Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Benzyl *N*-[1-(furan-2-yl)ethylidene]hydrazinecarbodithioate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.047
Data-to-parameter ratio = 9.8

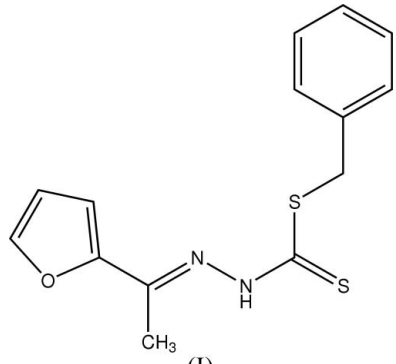
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 17 May 2005
Accepted 1 July 2005
Online 9 July 2005

The title compound, $C_{14}H_{12}N_2S_2O$, contains a dithiocarbazate group. The phenyl ring is disordered and perpendicular [dihedral angle of 48.0 (3)°] to the rest of the molecule, which is planar.

Comment

Dithiocarbazate derivatives have been widely studied and have great potential biological activity as anticancer and antimicrobial drugs (Bharti *et al.*, 2000) and in radiopharmaceutical applications (Boschi *et al.*, 2003). This functional group is of particular interest because it is easily tuned by reaction with different aldehydes or ketones to give varied geometries for chelation to transition metals. In the structure of the title compound, (I), we were interested in studying the effect of introducing a furan ring to determine if it can also participate in chelation to a metal centre. The previously reported Cd^{II} complex of this ligand (Tarafder *et al.*, 2002*b*) indicated that it only forms a bis-chelating bidentate ligand without O coordination. The biological activity of the compound and its analytical characterization have also been reported (Tarafder *et al.*, 2002*a*).



(I)

Compound (I) (Figs. 1–3) crystallizes in the unprotonated thione form with a C=S bond length of 1.664 (2) Å, which is slightly longer than that previously reported for a dithiocarbazate Schiff base [1.6503 (17) Å; Chan *et al.*, 2003]. This is in accordance with other experimental characterizations, which indicate that this type of compound forms the thione tautomer in the solid state. The formation of the Cd^{II} complex occurs through coordination at the azomethane N atom and thiolate S atom (Tarafder *et al.*, 2002*b*) but does not show any bond-length change: N1—N2 = 1.381 (2) Å in (I).

The molecule crystallizes in the conformer in which the N1—N2 bond adopts a *trans* geometry with respect to C12=S2, while the *S*-benzyl group adopts a *cis* geometry. The

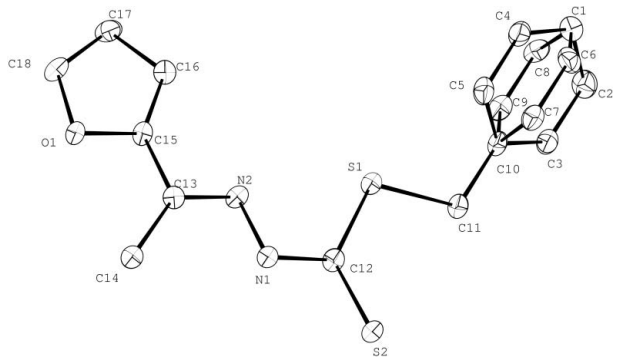


Figure 1
The molecular structure of (I). with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown. H atoms have been omitted.

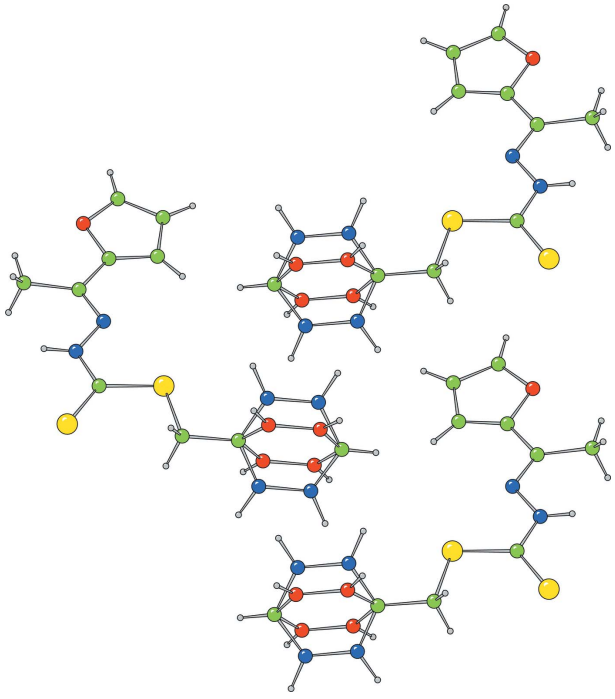


Figure 2
A projection along the *a* axis of part of the packing of (I), showing that the phenyl groups form a layer in the crystal structure. The alternative orientations of the phenyl C atoms are coloured red and blue.

furan and phenyl groups are *cis* to each other across N2/N1/C12/S1. The C13═N2 bond [1.289 (3) Å] is formed from the condensation reaction. The C14 methyl group is *cis* to the furyl O atom in this free ligand but transforms to *trans* upon chelation to Cd^{II} (Tarafder *et al.*, 2002*b*), even though the O atom does not coordinate to the metal centre. The S1—C12═S2 angle is maintained at 125.22 (12)° after coordination [125.22 (12)° in (I)].

Experimental

The Schiff base ligand was prepared according to the literature method of Tarafder *et al.* (2002*a*). *S*-Benzyldithiocarbazate (1.98 g, 0.1 mol) in absolute ethanol (40 ml) was added to an equimolar quantity of 2-furylmethylketone in absolute ethanol (50 ml). The mixture was heated over a steam bath for 10 min and then cooled to 273 K in an ice bath. The Schiff base which precipitated was filtered, washed with cold ethanol and dried *in vacuo* over silica gel, giving a dark-orange product (yield 80%, m.p 406 K). Yellow single crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation of an ethanol solution over a period of three weeks.

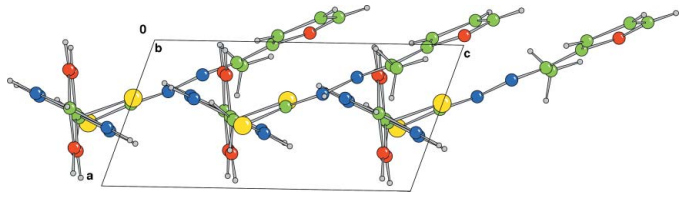


Figure 3
A projection along the *b* axis of a section of the crystal structure of (I). The alternative orientations of the phenyl C atoms are coloured red and blue. Note that if alternate red and blue phenyl groups are selected in any layer, there are no short intermolecular clashes.

Crystal data

$C_{14}H_{14}N_2OS_2$
M_r = 290.41
Monoclinic, $P2_1/c$
a = 4.7347 (1) Å
b = 32.6510 (7) Å
c = 9.3959 (2) Å
β = 109.0305 (9)°
V = 1373.15 (5) Å^3
Z = 4
D_x = 1.405 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2559 reflections
θ = 5–27°
μ = 0.38 mm^{-1}
T = 150 K
Block, yellow
0.40 × 0.30 × 0.30 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.89, T_{max} = 0.89
5121 measured reflections
3055 independent reflections
2036 reflections with $I > 3\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.5°
$h = -6 \rightarrow 6$
$k = -38 \rightarrow 42$
$l = -12 \rightarrow 12$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.047
S = 1.09
2036 reflections
208 parameters
H-atom parameters constrained
Chebychev polynomial, with A_i coefficients 1.29, 0.798, 1.02
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C12—N1	1.343 (3)	C15—O1	1.374 (2)
C12—S1	1.749 (2)	C16—C17	1.423 (3)
C12—S2	1.664 (2)	C17—C18	1.330 (3)
C13—N2	1.289 (3)	C18—O1	1.364 (3)
C15—C16	1.344 (3)	N1—N2	1.381 (2)
N1—C12—S1	113.77 (15)	C12—N1—N2	119.35 (17)
N1—C12—S2	121.00 (16)	C12—N1—H3	119.4
S1—C12—S2	125.22 (12)	N1—N2—C13	116.37 (18)
C14—C13—N2	125.2 (2)	C15—O1—C18	106.40 (16)
C15—C13—N2	115.42 (18)	C11—S1—C12	101.75 (10)

The phenyl group was seen to be disordered. The site

occupancy factors for the two orientations refined to 0.508 (4):0.492 (4), in close agreement with the value of 0.5:0.5 which would be required by strict alternation of the two orientations in each molecular layer (Figs. 2 and 3). All H atoms (including those of the disordered phenyl group) were located in a difference map, but those attached to C atoms were repositioned geometrically. All H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–98 and N—H = 0.85 Å) and isotropic atomic displacement parameters [U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom], after which they were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *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*.

KTJ gratefully acknowledges MOSTI, Malaysia, for an attachment grant under an NSF scholarship, and the Chemical Crystallography Laboratory, University of Oxford, for instrumental facilities.

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supporting information

Acta Cryst. (2005). E**61**, o2441–o2443 [https://doi.org/10.1107/S1600536805020969]

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$h = -6 \rightarrow 6$
$k = -38 \rightarrow 42$
$l = -12 \rightarrow 12$

Refinement

Refinement on F
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.047$
$S = 1.09$
2036 reflections
208 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-atom parameters constrained
Chebychev polynomial, *w*ith A_i coefficients 1.29, 0.798, 1.02
$(\Delta/\sigma)_{max} = 0.000357$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.4734 (5)	0.27775 (7)	0.3069 (2)	0.0290	
C2	0.3756 (10)	0.25222 (14)	0.1810 (5)	0.0299	0.5079
C3	0.3952 (9)	0.20941 (13)	0.1950 (4)	0.0249	0.5079

C4	0.6012 (10)	0.25859 (14)	0.4492 (5)	0.0306	0.5079
C5	0.6238 (10)	0.21637 (13)	0.4617 (5)	0.0275	0.5079
C6	0.7425 (10)	0.26000 (13)	0.3674 (5)	0.0283	0.4921
C7	0.7646 (10)	0.21747 (13)	0.3807 (4)	0.0248	0.4921
C8	0.2116 (10)	0.25508 (14)	0.2590 (5)	0.0263	0.4921
C9	0.2317 (10)	0.21287 (14)	0.2720 (5)	0.0272	0.4921
C10	0.5141 (4)	0.19259 (6)	0.3337 (2)	0.0232	
C11	0.5367 (5)	0.14628 (6)	0.3472 (2)	0.0267	
C12	0.4384 (5)	0.07792 (6)	0.4993 (2)	0.0246	
C13	0.1442 (5)	0.06134 (6)	0.7908 (2)	0.0265	
C14	0.1635 (7)	0.01591 (7)	0.8110 (3)	0.0443	
C15	0.0181 (5)	0.08592 (6)	0.8846 (2)	0.0253	
C16	−0.0427 (5)	0.12595 (7)	0.8912 (2)	0.0291	
C17	−0.1686 (5)	0.13048 (7)	1.0087 (3)	0.0302	
C18	−0.1758 (6)	0.09333 (7)	1.0655 (3)	0.0348	
N1	0.3493 (4)	0.05880 (5)	0.6039 (2)	0.0267	
N2	0.2315 (4)	0.08155 (6)	0.69490 (19)	0.0261	
O1	−0.0656 (4)	0.06489 (5)	0.99101 (19)	0.0371	
S1	0.39774 (13)	0.131167 (15)	0.49885 (6)	0.0269	
S2	0.57251 (14)	0.051604 (17)	0.38374 (7)	0.0331	
H1	0.4624	0.3071	0.2978	0.0439*	
H2	0.4164	0.1338	0.2560	0.0358*	
H3	0.3655	0.0330	0.6123	0.0360*	
H4	0.3649	0.0066	0.8272	0.0867*	
H6	0.1066	0.0078	0.8963	0.0868*	
H9	−0.2466	0.0872	1.1437	0.0520*	
H82	0.0317	0.0027	0.7226	0.0868*	
H83	−0.2339	0.1546	1.0406	0.0412*	
H84	0.7390	0.1380	0.3682	0.0359*	
H85	−0.0078	0.1467	0.8314	0.0400*	
H61	0.9266	0.2773	0.4029	0.0284*	0.4921
H71	0.9660	0.2046	0.4253	0.0250*	0.4921
H41	0.6761	0.2759	0.5418	0.0329*	0.5079
H51	0.7184	0.2032	0.5622	0.0281*	0.5079
H81	0.0133	0.2689	0.2162	0.0266*	0.4921
H91	0.0448	0.1961	0.2374	0.0281*	0.4921
H21	0.2897	0.2647	0.0788	0.0293*	0.5079
H31	0.3225	0.1916	0.1038	0.0256*	0.5079

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0354 (12)	0.0245 (10)	0.0300 (10)	−0.0012 (8)	0.0148 (9)	0.0016 (8)
C2	0.030 (2)	0.033 (2)	0.025 (2)	0.0038 (17)	0.0062 (17)	0.0059 (16)
C3	0.026 (2)	0.029 (2)	0.0213 (18)	−0.0073 (16)	0.0103 (15)	−0.0039 (16)
C4	0.040 (2)	0.029 (2)	0.030 (2)	−0.0112 (18)	0.0206 (19)	−0.0068 (17)
C5	0.032 (2)	0.032 (2)	0.0207 (18)	−0.0029 (17)	0.0105 (16)	0.0044 (16)
C6	0.034 (2)	0.023 (2)	0.028 (2)	−0.0084 (18)	0.0102 (18)	0.0001 (17)

C7	0.025 (2)	0.031 (2)	0.0196 (18)	−0.0014 (16)	0.0079 (15)	−0.0007 (16)
C8	0.027 (2)	0.031 (2)	0.0225 (19)	0.0066 (17)	0.0090 (16)	−0.0020 (16)
C9	0.026 (2)	0.033 (2)	0.025 (2)	−0.0009 (17)	0.0117 (16)	−0.0018 (17)
C10	0.0228 (10)	0.0281 (10)	0.0230 (10)	−0.0006 (7)	0.0132 (8)	0.0014 (8)
C11	0.0317 (11)	0.0266 (10)	0.0276 (10)	−0.0033 (8)	0.0175 (8)	−0.0001 (8)
C12	0.0284 (11)	0.0253 (10)	0.0221 (9)	−0.0007 (8)	0.0111 (8)	−0.0004 (8)
C13	0.0341 (11)	0.0220 (10)	0.0278 (10)	0.0005 (8)	0.0162 (9)	0.0014 (8)
C14	0.079 (2)	0.0241 (10)	0.0492 (14)	0.0063 (12)	0.0478 (15)	0.0040 (11)
C15	0.0305 (11)	0.0251 (10)	0.0255 (10)	−0.0008 (8)	0.0163 (8)	0.0018 (8)
C16	0.0389 (12)	0.0242 (10)	0.0286 (11)	−0.0002 (9)	0.0173 (9)	0.0014 (8)
C17	0.0349 (12)	0.0282 (11)	0.0321 (11)	0.0003 (9)	0.0171 (9)	−0.0071 (9)
C18	0.0500 (15)	0.0332 (12)	0.0324 (12)	0.0014 (10)	0.0286 (11)	−0.0040 (9)
N1	0.0387 (10)	0.0211 (8)	0.0262 (9)	0.0006 (7)	0.0187 (8)	0.0002 (7)
N2	0.0316 (10)	0.0261 (9)	0.0254 (9)	0.0016 (7)	0.0160 (8)	−0.0013 (7)
O1	0.0643 (12)	0.0247 (7)	0.0383 (9)	0.0020 (8)	0.0387 (8)	0.0028 (7)
S1	0.0364 (3)	0.0234 (3)	0.0279 (3)	0.0033 (2)	0.0199 (2)	0.0022 (2)
S2	0.0526 (4)	0.0242 (3)	0.0346 (3)	−0.0005 (2)	0.0310 (3)	−0.0020 (2)

Geometric parameters (Å, º)

C1—C2	1.397 (5)	C10—C11	1.518 (3)
C1—C4	1.421 (5)	C11—S1	1.822 (2)
C1—H1	0.961	C11—H2	0.951
C1—C6	1.345 (5)	C11—H84	0.952
C1—C8	1.387 (5)	C12—N1	1.343 (3)
C1—H1	0.961	C12—S1	1.749 (2)
C2—C3	1.404 (6)	C12—S2	1.664 (2)
C2—H21	1.000	C13—C14	1.494 (3)
C3—C10	1.356 (5)	C13—C15	1.456 (3)
C3—H31	1.000	C13—N2	1.289 (3)
C4—C5	1.385 (6)	C14—H4	0.964
C4—H41	1.000	C14—H6	0.962
C5—C10	1.383 (5)	C14—H82	0.962
C5—H51	1.000	C15—C16	1.344 (3)
C6—C7	1.395 (6)	C15—O1	1.374 (2)
C6—H61	1.000	C16—C17	1.423 (3)
C7—C10	1.386 (5)	C16—H85	0.928
C7—H71	1.000	C17—C18	1.330 (3)
C8—C9	1.384 (6)	C17—H83	0.930
C8—H81	1.000	C18—O1	1.364 (3)
C9—C10	1.434 (5)	C18—H9	0.924
C9—H91	1.000	N1—N2	1.381 (2)
C10—C11	1.518 (3)	N1—H3	0.848
C2—C1—C4	117.1 (3)	C10—C11—S1	107.55 (14)
C2—C1—H1	121.8	C10—C11—H2	110.2
C4—C1—H1	121.1	S1—C11—H2	109.0
C6—C1—C8	122.0 (3)	C10—C11—H84	109.8

C6—C1—H1	118.9	S1—C11—H84	110.9
C8—C1—H1	119.1	H2—C11—H84	109.4
C1—C2—C3	121.4 (4)	N1—C12—S1	113.77 (15)
C1—C2—H21	119.3	N1—C12—S2	121.00 (16)
C3—C2—H21	119.3	S1—C12—S2	125.22 (12)
C2—C3—C10	119.1 (3)	C14—C13—C15	119.37 (18)
C2—C3—H31	120.4	C14—C13—N2	125.2 (2)
C10—C3—H31	120.4	C15—C13—N2	115.42 (18)
C1—C4—C5	121.0 (4)	C13—C14—H4	110.4
C1—C4—H41	119.5	C13—C14—H6	110.8
C5—C4—H41	119.5	H4—C14—H6	108.3
C4—C5—C10	119.2 (4)	C13—C14—H82	109.8
C4—C5—H51	120.4	H4—C14—H82	109.0
C10—C5—H51	120.4	H6—C14—H82	108.5
C1—C6—C7	120.0 (4)	C13—C15—C16	134.45 (19)
C1—C6—H61	120.0	C13—C15—O1	115.96 (18)
C7—C6—H61	120.0	C16—C15—O1	109.58 (18)
C6—C7—C10	121.6 (4)	C15—C16—C17	106.70 (19)
C6—C7—H71	119.2	C15—C16—H85	126.7
C10—C7—H71	119.2	C17—C16—H85	126.6
C1—C8—C9	118.3 (4)	C16—C17—C18	106.75 (19)
C1—C8—H81	120.8	C16—C17—H83	127.3
C9—C8—H81	120.8	C18—C17—H83	126.0
C8—C9—C10	121.6 (4)	C17—C18—O1	110.56 (19)
C8—C9—H91	119.2	C17—C18—H9	125.5
C10—C9—H91	119.2	O1—C18—H9	124.0
C5—C10—C3	122.0 (3)	C12—N1—N2	119.35 (17)
C5—C10—C11	119.4 (2)	C12—N1—H3	119.4
C3—C10—C11	118.7 (2)	N2—N1—H3	121.3
C9—C10—C7	116.5 (3)	N1—N2—C13	116.37 (18)
C9—C10—C11	121.7 (2)	C15—O1—C18	106.40 (16)
C7—C10—C11	121.8 (2)	C11—S1—C12	101.75 (10)