(Z)-N,N-Dimethyl-2-[phenyl(pyridin-2-yl)methylidene]hydrazinecarbothioamide

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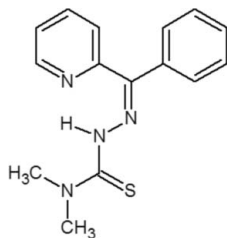Correspondence e-mail: eesans@yahoo.com

The title compound, $C_{15}H_{16}N_4S$, exists in the Z conformation with the thionyl S atom lying *cis* to the azomethine N atom. The shortening of the N—N distance [1.3697 (17) Å] is due to extensive delocalization with the pyridine ring. The hydrazine–carbothioamide unit is almost planar, with a maximum deviation of 0.013 (2) Å for the amide N atom. The stability of this conformation is favoured by the formation of an intramolecular N—H⋯N hydrogen bond. The packing of the molecules involves no classical intermolecular hydrogen-bonding interactions; however, a C—H⋯π interaction occurs.

Related literature

For abackground to hydrazinecarbothioamide and its derivatives, see: Beraldo & Gambino (2004). For the synthesis, see: Joseph *et al.* (2006). For related structures of hydrazinecarbothioamides, see: Philip *et al.* (2006); Arumugam *et al.* (2011). For related structures, see: Seena *et al.* (2008); Usman *et al.* (2002); Huheey *et al.* (1993); Joseph *et al.* (2004).

Experimental

Crystal data

$C_{15}H_{16}N_4S$	b = 8.888 (2) Å
M_r = 284.39	c = 16.256 (4) Å
Monoclinic, $P2_1/c$	β = 94.528 (3)°
a = 10.011 (2) Å	V = 1441.9 (6) Å^3
Z = 4	T = 153 K
Mo $K\alpha$ radiation	0.32 × 0.28 × 0.22 mm
μ = 0.22 mm^{-1}	

Data collection

Bruker P4 diffractometer	14231 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004) T_{min} = 0.932, T_{max} = 0.953	2828 independent reflections 2405 reflections with $I > 2\sigma(I)$ R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.110	
S = 1.06	
2828 reflections	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
188 parameters	$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

Cg is the centroid of the N1/C8–C12 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3′⋯N1	0.837 (17)	1.869 (17)	2.602 (2)	145.4 (15)
C5—H5⋯Cg^i	0.93	2.66	3.536 (2)	157

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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supplementary materials

(*Z*)-*N*,*N*-Dimethyl-2-[phenyl(pyridin-2-yl)methylidene]hydrazinecarbothioamide

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Comment

A large number of studies have been devoted to the search for derivatives of hydrazinecarbothioamide, which have been used as drugs and have the ability to form complexes. The biological activity of these compounds depends on the parent aldehyde or ketone (Beraldo & Gambino, 2004). Derivatives of hydrazinecarbothioamide constitute an important group of multidentate ligands with potential binding sites available for a wide variety of metal ions. These thiourea derivatives find substantial applications in different facets of contemporary scientific research.

The title compound (Z)-2-N,N-dimethyl-2-[phenyl(pyridin-2-yl)methylidene]hydrazinecarbothioamide is found to exist in Z configuration. A perspective view of the molecular structure of the title compound, along with the atom-labeling scheme, is given in Fig. 1. The S1= C13–N3–N2 torsion-angle [14.4 (2)°] indicates that thionyl atom S1 is positioned cis to azomethane nitrogen atom N2. The hydrazinecarbothioamide moiety adopts an extended conjugation, with electron delocalization throughout the N4/C13/S1/N3/N2 group. The fact that the compound exists in the thione form is confirmed by the N3—N2, N4—C13 and C13=S1 bond distances. The C13=S1 bond distance is close to that expected for a C=S double bond of 1.60 Å (Huheey *et al.*, 1993). The N3—N2 bond distance is very close to the reported similar substituted hydrazinecarbothioamide (Joseph *et al.*, 2004). The resonance form involving pyridine ring would account for the shortening of the N—N distance through extensive electron delocalization.

The hydrazinecarbothioamide moiety, comprising atoms N3, C13, S1 and N4, is almost planar with the maximum deviation of 0.013 (2) Å for atom N4. The pyridyl ring and phenyl ring are not in the same plane and the pyridyl ring is twisted significantly from the hydrazinecarbothioamide plane, with a torsionl angle of -176.3 (2)°.

Two types of intramolecular (classical and non-classical) hydrogen bond interactions are found in this molecule. A classical hydrogen bonding interaction between the hydrogen attached to the N3 nitrogen and the N1 nitrogen with the D⋯A distance of 2.602 (2) Å and the non-classical hydrogen bonding interaction between one of the hydrogen atom attached to the C14 atom and the S1 atom of the molecule with a D⋯A distance of 3.030 (2) Å as described in Table 1.

Fig. 2 shows the packing diagram of the title compound. Packing of these molecules does not include any classical intermolecular hydrogen bonding interactions in its molecular array. However, it may be directed by the C—H⋯π interaction between the pyridine ring and the hydrogen attached at C5 carbon atom of the phenyl ring of the another molecule. There are four very weak π–π interactions present in this molecular array with the distances of 5.5874 (17), 4.8708 (15), 5.5455 (17) and 4.9165 (15) Å between the centroids of the corresponding rings involving interactions.

Experimental

The title compound was prepared by adapting a reported procedure (Joseph *et al.*, 2006) by refluxing a mixture of methanolic solutions of 2-benzoylpyridine (11 mmol, 2.032 g) and N,N-dimethylhydrazinecarbothioamide (11 mmol, 1.320 g) for five hours after adding 5 drops of acetic acid. Yellow crystals were collected, washed with few drops of methanol and dried

over P_4O_{10} in vacuo. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation from its methanolic solution.

Refinement

All H atoms on C were placed in calculated positions, guided by difference maps, with C—H bond distances 0.93–0.96 Å. H atoms were assigned as U_{iso}=1.2Ueq (1.5 for Me). N3—H3' hydrogen was located from difference maps and restrained using *DFIX* instruction.

Figures
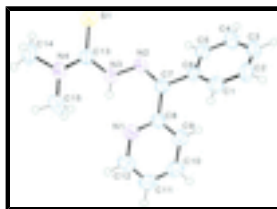
Fig. 1. The molecular structure of the title compound with displacement ellipsoids are drawn at 50% probability level.
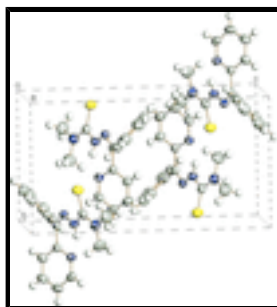
Fig. 2. Packing diagram of the title compound, the unit cell is viewed down the *a* axis.

(*Z*)-*N*,*N*-Dimethyl-2-[phenyl(pyridin-2- yl)methylidene]hydrazinecarbothioamide

Crystal data

$C_{15}H_{16}N_4S$	$F(000) = 600.0$
$M_r = 284.39$	$D_x = 1.310$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8120 reflections
$a = 10.011$ (2) Å	$\theta = 2.0–26.0°$
$b = 8.888$ (2) Å	$\mu = 0.22$ mm^{-1}
$c = 16.256$ (4) Å	$T = 153$ K
$\beta = 94.528$ (3)°	Block, yellow
$V = 1441.9$ (6) Å^3	$0.32 \times 0.28 \times 0.22$ mm
$Z = 4$	

Data collection

Bruker P4 diffractometer	2828 independent reflections

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 8.33 pixels mm^{-1}

ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2004)

$T_{min} = 0.932$, $T_{max} = 0.953$

14231 measured reflections

2405 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$

$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$

$h = -12 \rightarrow 12$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.110$

$S = 1.06$

2828 reflections

188 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.2366P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.014$

$\Delta\rho_{max} = 0.19$ e Å^{-3}

$\Delta\rho_{min} = -0.20$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc^{2}λ^3/sin(2θ)]$^{-1/4}$

Extinction coefficient: 0.0104 (16)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$
S1	0.75460 (4)	0.15132 (5)	0.31975 (3)	0.05808 (18)
N1	0.98755 (14)	0.68420 (14)	0.33757 (8)	0.0466 (3)
N2	0.99018 (12)	0.35758 (13)	0.36663 (7)	0.0413 (3)
N3	0.87523 (12)	0.42001 (16)	0.33015 (8)	0.0459 (3)
N4	0.68025 (13)	0.41370 (17)	0.25113 (9)	0.0552 (4)
C1	1.33165 (15)	0.42244 (19)	0.39734 (10)	0.0496 (4)
H1	1.3333	0.4983	0.3580	0.059*

C2	1.44999 (16)	0.3531 (2)	0.42682 (12)	0.0584 (5)
H2	1.5307	0.3820	0.4069	0.070*
C3	1.44848 (18)	0.2420 (2)	0.48527 (12)	0.0604 (5)
H3	1.5280	0.1956	0.5048	0.072*
C4	1.32983 (18)	0.1993 (2)	0.51494 (11)	0.0586 (5)
H4	1.3291	0.1248	0.5551	0.070*
C5	1.21090 (16)	0.26692 (18)	0.48536 (10)	0.0474 (4)
H5	1.1305	0.2368	0.5053	0.057*
C6	1.21111 (14)	0.37895 (16)	0.42634 (9)	0.0386 (3)
C7	1.08395 (14)	0.45037 (16)	0.39224 (8)	0.0383 (3)
C8	1.07742 (14)	0.61797 (16)	0.39196 (9)	0.0404 (3)
C9	1.15590 (16)	0.70179 (18)	0.44910 (10)	0.0499 (4)
H9	1.2173	0.6546	0.4865	0.060*
C10	1.14187 (19)	0.85641 (19)	0.44978 (13)	0.0600 (5)
H10	1.1928	0.9143	0.4882	0.072*
C11	1.05114 (18)	0.92430 (19)	0.39262 (12)	0.0574 (4)
H11	1.0408	1.0283	0.3912	0.069*
C12	0.97729 (18)	0.83393 (18)	0.33834 (11)	0.0527 (4)
H12	0.9165	0.8793	0.2998	0.063*
C13	0.77074 (15)	0.33429 (18)	0.29902 (9)	0.0442 (4)
C14	0.56134 (19)	0.3425 (3)	0.21167 (14)	0.0755 (6)
H14A	0.5778	0.3140	0.1564	0.113*
H14B	0.4877	0.4119	0.2101	0.113*
H14C	0.5400	0.2547	0.2424	0.113*
C15	0.6980 (2)	0.5728 (2)	0.23277 (14)	0.0770 (6)
H15A	0.6945	0.6306	0.2824	0.115*
H15B	0.6279	0.6051	0.1930	0.115*
H15C	0.7833	0.5874	0.2108	0.115*
H3'	0.8833 (15)	0.511 (2)	0.3188 (9)	0.043 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0506 (3)	0.0477 (3)	0.0740 (3)	−0.00580 (18)	−0.0075 (2)	−0.00052 (19)
N1	0.0516 (8)	0.0409 (7)	0.0469 (7)	0.0035 (6)	0.0016 (6)	0.0030 (5)
N2	0.0353 (6)	0.0410 (7)	0.0462 (7)	0.0030 (5)	−0.0045 (5)	0.0000 (5)
N3	0.0394 (7)	0.0388 (7)	0.0574 (8)	0.0035 (5)	−0.0087 (6)	0.0003 (6)
N4	0.0427 (7)	0.0588 (9)	0.0613 (8)	0.0069 (6)	−0.0143 (6)	−0.0006 (7)
C1	0.0441 (9)	0.0505 (9)	0.0542 (9)	0.0001 (7)	0.0042 (7)	0.0044 (7)
C2	0.0347 (8)	0.0697 (12)	0.0705 (11)	0.0005 (8)	0.0022 (8)	−0.0032 (9)
C3	0.0425 (9)	0.0639 (11)	0.0711 (11)	0.0098 (8)	−0.0182 (8)	−0.0052 (9)
C4	0.0562 (10)	0.0552 (10)	0.0611 (10)	0.0010 (8)	−0.0157 (8)	0.0113 (8)
C5	0.0418 (8)	0.0478 (9)	0.0513 (9)	−0.0055 (7)	−0.0045 (7)	0.0039 (7)
C6	0.0363 (7)	0.0361 (7)	0.0421 (8)	0.0002 (6)	−0.0042 (6)	−0.0050 (6)
C7	0.0372 (7)	0.0394 (7)	0.0380 (7)	0.0016 (6)	0.0014 (6)	−0.0007 (6)
C8	0.0373 (7)	0.0400 (8)	0.0442 (8)	0.0019 (6)	0.0058 (6)	0.0004 (6)
C9	0.0448 (9)	0.0463 (9)	0.0577 (9)	−0.0007 (7)	−0.0016 (7)	−0.0048 (7)
C10	0.0582 (11)	0.0457 (10)	0.0756 (12)	−0.0065 (8)	0.0024 (9)	−0.0123 (8)

C11	0.0634 (11)	0.0360 (8)	0.0745 (11)	−0.0007 (8)	0.0162 (9)	−0.0006 (8)
C12	0.0595 (10)	0.0438 (9)	0.0553 (9)	0.0074 (7)	0.0069 (8)	0.0092 (7)
C13	0.0373 (8)	0.0499 (9)	0.0444 (8)	0.0043 (6)	−0.0021 (6)	−0.0052 (6)
C14	0.0502 (11)	0.0935 (16)	0.0781 (13)	0.0042 (10)	−0.0250 (10)	−0.0092 (11)
C15	0.0699 (13)	0.0660 (13)	0.0902 (15)	0.0183 (10)	−0.0245 (11)	0.0121 (11)

Geometric parameters (Å, °)

S1—C13	1.6712 (17)	C5—C6	1.383 (2)
N1—C12	1.335 (2)	C5—H5	0.9300
N1—C8	1.3461 (19)	C6—C7	1.4898 (19)
N2—C7	1.2934 (18)	C7—C8	1.491 (2)
N2—N3	1.3697 (17)	C8—C9	1.386 (2)
N3—C13	1.3591 (19)	C9—C10	1.381 (2)
N3—H3'	0.837 (17)	C9—H9	0.9300
N4—C13	1.3466 (19)	C10—C11	1.385 (3)
N4—C14	1.452 (2)	C10—H10	0.9300
N4—C15	1.459 (3)	C11—C12	1.366 (2)
C1—C6	1.385 (2)	C11—H11	0.9300
C1—C2	1.387 (2)	C12—H12	0.9300
C1—H1	0.9300	C14—H14A	0.9600
C2—C3	1.371 (3)	C14—H14B	0.9600
C2—H2	0.9300	C14—H14C	0.9600
C3—C4	1.370 (3)	C15—H15A	0.9600
C3—H3	0.9300	C15—H15B	0.9600
C4—C5	1.385 (2)	C15—H15C	0.9600
C4—H4	0.9300		
C12—N1—C8	118.54 (14)	N1—C8—C7	117.75 (13)
C7—N2—N3	116.40 (12)	C9—C8—C7	120.85 (13)
C13—N3—N2	121.99 (13)	C10—C9—C8	119.18 (16)
C13—N3—H3'	123.1 (11)	C10—C9—H9	120.4
N2—N3—H3'	113.3 (11)	C8—C9—H9	120.4
C13—N4—C14	121.18 (15)	C9—C10—C11	119.31 (16)
C13—N4—C15	122.61 (14)	C9—C10—H10	120.3
C14—N4—C15	116.16 (14)	C11—C10—H10	120.3
C6—C1—C2	120.13 (16)	C12—C11—C10	118.02 (15)
C6—C1—H1	119.9	C12—C11—H11	121.0
C2—C1—H1	119.9	C10—C11—H11	121.0
C3—C2—C1	120.23 (16)	N1—C12—C11	123.63 (16)
C3—C2—H2	119.9	N1—C12—H12	118.2
C1—C2—H2	119.9	C11—C12—H12	118.2
C4—C3—C2	120.04 (16)	N4—C13—N3	112.61 (14)
C4—C3—H3	120.0	N4—C13—S1	123.72 (12)
C2—C3—H3	120.0	N3—C13—S1	123.65 (11)
C3—C4—C5	120.19 (16)	N4—C14—H14A	109.5
C3—C4—H4	119.9	N4—C14—H14B	109.5
C5—C4—H4	119.9	H14A—C14—H14B	109.5
C6—C5—C4	120.31 (15)	N4—C14—H14C	109.5
C6—C5—H5	119.8	H14A—C14—H14C	109.5

C4—C5—H5	119.8	H14B—C14—H14C	109.5
C5—C6—C1	119.09 (14)	N4—C15—H15A	109.5
C5—C6—C7	121.12 (13)	N4—C15—H15B	109.5
C1—C6—C7	119.77 (13)	H15A—C15—H15B	109.5
N2—C7—C6	115.17 (12)	N4—C15—H15C	109.5
N2—C7—C8	127.26 (13)	H15A—C15—H15C	109.5
C6—C7—C8	117.56 (12)	H15B—C15—H15C	109.5
N1—C8—C9	121.30 (14)		
C7—N2—N3—C13	178.44 (14)	N2—C7—C8—N1	−23.7 (2)
C6—C1—C2—C3	−0.5 (3)	C6—C7—C8—N1	157.05 (13)
C1—C2—C3—C4	−0.2 (3)	N2—C7—C8—C9	152.63 (15)
C2—C3—C4—C5	0.8 (3)	C6—C7—C8—C9	−26.6 (2)
C3—C4—C5—C6	−0.7 (3)	N1—C8—C9—C10	−0.4 (2)
C4—C5—C6—C1	0.0 (2)	C7—C8—C9—C10	−176.54 (16)
C4—C5—C6—C7	178.48 (14)	C8—C9—C10—C11	−0.9 (3)
C2—C1—C6—C5	0.6 (2)	C9—C10—C11—C12	1.0 (3)
C2—C1—C6—C7	−177.91 (14)	C8—N1—C12—C11	−1.5 (3)
N3—N2—C7—C6	−175.96 (12)	C10—C11—C12—N1	0.2 (3)
N3—N2—C7—C8	4.8 (2)	C14—N4—C13—N3	179.72 (16)
C5—C6—C7—N2	−50.15 (19)	C15—N4—C13—N3	2.5 (2)
C1—C6—C7—N2	128.32 (15)	C14—N4—C13—S1	−1.7 (2)
C5—C6—C7—C8	129.21 (15)	C15—N4—C13—S1	−178.84 (15)
C1—C6—C7—C8	−52.32 (19)	N2—N3—C13—N4	−166.98 (14)
C12—N1—C8—C9	1.5 (2)	N2—N3—C13—S1	14.4 (2)
C12—N1—C8—C7	177.81 (14)		

Hydrogen-bond geometry (Å, °)

Cg is the centroid of the N1/C8–C12 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3'···N1	0.837 (17)	1.869 (17)	2.602 (2)	145.4 (15)
C14—H14C···S1	0.96	2.57	3.030 (2)	109.
C5—H5···Cg^{i}	0.93	2.66	3.536 (2)	157

Symmetry codes: (i) −x+2, −y+1, −z+1.

Fig. 1

Fig. 2