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N-Phenylindazole-1-thiocarboxamide

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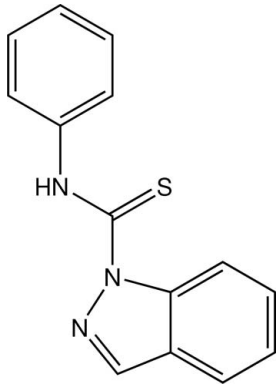
Key indicators: single-crystal X-ray study; T = 98 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.069; data-to-parameter ratio = 13.5.

The title compound, $C_{14}H_{11}N_3S$, exists as a thione and has a Z conformation about the central C—N bond. The phenyl ring is twisted out of the plane defining the rest of the molecule [dihedral angle = 64.73 (8)°]. In the crystal structure, molecules associate into pairs *via* N—H···N bonds and stack into columns *via* C—H···π interactions.

Related literature

For related literature, see: Hossaini Sadr, Sardroodi *et al.* (2005); Hossaini Sadr, Jalili *et al.* (2005); Henderson *et al.* (2006).



Experimental

Crystal data

$C_{14}H_{11}N_3S$
M_r = 253.32
Monoclinic, $C2$
a = 20.408 (8) Å
b = 5.690 (2) Å
c = 11.949 (5) Å
β = 121.110 (14)°
V = 1188.0 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 98 (2) K
0.42 × 0.12 × 0.02 mm

Data collection

Rigaku AFC12κ/SATURN724 diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.506, T_{max} = 1.000
(expected range = 0.503–0.995)
6334 measured reflections
2202 independent reflections
2160 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.069
S = 1.05
2202 reflections
163 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Absolute structure: Flack (1983), 846 Friedel pairs
Flack parameter: 0.03 (7)

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

Cg is the centroid of the C9–C14 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N2^{i}	0.88	2.30	3.097 (3)	151
C5—H5···S1^{ii}	0.95	3.14	3.881 (2)	136
C6—H6···S1^{iii}	0.95	3.17	4.040 (3)	153
C1—H1···*Cg*^{iv}	0.95	2.47	3.389 (3)	164

Symmetry codes: (i) $-x+1, y, -z$; (ii) $-x+1, y+1, -z+1$; (iii) $-x+1, y, -z+1$; (iv) $-x+1, y+1, -z$.

Data collection: *CrystalClear* (Rigaku Americas Corporation, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2071).

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supplementary materials

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N-Phenylindazole-1-thiocarboxamide

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Comment

The preparation and crystal structures of series of compounds containing molecules related to the title compound (I), *i.e.* with the general formula PhNC(=S)*R* (*R* = pyrazolyl, 3,5-dimethylpyrazolyl and 3,5-diphenylpyrazolyl) and PhNC(=S)NRR' (*R* = alkyl or aryl) have been reported recently (Hossaini Sadr, Sardroodi *et al.*, 2005; Hossaini Sadr, Jalili *et al.*, 2005; Henderson *et al.*, 2006). Compound (I) exists as a thione, C8=S1 is 1.6545 (19) Å, and the conformation about the C8—N3 bond is *Z*. The molecule is non-planar as the phenyl ring is twisted out of the plane of the central chromophore as manifested in the C8/N3/C9/C10 torsion angle of 51.7 (2)°. In the crystal structure, molecules related by 2-fold symmetry associate *via* N—H···N hydrogen bonds, Table 1. Pairs of molecules are connected by C—H···π interactions [C1—H1···*Cg*(C9—C14) = 2.47 Å for symmetry operation $1 - x, 1 + y, -z$] on either side to form columns parallel to the *b* axis. Connections between columns are afforded by weak C—H···S interactions; the S1 forms two such contacts with different molecules of the adjacent chain, Table 1. A view of the unit-cell contents is shown in Fig. 2.

Experimental

A solution of indazole (1.18 g, 10 mmol) in dry n-hexane (25 ml) was treated with solid NaH (55%, 0.44 g, 10 mmol) under an N_2 atmosphere. Liberation of H_2 stopped after 3 h stirring. PhNCS (1.2 ml, 10 mmol) was added to the resulting suspension of [Na][Indz] and the reaction was continued overnight at r.t. The suspension was filtered using a fritted funnel and the collected white solid, [Na][PhNCSIndz], was washed with cold n-hexane (3 *x* 10 ml) and dried *in vacuo*; yield 2.60 g, 95%. *M*.p. = 240 °C (melting along with colour change and decomposition). Colourless crystals of (I) were obtained unintentionally as the decomposition product of an authenticated sample of $Bu_2Sn(PhNCSIndz)_2$ during attempts to grow crystals from heptane solution in air; *M*.p. = 90 °C.

Refinement

All C– and N-bound H atoms were included in the riding-model approximation, with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C, N)$.

Figures

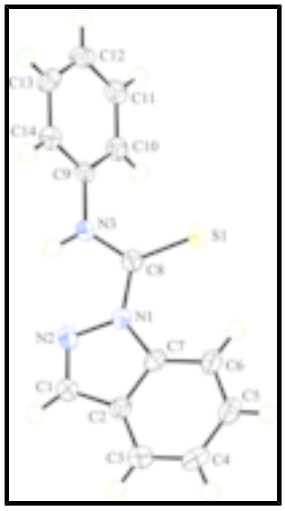

Fig. 1. Molecular structure of (I) showing atom-labelling scheme and displacement ellipsoids at the 70% probability level.

Fig. 2. View of the crystal packing in (I) down the *b* axis. The N—H···N hydrogen bonds are shown as orange-dashed lines. Colour code: yellow (sulfur), red (oxygen), blue (nitrogen), grey (carbon) and green (hydrogen).

N-Phenylindazole-1-thiocarboxamide

Crystal data

$C_{14}H_{11}N_3S$	F_{000} = 528
M_r = 253.32	D_x = 1.416 Mg m^{-3}
Monoclinic, *C*2	Mo *K*α radiation λ = 0.71070 Å
Hall symbol: C 2y	Cell parameters from 5144 reflections
a = 20.408 (8) Å	θ = 3.4–29.6º
b = 5.690 (2) Å	μ = 0.26 mm^{-1}
c = 11.949 (5) Å	*T* = 98 (2) K
β = 121.110 (14)º	Prism, colourless
V = 1188.0 (8) Å^3	0.42 × 0.12 × 0.02 mm
Z = 4	

Data collection

Rigaku AFC12κ/SATURN724 diffractometer	2202 independent reflections
Radiation source: fine-focus sealed tube	2160 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.023
T = 98(2) K	θ_{max} = 26.5º
ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	*h* = −25→25
T_{min} = 0.506, T_{max} = 1.000	*k* = −7→6

6334 measured reflections

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.069$

$S = 1.05$

2202 reflections

163 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 1.0876P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.22$ e Å^{-3}

$\Delta\rho_{min} = -0.19$ e Å^{-3}

Extinction correction: none

Absolute structure: Flack (1983), 845 Friedel pairs

Flack parameter: 0.03 (7)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.53512 (3)	0.82070 (8)	0.39615 (4)	0.02211 (12)
N1	0.45431 (9)	1.0153 (3)	0.15952 (14)	0.0166 (3)
N2	0.43439 (9)	1.0280 (3)	0.02939 (14)	0.0192 (3)
N3	0.55419 (8)	0.7817 (3)	0.19105 (13)	0.0170 (3)
H3	0.5407	0.8284	0.1118	0.020*
C1	0.38502 (11)	1.1986 (4)	−0.02293 (18)	0.0205 (4)
H1	0.3618	1.2443	−0.1119	0.025*
C2	0.36965 (9)	1.3095 (4)	0.06872 (15)	0.0183 (4)
C3	0.32405 (11)	1.4985 (4)	0.0617 (2)	0.0230 (4)
H3A	0.2935	1.5815	−0.0178	0.028*
C4	0.32458 (11)	1.5613 (4)	0.1736 (2)	0.0244 (4)
H4	0.2943	1.6899	0.1717	0.029*
C5	0.36970 (11)	1.4360 (4)	0.29058 (19)	0.0237 (4)
H5	0.3689	1.4827	0.3662	0.028*
C6	0.41493 (11)	1.2485 (4)	0.29997 (17)	0.0215 (4)
H6	0.4448	1.1652	0.3796	0.026*
C7	0.41481 (10)	1.1861 (3)	0.18606 (17)	0.0167 (4)
C8	0.51513 (10)	0.8685 (3)	0.24509 (16)	0.0174 (4)
C9	0.61595 (10)	0.6190 (3)	0.25473 (16)	0.0154 (4)
C10	0.60810 (11)	0.4125 (4)	0.30926 (17)	0.0189 (4)

H10	0.5610	0.3779	0.3039	0.023*
C11	0.66871 (11)	0.2582 (3)	0.37105 (17)	0.0205 (4)
H11	0.6635	0.1188	0.4095	0.025*
C12	0.73743 (10)	0.3055 (4)	0.37739 (16)	0.0208 (4)
H12	0.7793	0.1996	0.4207	0.025*
C13	0.74437 (11)	0.5080 (3)	0.32012 (18)	0.0201 (4)
H13	0.7908	0.5393	0.3226	0.024*
C14	0.68392 (10)	0.6660 (3)	0.25904 (17)	0.0185 (4)
H14	0.6891	0.8054	0.2205	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0249 (2)	0.0273 (3)	0.0173 (2)	0.0050 (2)	0.01318 (17)	0.0041 (2)
N1	0.0174 (8)	0.0192 (8)	0.0148 (7)	0.0017 (6)	0.0094 (6)	0.0010 (6)
N2	0.0223 (8)	0.0217 (9)	0.0152 (7)	0.0009 (7)	0.0109 (6)	0.0016 (6)
N3	0.0174 (7)	0.0209 (9)	0.0143 (6)	0.0022 (6)	0.0093 (6)	0.0031 (6)
C1	0.0216 (9)	0.0223 (10)	0.0186 (9)	0.0037 (8)	0.0111 (7)	0.0034 (8)
C2	0.0162 (8)	0.0204 (9)	0.0195 (8)	−0.0004 (9)	0.0101 (7)	−0.0003 (9)
C3	0.0210 (10)	0.0219 (10)	0.0248 (10)	0.0021 (8)	0.0110 (8)	0.0013 (8)
C4	0.0196 (10)	0.0234 (11)	0.0323 (10)	0.0033 (8)	0.0149 (8)	−0.0027 (8)
C5	0.0217 (10)	0.0288 (11)	0.0236 (10)	−0.0023 (9)	0.0139 (8)	−0.0074 (8)
C6	0.0201 (9)	0.0276 (12)	0.0203 (9)	−0.0011 (8)	0.0129 (8)	−0.0024 (8)
C7	0.0145 (9)	0.0161 (9)	0.0213 (9)	−0.0019 (7)	0.0105 (7)	−0.0022 (7)
C8	0.0162 (8)	0.0189 (11)	0.0170 (8)	−0.0020 (7)	0.0086 (7)	−0.0004 (7)
C9	0.0168 (9)	0.0154 (9)	0.0116 (8)	0.0008 (7)	0.0056 (7)	−0.0005 (7)
C10	0.0191 (9)	0.0203 (9)	0.0168 (8)	−0.0011 (8)	0.0091 (7)	−0.0006 (7)
C11	0.0240 (10)	0.0197 (11)	0.0168 (8)	−0.0001 (8)	0.0097 (7)	−0.0007 (7)
C12	0.0175 (8)	0.0219 (9)	0.0180 (8)	0.0024 (9)	0.0055 (7)	−0.0035 (8)
C13	0.0182 (9)	0.0213 (10)	0.0219 (9)	−0.0016 (8)	0.0112 (8)	−0.0058 (8)
C14	0.0199 (9)	0.0181 (10)	0.0182 (9)	−0.0020 (7)	0.0104 (7)	−0.0018 (7)

Geometric parameters (Å, °)

S1—C8	1.6545 (19)	C5—C6	1.377 (3)
N1—N2	1.391 (2)	C5—H5	0.9500
N1—C7	1.399 (2)	C6—C7	1.405 (3)
N1—C8	1.405 (2)	C6—H6	0.9500
N2—C1	1.303 (3)	C9—C14	1.387 (3)
N3—C8	1.352 (2)	C9—C10	1.393 (3)
N3—C9	1.426 (2)	C10—C11	1.379 (3)
N3—H3	0.8800	C10—H10	0.9500
C1—C2	1.432 (3)	C11—C12	1.391 (3)
C1—H1	0.9500	C11—H11	0.9500
C2—C3	1.396 (3)	C12—C13	1.384 (3)
C2—C7	1.405 (3)	C12—H12	0.9500
C3—C4	1.378 (3)	C13—C14	1.390 (3)
C3—H3A	0.9500	C13—H13	0.9500
C4—C5	1.407 (3)	C14—H14	0.9500

C4—H4	0.9500		
N2—N1—C7	110.34 (14)	N1—C7—C2	106.18 (15)
N2—N1—C8	118.84 (14)	N1—C7—C6	132.99 (17)
C7—N1—C8	130.08 (15)	C2—C7—C6	120.82 (18)
C1—N2—N1	106.36 (15)	N3—C8—N1	112.77 (15)
C8—N3—C9	123.98 (14)	N3—C8—S1	125.95 (14)
C8—N3—H3	118.0	N1—C8—S1	121.26 (13)
C9—N3—H3	118.0	C14—C9—C10	120.00 (17)
N2—C1—C2	112.47 (17)	C14—C9—N3	119.07 (16)
N2—C1—H1	123.8	C10—C9—N3	120.92 (17)
C2—C1—H1	123.8	C11—C10—C9	119.97 (18)
C3—C2—C7	121.21 (16)	C11—C10—H10	120.0
C3—C2—C1	134.13 (17)	C9—C10—H10	120.0
C7—C2—C1	104.65 (17)	C10—C11—C12	120.40 (18)
C4—C3—C2	118.07 (18)	C10—C11—H11	119.8
C4—C3—H3A	121.0	C12—C11—H11	119.8
C2—C3—H3A	121.0	C13—C12—C11	119.46 (18)
C3—C4—C5	120.36 (19)	C13—C12—H12	120.3
C3—C4—H4	119.8	C11—C12—H12	120.3
C5—C4—H4	119.8	C12—C13—C14	120.55 (17)
C6—C5—C4	122.72 (18)	C12—C13—H13	119.7
C6—C5—H5	118.6	C14—C13—H13	119.7
C4—C5—H5	118.6	C9—C14—C13	119.60 (18)
C5—C6—C7	116.82 (17)	C9—C14—H14	120.2
C5—C6—H6	121.6	C13—C14—H14	120.2
C7—C6—H6	121.6		
C7—N1—N2—C1	0.2 (2)	C5—C6—C7—N1	177.58 (19)
C8—N1—N2—C1	−170.97 (16)	C5—C6—C7—C2	−0.7 (3)
N1—N2—C1—C2	0.3 (2)	C9—N3—C8—N1	−176.69 (16)
N2—C1—C2—C3	178.1 (2)	C9—N3—C8—S1	5.0 (3)
N2—C1—C2—C7	−0.7 (2)	N2—N1—C8—N3	9.0 (2)
C7—C2—C3—C4	0.1 (3)	C7—N1—C8—N3	−160.10 (18)
C1—C2—C3—C4	−178.5 (2)	N2—N1—C8—S1	−172.60 (13)
C2—C3—C4—C5	−0.4 (3)	C7—N1—C8—S1	18.3 (3)
C3—C4—C5—C6	0.2 (3)	C8—N3—C9—C14	−129.93 (19)
C4—C5—C6—C7	0.4 (3)	C8—N3—C9—C10	51.7 (2)
N2—N1—C7—C2	−0.61 (19)	C14—C9—C10—C11	2.0 (3)
C8—N1—C7—C2	169.24 (17)	N3—C9—C10—C11	−179.65 (16)
N2—N1—C7—C6	−179.06 (19)	C9—C10—C11—C12	−1.1 (3)
C8—N1—C7—C6	−9.2 (3)	C10—C11—C12—C13	−0.6 (3)
C3—C2—C7—N1	−178.21 (17)	C11—C12—C13—C14	1.4 (3)
C1—C2—C7—N1	0.76 (19)	C10—C9—C14—C13	−1.2 (3)
C3—C2—C7—C6	0.5 (3)	N3—C9—C14—C13	−179.58 (16)
C1—C2—C7—C6	179.44 (17)	C12—C13—C14—C9	−0.5 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N3—H3···N2^{i}	0.88	2.30	3.097 (3)	151
C5—H5···S1^{ii}	0.95	3.14	3.881 (2)	136
C6—H6···S1^{iii}	0.95	3.17	4.040 (3)	153
C1—H1···Cg(C9–C14)^{iv}	0.95	???	2.47	???

Symmetry codes: (i) −*x*+1, *y*, −*z*; (ii) −*x*+1, *y*+1, −*z*+1; (iii) −*x*+1, *y*, −*z*+1; (iv) −*x*+1, *y*+1, −*z*.

Fig. 1

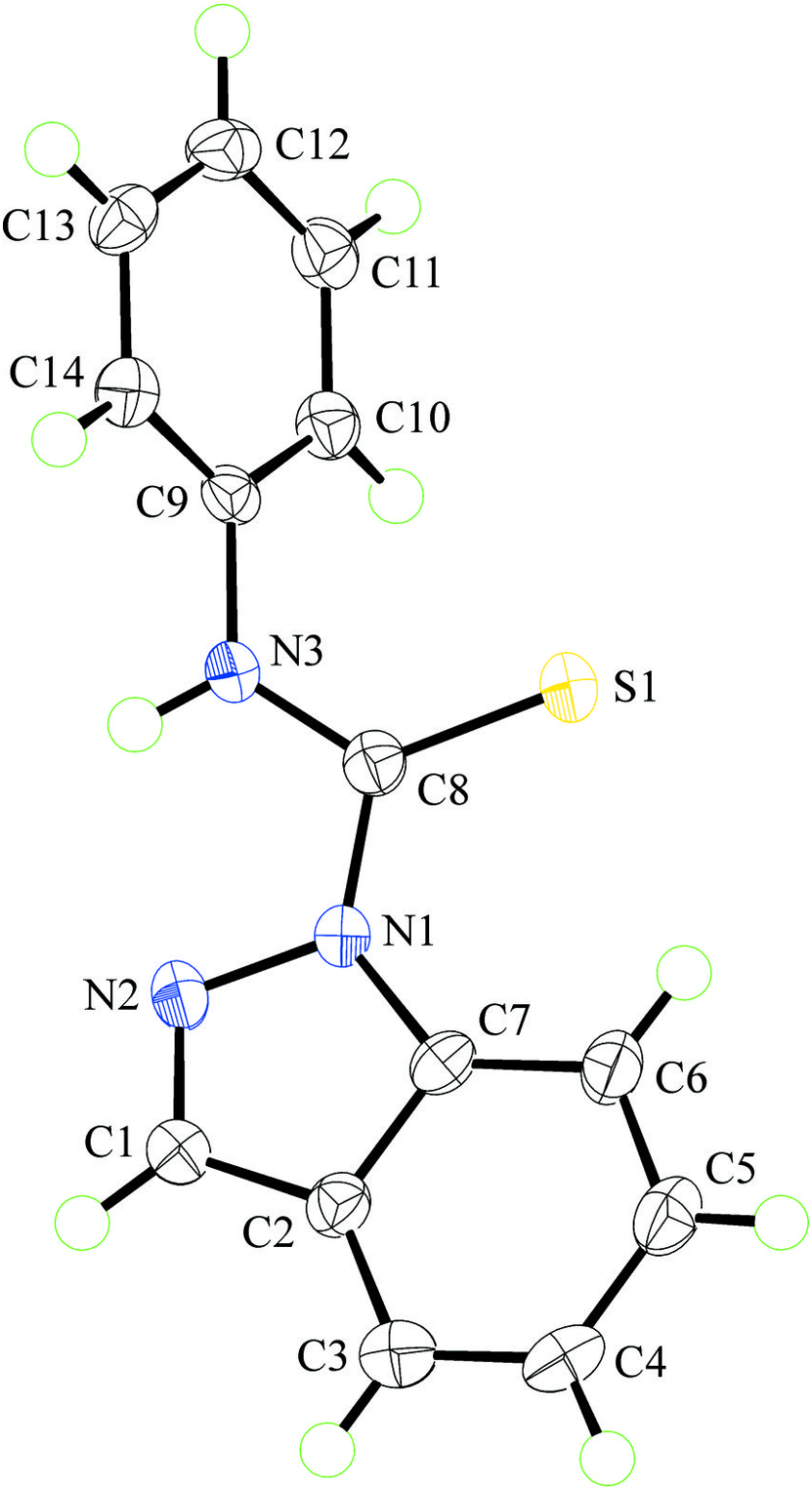

Fig. 2