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2-Quinolylmethyl *N*′-[1-(*m*-tolyl)ethylidene]hydrazinecarbodithioate

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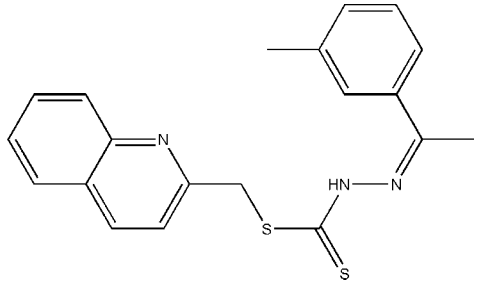
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.061; wR factor = 0.095; data-to-parameter ratio = 18.4.

The title compound, $C_{20}H_{19}N_3S_2$, crystallized as a *cis–trans* conformer in which the quinoline ring system is *cis* across the C—S bond but adopts a *trans* geometry with respect to the C—N bond. The compound exists in the thione form with the presence of a C=S bond.

Related literature

The dithiocarbazate ligand used to prepare the title compound is *S*-quinolin-2-ylmethyldithiocarbazate. This compound was prepared as described by How *et al.* (2007). Interatomic parameters for similar compounds are reported by Chan *et al.* (2003), Khoo *et al.* (2005) and How *et al.* (2007).



Experimental

Crystal data

$C_{20}H_{19}N_3S_2$
M_r = 365.52
Triclinic, $P\overline{1}$
a = 7.7423 (2) Å
b = 8.2816 (2) Å
c = 14.0409 (4) Å
α = 81.2501 (13)°
β = 80.5729 (13)°
γ = 85.7886 (13)°
V = 876.70 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 150 K
0.48 × 0.12 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.79, T_{max} = 0.98
14454 measured reflections
4155 independent reflections
4155 reflections with $I > -3\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.095
S = 0.93
4155 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C9—N10	1.352 (2)	N10—N11	1.3803 (19)
C9—S21	1.6593 (17)		
S8—C9—S21	126.92 (10)	C9—N10—N11	117.61 (13)
N10—C9—S21	120.76 (12)		

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: LW2012).

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supplementary materials

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2-Quinolylmethyl *N*'-[1-(*m*-tolyl)ethylidene]hydrazinecarbodithioate

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

Comment

S-quinolin-2-ylmethyldithiocarbazate, a new dithiocarbazate derivative has been introduced. This dithiocarbazate derivative ligand contains a quinoline ring [How, *et al.*, 2007]. This new ligand were used to synthesized new Schiff bases. It is likely that these compound will be of interest for further research.

The C9—N10 bond [1.352 (2) Å] is comparable with the literature value and showed a 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 1.6593 (17) Å, which is shorter than in *S*-quinolin-2-ylmethyldithiocarbazate [1.6804 (14) Å; How, *et al.*, 2007] but 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 molecule contains three planar fragments *viz*. the quinoline ring, dithiocarbazate moiety and the benzyl group. [Fig. 1.]. The dihedral angle between the planar quinoline ring and the dithiocarbazate moiety is 103.7°. The dihedral angle between the dithiocarbazate moiety with the benzyl group is 17.2°.

Bond angle N11—N10—C9 [117.61 (13)°] is slightly shorter than other Schiff bases. [119.20 (14)°; Chan *et al.*, 2003] and [119.35 (17)°; Khoo *et al.*, 2005]. However, S21—C9—S8 [126.92 (10)°] is slightly longer. [125.60 (10)°; Chan *et al.*, 2003] and [125.22 (12)°; Khoo *et al.*, 2005]. This is due to the twisting of both benzyl ring and the quinoline ring for stabilization.

The isolated molecule is *L* shaped [Fig. 2.]. Viewed along the *a* axis, the molecule packed in hearing-bone columns with pairs of quinoline rings residues lying parallel [Fig. 3.] and overlapping (mean separation 3.4 Å), corresponding to a reasonably strong π-π interaction between the quinoline rings. [Fig. 4.] Pairs of methyl benzyl residues are also almost parellel (mean separation 3.7 Å), but there is no overlap between the aromatic moieties. The moiety C7/S8/C9/N10/N11/C12/S21 behaves as a rigid group (TLS *R*-factor= 0.085).

Experimental

S-quinolin-2-ylmethyldithiocarbazate (0.02 mol) [How, *et al.*, 2007] was dissolved in hot absolute ethanol (30 ml) with dropwise addition of equimolar amount of 3-methylacetophenone. The mixture was left heated with stirring to reduce half the volume. Precipitate formed were filtered and washed with a little ice-cold ethanol. The crude yellow product was recrystallized from ethanol. Yellow single crystals were formed upon slow evaporation of an ethanol solution. (Yield = 70%, *M*.p = 437.7–438.5 K)

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

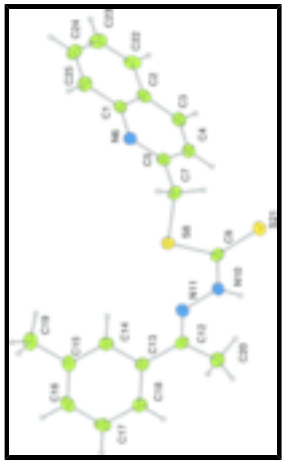

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

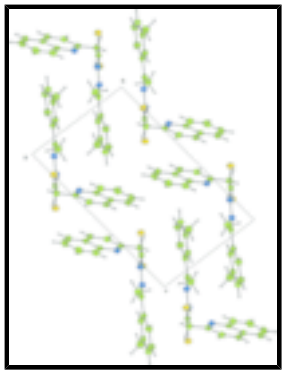

Fig. 2. The packing diagram of the molecules viewed along the *a* axis.

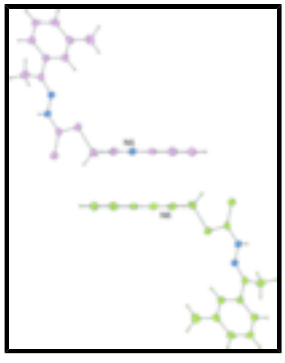

Fig. 3. The quinoline rings are parallel to each other.

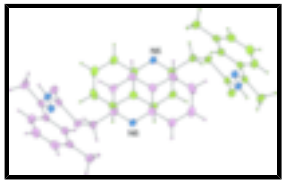

Fig. 4. The overlapping of the quinoline rings due to the π-π interaction.

2-Quinolylmethyl *N*'-[1-(*m*-tolyl)ethylidene]hydrazinecarbodithioate

Crystal data

$C_{20}H_{19}N_3S_2$	F_{000} = 384
M_r = 365.52	D_x = 1.385 Mg m^{-3}
Triclinic, $P\overline{1}$	Melting point: 438.5 K
a = 7.7423 (2) Å	Mo $K\alpha$ radiation λ = 0.71073 Å
b = 8.2816 (2) Å	Cell parameters from 3785 reflections
c = 14.0409 (4) Å	θ = 5–28º
α = 81.2501 (13)º	μ = 0.31 mm^{-1}
β = 80.5729 (13)º	T = 150 K
γ = 85.7886 (13)º	Plate, yellow
V = 876.70 (4) Å^3	0.48 × 0.12 × 0.06 mm
Z = 2	

Data collection

Nonius KappaCCD diffractometer	4155 reflections with $I > -3\sigma(I)$
Monochromator: graphite	R_{int} = 0.043
T = 150 K	θ_{max} = 27.9º
ω scans	θ_{min} = 5.1º
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	h = −9→10
T_{min} = 0.79, T_{max} = 0.98	k = −10→10
14454 measured reflections	l = −18→18
4155 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.061	Method = Modified Sheldrick w = 1/[\s^2^(F^2^) + (0.04P)^2^ + 0.22P] , where P = (max(F_o^2^,0) + 2F_c^2^)/3
$wR(F^2)$ = 0.095	$(\Delta/\sigma)_{max}$ = 0.0003
S = 0.93	$\Delta\rho_{max}$ = 0.52 e Å^{-3}
4155 reflections	$\Delta\rho_{min}$ = −0.45 e Å^{-3}
226 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	−0.0600 (2)	0.1649 (2)	0.37590 (12)	0.0210
C2	0.0184 (2)	0.2108 (2)	0.45150 (12)	0.0218
C3	0.1944 (2)	0.1553 (2)	0.45653 (13)	0.0227
C4	0.2799 (2)	0.0608 (2)	0.39084 (12)	0.0228
C5	0.1915 (2)	0.0177 (2)	0.31810 (12)	0.0205
N6	0.02722 (17)	0.06871 (17)	0.30981 (10)	0.0204
C7	0.2821 (2)	−0.0930 (2)	0.24793 (13)	0.0223
S8	0.45390 (5)	0.00735 (5)	0.15921 (3)	0.0227
C9	0.6441 (2)	−0.0558 (2)	0.21229 (12)	0.0207
N10	0.78668 (17)	0.02300 (17)	0.16409 (10)	0.0219
N11	0.76719 (18)	0.12944 (17)	0.08037 (10)	0.0220
C12	0.8989 (2)	0.2090 (2)	0.03342 (12)	0.0207
C13	0.8649 (2)	0.3172 (2)	−0.05711 (12)	0.0206
C14	0.6920 (2)	0.3671 (2)	−0.07123 (13)	0.0226
C15	0.6572 (2)	0.4663 (2)	−0.15533 (13)	0.0232
C16	0.7980 (2)	0.5155 (2)	−0.22723 (13)	0.0277
C17	0.9683 (2)	0.4654 (2)	−0.21536 (13)	0.0289
C18	1.0018 (2)	0.3675 (2)	−0.13044 (13)	0.0257
C19	0.4721 (2)	0.5204 (2)	−0.17004 (14)	0.0312
C20	1.0788 (2)	0.1982 (2)	0.06223 (13)	0.0275
S21	0.65894 (5)	−0.19488 (5)	0.30940 (3)	0.0245
C22	−0.0797 (2)	0.3076 (2)	0.51814 (13)	0.0272
C23	−0.2492 (2)	0.3583 (2)	0.50908 (14)	0.0315
C24	−0.3267 (2)	0.3139 (2)	0.43410 (14)	0.0309
C25	−0.2357 (2)	0.2197 (2)	0.36890 (14)	0.0264
H31	0.2520	0.1821	0.5049	0.0288*
H41	0.3961	0.0216	0.3934	0.0267*
H71	0.3351	−0.1901	0.2842	0.0269*
H72	0.1962	−0.1268	0.2120	0.0265*
H141	0.5976	0.3328	−0.0224	0.0273*
H161	0.7761	0.5849	−0.2840	0.0337*
H171	1.0622	0.4989	−0.2641	0.0341*
H181	1.1171	0.3356	−0.1222	0.0295*
H191	0.4597	0.6381	−0.1801	0.0469*
H192	0.3907	0.4809	−0.1141	0.0466*
H193	0.4445	0.4798	−0.2257	0.0463*
H201	1.1334	0.3001	0.0399	0.0415*
H202	1.0724	0.1749	0.1311	0.0415*
H203	1.1508	0.1128	0.0336	0.0421*
H221	−0.0266	0.3374	0.5687	0.0329*
H231	−0.3129	0.4241	0.5535	0.0372*
H241	−0.4440	0.3492	0.4284	0.0361*
H251	−0.2890	0.1901	0.3188	0.0310*
H1	0.8843	0.0107	0.1888	0.0281*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0220 (8)	0.0180 (8)	0.0207 (9)	−0.0026 (7)	−0.0008 (7)	0.0026 (7)
C2	0.0249 (8)	0.0184 (8)	0.0203 (9)	−0.0055 (7)	−0.0004 (7)	0.0018 (7)
C3	0.0238 (8)	0.0237 (9)	0.0208 (9)	−0.0049 (7)	−0.0045 (7)	−0.0011 (7)
C4	0.0189 (8)	0.0255 (9)	0.0232 (9)	−0.0019 (7)	−0.0042 (7)	0.0007 (7)
C5	0.0192 (8)	0.0205 (9)	0.0205 (9)	−0.0055 (7)	−0.0012 (6)	0.0011 (7)
N6	0.0177 (7)	0.0213 (7)	0.0209 (7)	−0.0029 (6)	−0.0015 (5)	0.0001 (6)
C7	0.0173 (8)	0.0245 (9)	0.0253 (9)	−0.0015 (7)	−0.0026 (7)	−0.0041 (7)
S8	0.0171 (2)	0.0292 (2)	0.0207 (2)	−0.00164 (17)	−0.00296 (16)	0.00023 (18)
C9	0.0187 (8)	0.0211 (9)	0.0226 (9)	0.0015 (7)	−0.0019 (7)	−0.0066 (7)
N10	0.0178 (7)	0.0264 (8)	0.0201 (7)	−0.0009 (6)	−0.0039 (6)	0.0022 (6)
N11	0.0210 (7)	0.0237 (8)	0.0199 (7)	−0.0006 (6)	−0.0022 (6)	0.0000 (6)
C12	0.0177 (8)	0.0222 (9)	0.0229 (9)	0.0002 (7)	−0.0026 (7)	−0.0068 (7)
C13	0.0203 (8)	0.0201 (9)	0.0214 (9)	−0.0018 (7)	−0.0015 (6)	−0.0043 (7)
C14	0.0212 (8)	0.0242 (9)	0.0224 (9)	−0.0030 (7)	−0.0019 (7)	−0.0047 (7)
C15	0.0278 (9)	0.0197 (9)	0.0240 (9)	−0.0002 (7)	−0.0074 (7)	−0.0062 (7)
C16	0.0369 (10)	0.0226 (9)	0.0220 (9)	−0.0012 (8)	−0.0047 (7)	0.0014 (7)
C17	0.0301 (9)	0.0250 (9)	0.0272 (10)	−0.0050 (8)	0.0054 (8)	0.0012 (8)
C18	0.0220 (8)	0.0256 (9)	0.0280 (10)	−0.0021 (7)	−0.0016 (7)	−0.0010 (8)
C19	0.0308 (10)	0.0322 (10)	0.0324 (11)	0.0019 (8)	−0.0125 (8)	−0.0037 (8)
C20	0.0204 (8)	0.0351 (10)	0.0266 (10)	−0.0039 (8)	−0.0058 (7)	0.0001 (8)
S21	0.0228 (2)	0.0262 (2)	0.0226 (2)	−0.00006 (18)	−0.00369 (17)	0.00191 (18)
C22	0.0316 (9)	0.0247 (9)	0.0242 (9)	−0.0053 (8)	0.0018 (7)	−0.0051 (8)
C23	0.0338 (10)	0.0221 (9)	0.0353 (11)	−0.0001 (8)	0.0055 (8)	−0.0061 (8)
C24	0.0231 (9)	0.0284 (10)	0.0377 (11)	0.0025 (8)	0.0004 (8)	−0.0014 (9)
C25	0.0227 (8)	0.0254 (9)	0.0299 (10)	−0.0009 (7)	−0.0034 (7)	−0.0010 (8)

Geometric parameters (Å, °)

C1—C2	1.417 (2)	C13—C18	1.390 (2)
C1—N6	1.375 (2)	C14—C15	1.386 (2)
C1—C25	1.416 (2)	C14—H141	0.944
C2—C3	1.415 (2)	C15—C16	1.398 (3)
C2—C22	1.414 (3)	C15—C19	1.507 (2)
C3—C4	1.358 (2)	C16—C17	1.382 (3)
C3—H31	0.932	C16—H161	0.941
C4—C5	1.419 (2)	C17—C18	1.386 (2)
C4—H41	0.939	C17—H171	0.940
C5—N6	1.328 (2)	C18—H181	0.933
C5—C7	1.503 (2)	C19—H191	0.963
C7—S8	1.8210 (16)	C19—H192	0.954
C7—H71	0.985	C19—H193	0.957
C7—H72	0.978	C20—H201	0.958
S8—C9	1.7679 (16)	C20—H202	0.951
C9—N10	1.352 (2)	C20—H203	0.963
C9—S21	1.6593 (17)	C22—C23	1.368 (3)

N10—N11	1.3803 (19)	C22—H221	0.948
N10—H1	0.875	C23—C24	1.400 (3)
N11—C12	1.287 (2)	C23—H231	0.945
C12—C13	1.489 (2)	C24—C25	1.367 (3)
C12—C20	1.506 (2)	C24—H241	0.946
C13—C14	1.408 (2)	C25—H251	0.942
C2—C1—N6	122.67 (15)	C15—C14—H141	119.1
C2—C1—C25	118.35 (17)	C14—C15—C16	118.53 (16)
N6—C1—C25	118.98 (15)	C14—C15—C19	121.25 (16)
C1—C2—C3	117.26 (16)	C16—C15—C19	120.21 (16)
C1—C2—C22	119.80 (16)	C15—C16—C17	120.91 (16)
C3—C2—C22	122.93 (16)	C15—C16—H161	119.3
C2—C3—C4	119.72 (16)	C17—C16—H161	119.8
C2—C3—H31	120.6	C16—C17—C18	120.06 (16)
C4—C3—H31	119.6	C16—C17—H171	120.3
C3—C4—C5	119.71 (15)	C18—C17—H171	119.6
C3—C4—H41	121.0	C13—C18—C17	120.55 (16)
C5—C4—H41	119.2	C13—C18—H181	119.6
C4—C5—N6	122.65 (16)	C17—C18—H181	119.8
C4—C5—C7	120.12 (15)	C15—C19—H191	109.8
N6—C5—C7	117.21 (14)	C15—C19—H192	110.7
C1—N6—C5	117.97 (14)	H191—C19—H192	108.1
C5—C7—S8	112.42 (11)	C15—C19—H193	110.0
C5—C7—H71	109.6	H191—C19—H193	109.1
S8—C7—H71	108.4	H192—C19—H193	109.0
C5—C7—H72	109.1	C12—C20—H201	109.5
S8—C7—H72	107.7	C12—C20—H202	110.9
H71—C7—H72	109.6	H201—C20—H202	108.8
C7—S8—C9	102.38 (8)	C12—C20—H203	110.5
S8—C9—N10	112.31 (12)	H201—C20—H203	108.8
S8—C9—S21	126.92 (10)	H202—C20—H203	108.2
N10—C9—S21	120.76 (12)	C2—C22—C23	120.19 (17)
C9—N10—N11	117.61 (13)	C2—C22—H221	119.3
C9—N10—H1	119.6	C23—C22—H221	120.5
N11—N10—H1	122.6	C22—C23—C24	120.11 (18)
N10—N11—C12	119.50 (13)	C22—C23—H231	119.4
N11—C12—C13	115.11 (14)	C24—C23—H231	120.5
N11—C12—C20	125.40 (15)	C23—C24—C25	121.11 (17)
C13—C12—C20	119.48 (14)	C23—C24—H241	119.6
C12—C13—C14	120.34 (15)	C25—C24—H241	119.3
C12—C13—C18	121.04 (15)	C1—C25—C24	120.43 (17)
C14—C13—C18	118.60 (15)	C1—C25—H251	119.1
C13—C14—C15	121.34 (16)	C24—C25—H251	120.5
C13—C14—H141	119.6		

Fig. 1

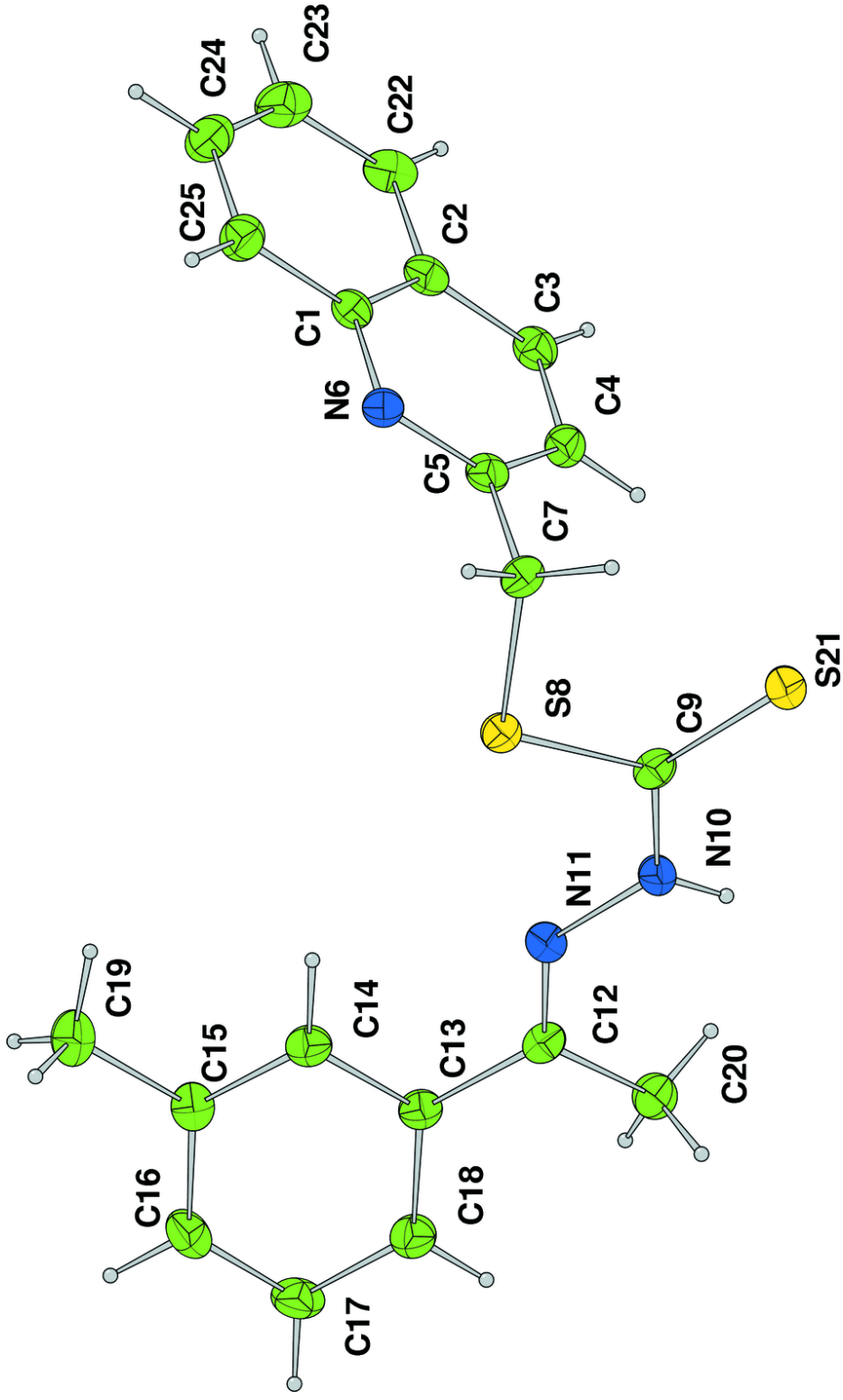
C24
C23
C22
C25
C2
C1
C3
N6
C4
C5
C7
S8
C9
S21
N10
N11
C19
C15
C14
C13
C12
C20
C16
C18
C17

Fig. 2

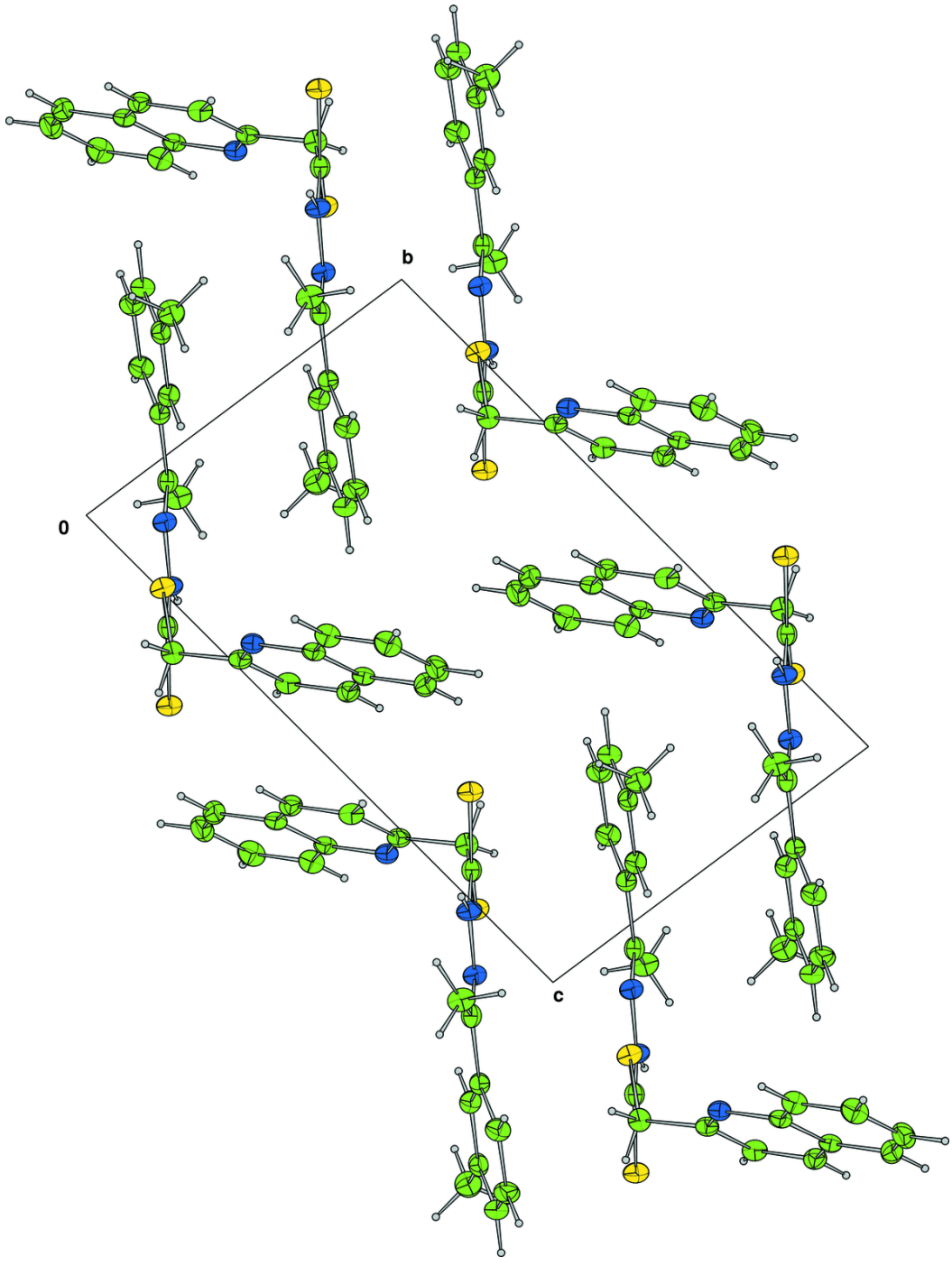

Fig. 3

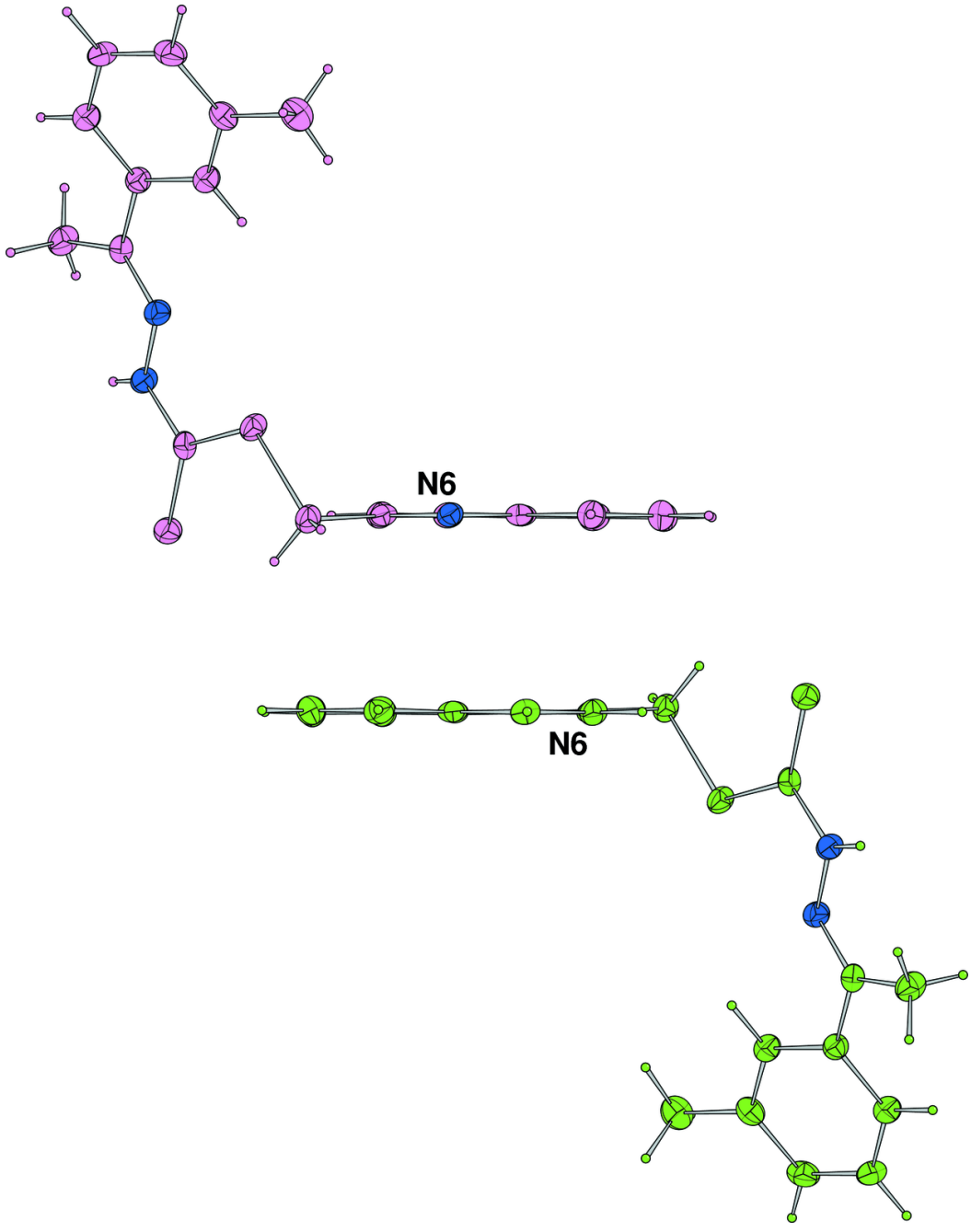

Fig. 4