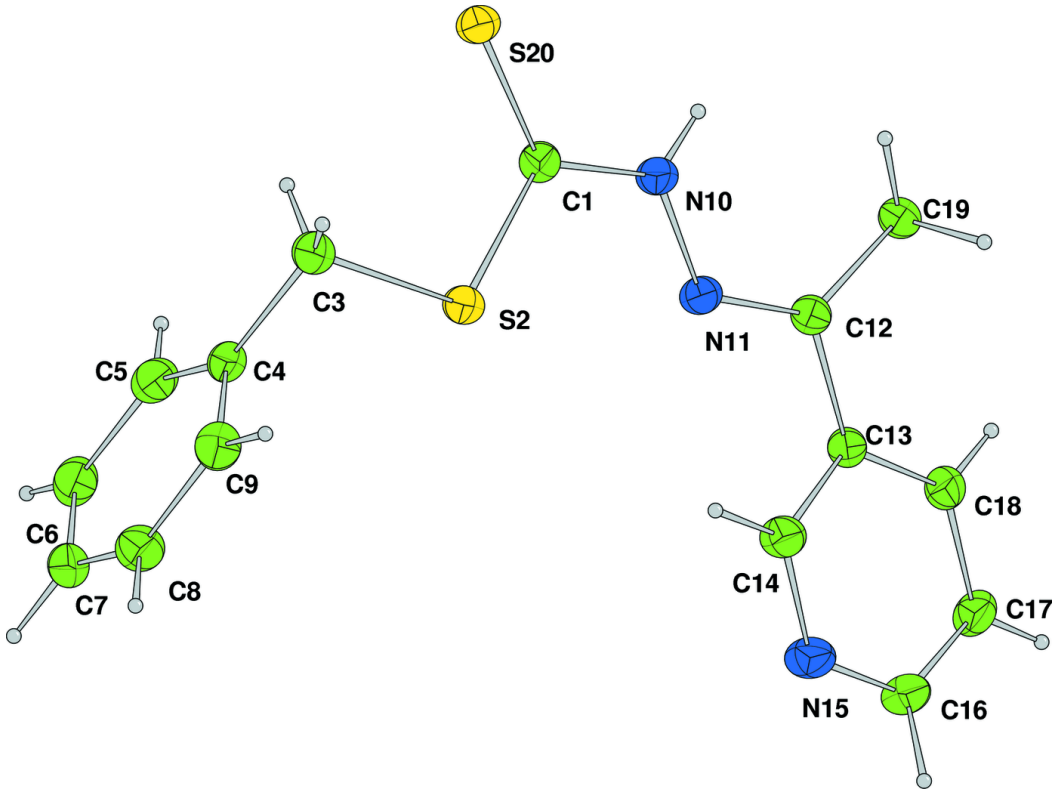
C6—C7	1.386 (2)	C16—H161	0.954
C6—H61	0.958	C17—C18	1.3893 (17)
C7—C8	1.384 (2)	C17—H171	0.939
C7—H71	0.964	C18—H181	0.955
C8—C9	1.3900 (19)	C19—H191	0.964
C8—H81	0.957	C19—H192	0.951
C9—H91	0.930	C19—H193	0.970
S2—C1—N10	112.64 (8)	C1—N10—H1	119.7
S2—C1—S20	124.99 (7)	N11—N10—H1	123.2
N10—C1—S20	122.37 (9)	N10—N11—C12	119.99 (10)
C1—S2—C3	101.04 (6)	N11—C12—C13	114.59 (10)
S2—C3—C4	107.01 (8)	N11—C12—C19	125.99 (11)
S2—C3—H31	109.4	C13—C12—C19	119.39 (10)
C4—C3—H31	110.9	C12—C13—C14	120.78 (10)
S2—C3—H32	107.0	C12—C13—C18	121.86 (10)
C4—C3—H32	112.0	C14—C13—C18	117.36 (11)
H31—C3—H32	110.4	C13—C14—N15	124.25 (11)
C3—C4—C5	120.05 (12)	C13—C14—H141	118.6
C3—C4—C9	121.04 (12)	N15—C14—H141	117.1
C5—C4—C9	118.91 (12)	C14—N15—C16	116.99 (11)
C4—C5—C6	120.52 (12)	N15—C16—C17	123.09 (11)
C4—C5—H51	119.4	N15—C16—H161	116.0
C6—C5—H51	120.1	C17—C16—H161	121.0
C5—C6—C7	120.05 (12)	C16—C17—C18	119.19 (11)
C5—C6—H61	119.7	C16—C17—H171	120.6
C7—C6—H61	120.3	C18—C17—H171	120.2
C6—C7—C8	119.96 (12)	C17—C18—C13	119.13 (11)
C6—C7—H71	120.1	C17—C18—H181	120.4
C8—C7—H71	119.9	C13—C18—H181	120.4
C7—C8—C9	119.91 (13)	C12—C19—H191	110.9
C7—C8—H81	120.5	C12—C19—H192	110.3
C9—C8—H81	119.6	H191—C19—H192	106.8
C4—C9—C8	120.65 (12)	C12—C19—H193	111.6
C4—C9—H91	119.4	H191—C19—H193	108.5
C8—C9—H91	120.0	H192—C19—H193	108.6
C1—N10—N11	116.92 (10)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H1···N15^{i}	0.87	2.32	3.171 (2)	165

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

Fig. 1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C1
N10
C19
C3
S2
N11
C12
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C4
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C9
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C6
C14
C8
C17
C7
N15
C16

Fig. 2

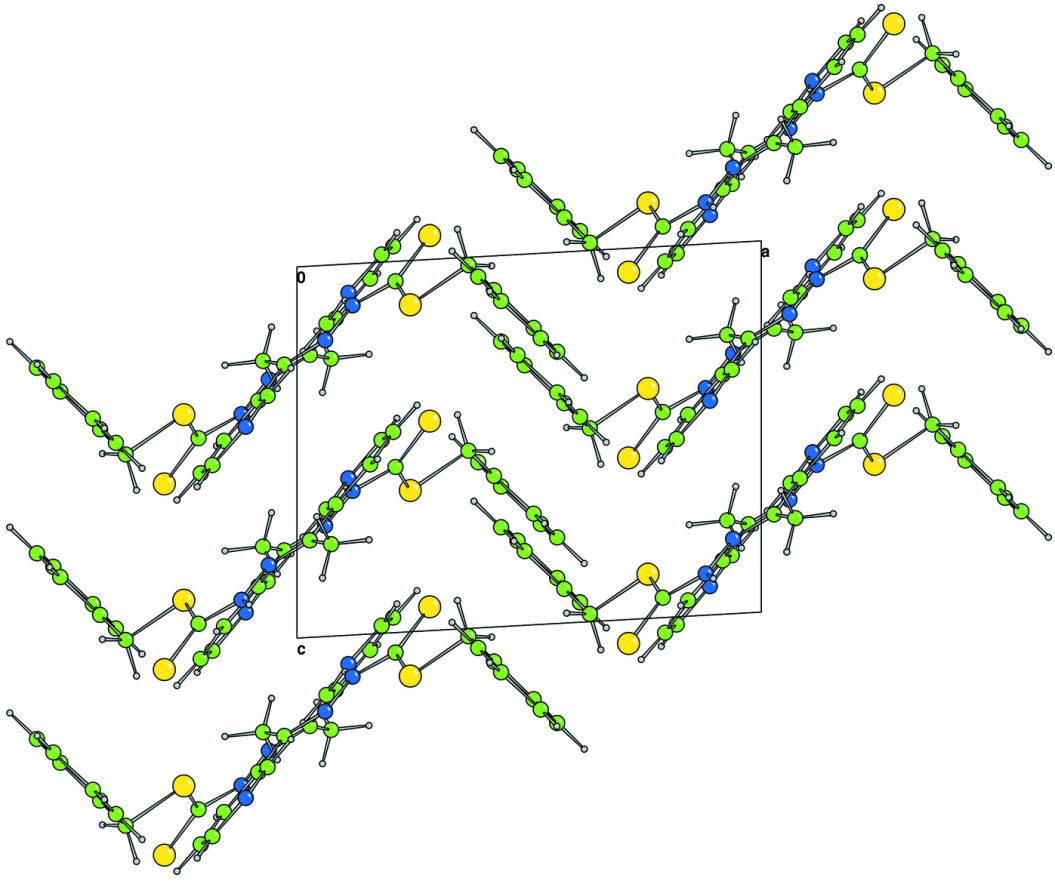

Fig. 3