N-[(R)-1-Phenylethyl]thiobenzamide

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The title compound, $C_{15}H_{15}NS$, crystallizes with two crystallographically independent and conformationally almost identical molecules in the asymmetric unit. Both molecules are non-planar, the dihedral angle between the two phenyl planes in each molecule being 76.41 (11) and 86.65 (10)°. An *anti* conformation of the amide and thio groups is observed in the thioamide fragment. In the solid state, the structure is stabilized by weak C—H···S intramolecular interactions, intermolecular N—H···S hydrogen bonds and C—H···π interactions.

Comment

Chiral ligands containing N and S donor atoms have received considerable attention in asymmetric catalysis (*e.g.* Begum *et al.*, 2006; Brunner *et al.*, 1996). Thioamides especially can act as anionic monodentate or bidentate, chelating or bridging ligands after deprotonation, and they can also provide a potential source of axial chirality owing to their non-planarity (Ach *et al.*, 2002; Artis & Lipton, 1998; Hossain *et al.*, 2003;). In this paper, we report the synthesis and crystal structure of N-[(R)-1-phenylethyl]thiobenzamide (I), with an aim to subsequently investigate the axial chirality of its metal complexes.

(I)
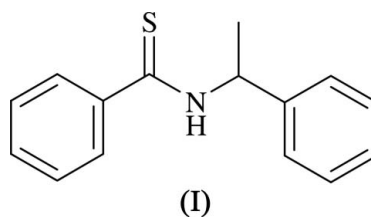
The title compound crystallizes with two crystallographically independent molecules, *A* and *B*, in the asymmetric unit (Fig. 1). Both molecules are non-planar, the dihedral angles between the two phenyl planes being 76.41 (11)° (in molecule *A*) and 86.65 (10)° (in molecule *B*). These values are comparable to the analogous dihedral angle of 71.7 (2)° in N-benzyl-2-methylfuran-3-thiocarboxanilide (Pavlović *et al.*, 2004). The angles between the two planes defined by the thioamide groups (S1/C7/N1) and the attached phenyl rings are 29.89 (11)° (in molecule *A*) and 34.43 (9)° (in molecule *B*). These values are larger than that of 19.1 (2)° in N-benzyl-2-methylfuran-3-thiocarboxanilide (Pavlović *et al.*, 2004), but much smaller than that of 83.0 (1)° in N,2-dimethylthionaphthamide (Ach *et al.*, 2002).

The bond distances and angles in (I) are within normal ranges (Allen *et al.*, 1987). The C7—S1 and N1–C7 bond distances (Table 1) are in agreement with those found in other
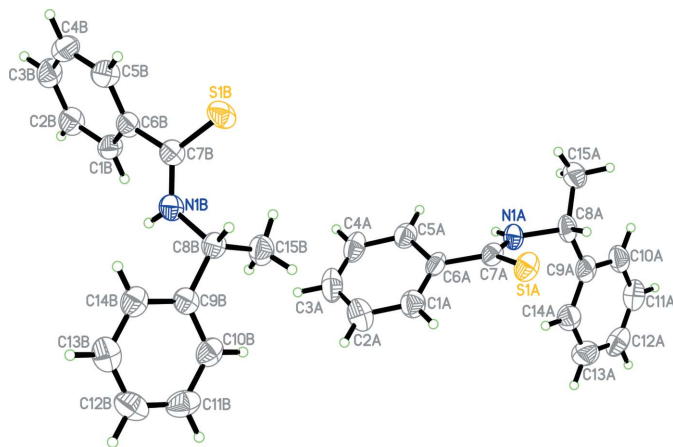
Figure 1
The asymmetric unit of (I), with the atom-labelling scheme; displacement ellipsoids are drawn at the 60% probability level.
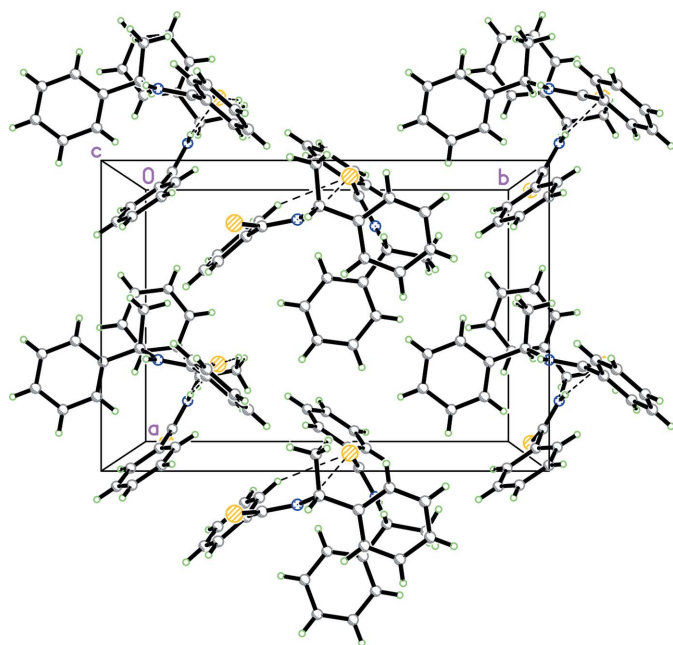

Figure 2
The crystal packing of (I), viewed down the *c* axis. Hydrogen bonds are shown as dashed lines.

thioamide compounds [C—S = 1.676 (3) Å in *N*-benzyl-2-methylfuran-3-thiocarboxanilide (Pavlović *et al.*, 2004), 1.667 (3) Å in *N*,2-dimethyl-3-thiofuramide (Popović *et al.*, 2001) and 1.688 (3) Å in *N*,2-dimethylthionaphthamide (Ach *et al.*, 2002); C—N = 1.327 (4) Å in *N*-benzyl-2-methylfuran-3-thiocarboxanilide, 1.335 (3) Å in *N*,2-dimethyl-3-thiofuramide and 1.334 (3) Å in *N*,2-dimethylthionaphthamide]. The short N1—C7 bond distance indicates significant double-bond character, in contrast to the N1—C8 bond distance (Table 1). However, the N1—C7 bond in (I) is still longer than the corresponding C═N distance [1.254 (9) Å] found for (I) acting as a deprotonated ligand in the complex bis{(1,5-cyclooctadiene)[*m*-N-(*R*)-1-phenylethyl)thiobenzamidato]-rhodium} (Brunner *et al.*, 1996).

In the crystal packing, molecules are connected into infinite chains along the *a* axis (Fig. 2) by N—H···S intermolecular hydrogen bonds between the amide group and the thioamide S atom (Table 2). The crystal structure is further stabilized by weak intramolecular C—H···S interactions and C—H···π interactions.

Experimental

A solution containing *O*-4-nitrobenzyl benzothioate (0.260 g, 1.0 mmol) and *N*-(*R*)-methylbenzylamine (0.122 g, 1.0 mmol) in dichloromethane (20 ml) was stirred overnight. The product *N*-[(*R*)-1-phenylethyl]thiobenzamide was separated by chromatography on silica gel (yield 0.18 g, 75%). Yellow needle-like single crystals of (I) of X-ray diffraction quality were obtained by slow evaporation of a dichloromethane/*n*-hexane (1:3) solution (m.p. 338–339 K).

Crystal data

$C_{15}H_{15}NS$	Mo $K\alpha$ radiation
$M_r = 241.35$	Cell parameters from 6772
Orthorhombic, $P2_12_12_1$	reflections
$a = 10.4149$ (3) Å	$\theta = 1.8–29.0°$
$b = 15.0106$ (5) Å	$\mu = 0.23$ mm^{-1}
$c = 16.3110$ (5) Å	$T = 100.0$ (1) K
$V = 2549.96$ (14) Å^3	Needle, yellow
$Z = 8$	$0.50 \times 0.24 \times 0.24$ mm
$D_x = 1.257$ Mg m^{-3}	

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	6772 independent reflections
	6150 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.056$
Absorption correction: multi-scan	$\theta_{max} = 29.0°$
(*SADABS*; Bruker, 2005)	$h = -12 \rightarrow 14$
$T_{min} = 0.936$, $T_{max} = 0.946$	$k = -20 \rightarrow 20$
50018 measured reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 0.9357P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} = 0.001$
6772 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
317 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Absolute structure: Flack (1983), 2982 Friedel pairs
	Flack parameter: 0.02 (6)

Table 1
Selected geometric parameters (Å, °).

S1A—C7A	1.688 (2)	S1B—C7B	1.681 (2)
N1A—C7A	1.321 (3)	N1B—C7B	1.322 (3)
N1A—C8A	1.473 (3)	N1B—C8B	1.476 (3)
C7A—N1A—C8A	126.46 (18)	C7B—N1B—C8B	125.49 (17)
N1A—C7A—C6A	115.71 (18)	N1B—C7B—C6B	116.18 (17)
N1A—C7A—S1A	123.48 (16)	N1B—C7B—S1B	123.30 (15)
C6A—C7A—S1A	120.81 (16)	C6B—C7B—S1B	120.51 (15)
C1A—C6A—C7A—N1A	149.5 (2)	C1B—C6B—C7B—N1B	−34.8 (3)
C5A—C6A—C7A—N1A	−30.0 (3)	C5B—C6B—C7B—N1B	145.5 (2)

Table 2
Hydrogen-bond geometry (Å, °).

$Cg1$, $Cg2$, $Cg3$ and $Cg4$ are the centroids of the phenyl rings C1A–C6A, C1B–C6B, C9A–C14A and C9B–C14B, respectively.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1A—H1NA⋯S1B[i]	0.83 (3)	2.65 (3)	3.4353 (18)	160 (3)
N1B—H1NB⋯S1A[ii]	0.83 (3)	2.78 (3)	3.4803 (18)	143 (3)
C1A—H1AA⋯S1A	0.93	2.76	3.126 (2)	105
C8A—H8AA⋯S1A	0.98	2.63	3.138 (2)	113
C5B—H5BA⋯S1B	0.93	2.83	3.152 (2)	102
C8B—H8BA⋯S1B	0.98	2.71	3.109 (2)	105
C14B—H14B⋯$Cg1$[iii]	0.93	2.83	3.547 (2)	135
C13A—H13A⋯$Cg2$[iv]	0.93	2.97	3.637 (3)	130
C15F—H15F⋯$Cg3$[iii]	0.96	3.11	3.845 (2)	134
C8A—H8AA⋯$Cg4$[iv]	0.98	2.98	3.852 (2)	148
C2B—H2BA⋯$Cg4$[v]	0.93	3.13	3.764 (2)	127

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{3}{2}, -y+1, z-\frac{1}{2}$; (iii) $x+1, y+1, z$; (iv) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$; (v) $-x+\frac{5}{2}, -y+1, z-\frac{1}{2}$.

H atoms attached to N were located in a difference map and refined isotropically. The remaining H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.98 Å; the $U_{\text{iso}}(\text{H})$ values were constrained to be $1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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