Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

trans–cis S-Benzyl dithiocarbazate

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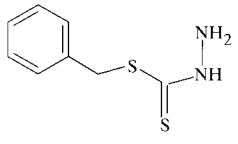
Received 30 May 2000
Accepted 26 June 2000

In the crystal structure of the title compound, $C_8H_{10}N_2S_2$, the molecules are linked by N—H···S hydrogen bonds between the imino group and the thione-S atoms to form a chain along the *b* axis. The dithiocarbazate moiety is rotated by 85.8 (2)° with respect to the phenyl ring.

Comment

There has been much interest in *S*-methyl dithiocarbazate and its behaviour towards transition metals (Weber, 1979; Battistoni *et al.*, 1971). According to NMR spectra (Gattegno & Giuliani, 1974), supported by theoretical studies (Andreocci *et al.*, 1974), there are three types of conformations, *viz*. *cis–cis, cis–trans* and *trans–cis*, based on the twist angle (°) along the N—C and C—S bonds, (0,0), (0,180) or (180,0), respectively. In the present structure, the corresponding angles are 179.5 (2) and 0.6 (2)°, respectively. The *cis–trans* conformation is observed in unsubstituted esters and *trans–cis* in substituted esters. Two conformers of *S*-methyl dithiocarbazate, namely *cis–trans* and *trans–cis*, were obtained in the solid state by recrystallization from ethanol at room temperature and from an ethanol–water mixture (2:3) below 273 K, respectively (Lanfredi *et al.*, 1977; Mattes & Weber, 1980). In our study of the interaction of *S*-benzyl dithiocarbazate with dimethyltin dichloride in acetonitrile, yellow crystals of the title compound, (I), suitable for X-ray crystallographic analysis, were obtained. The compound is a *trans–cis S*-benzyl dithiocarbazate.



(I)

The C═S distance of 1.678 (3) Å agrees well with the values in the literature of 1.681 (5) Å (Mattes & Weber, 1980), and 1.679 (4) and 1.670 (6) Å (Lanfredi *et al.*, 1977), being intermediate between the values of 1.82 Å for a C—S single bond and 1.56 Å for a C═S double bond (Suton, 1965). The C—N distance of 1.320 (3) Å is indicative of double-bond character. The bond angles S1—C8—S2 [125.4 (1)°] and N1—C8—S1 [113.5 (2)°] agree well with those observed for *trans–cis S*-methyl dithiocarbazate [125.5 (2) and 113.6 (3)°, respectively; Mattes & Weber, 1980], and are significantly different from the values of 116.2 (1) and 119.3 (1)°, respectively, observed for *cis–trans S*-methyl dithiocarbazate (Weber, 1979). This is a consequence of the participation of S2 in the hydrogen bond in the *trans–cis* conformer and of the change in the conformation of the *S*-ester groups.

The mean plane through N2/N1/C8/S2/S1/C7 is rotated by 85.8 (2)° with respect to the phenyl ring (Fig. 1). The H atom attached to the imino N atom has the potential to act as a hydrogen-bond donor. The intermolecular N—H···S hydrogen bonds involving the imino-N and thione-S atoms form a chain along the *b* axis (Fig. 2), as observed in *trans–cis S*-methyl dithiocarbazate (Mattes & Weber, 1980). The N···S^{i}

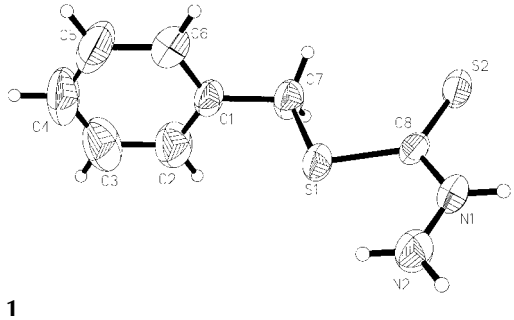


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

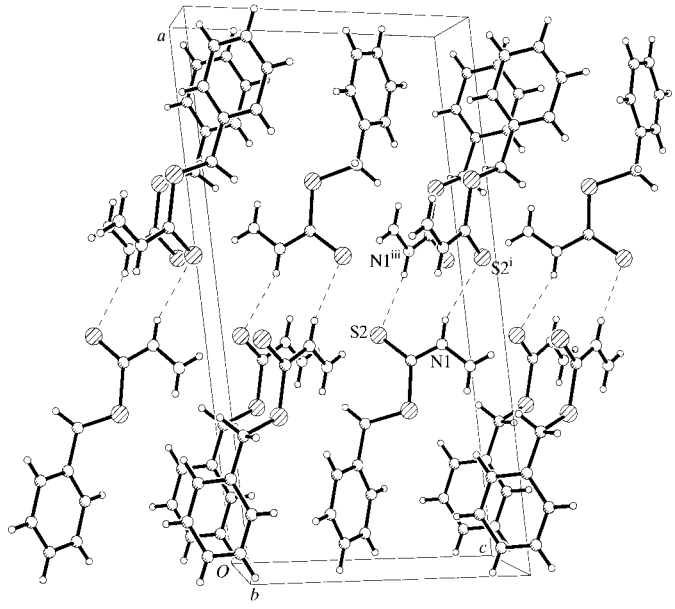


Figure 2
The packing of the molecules of (I) viewed down the *b* axis [symmetry codes: (i) $1-x, y+\frac{1}{2}, \frac{3}{2}-z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$].

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distance of 3.345 (2) Å [symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$] is significantly shorter than the same distance in *S*-methyl *N*,*N*-dimethyldithiocarbazate [3.480 (4) Å; Lanfredi *et al.*, 1977] and is comparable with the values of 3.389 (6) Å in *S*-methyl *β*-*N*-[4-(dimethylamino)benzylidene]dithiocarbazate (Zhao *et al.*, 1997), 3.343 (2) and 3.490 (3) Å in dimethylammonium dithiocarbazate (Wahlberg, 1978*a*), and 3.348 (3) Å in diisopropylammonium diisopropyldithiocarbamate (Wahlberg, 1978*b*). This value is at the upper end of the range described by Srinivasan & Chackko (1967). Moreover, atom H2*B* of the amino group is involved in two slightly longer N—H···S interactions [H2*B*···S2^{i} 3.413 (1) and N2···S2^{i} 3.780 (2) Å; H2*B*···S2^{ii} 3.295 (1) and N2···S2^{ii} 3.456 (2) Å; symmetry code: (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$], since it points towards the thione-S atoms of two different molecules.

Experimental

Hydrazine hydrate (10 g) was mixed with potassium hydroxide (11.4 g) in 90% ethanol (70 ml) and cooled to 273 K in an ice bath. The addition of carbon disulfide (15.2 g) with constant stirring over a period of 1 h formed two layers. The light-brown layer was separated, dissolved in cold 40% ethanol (60 ml) and kept in an ice bath. Benzyl chloride (25 g) was added dropwise with vigorous stirring of the mixture. A white product was formed after complete addition of the benzyl chloride. This product, (I), was filtered off and washed with water. After drying, it was recrystallized from benzene. An equimolar mixture of (I) and dimethyltin dichloride in ethanol, after a few days of evaporation, gave good crystals of (I), as identified by IR spectroscopy and elemental analysis.

Crystal data

$C_8H_{10}N_2S_2$
M_r = 198.30
Monoclinic, $P2_1/c$
a = 19.7221 (9) Å
b = 4.8605 (2) Å
c = 10.2699 (5) Å
β = 97.121 (1)°
V = 976.87 (8) Å^3
Z = 4
D_x = 1.348 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4301 reflections
θ = 3.12–28.42°
μ = 0.492 mm^{-1}
T = 293 (2) K
Parallelepiped, yellow
0.48 × 0.36 × 0.32 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.798, T_{max} = 0.859
6578 measured reflections
2398 independent reflections
1760 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 28.28°
$h = -24 \rightarrow 26$
$k = -6 \rightarrow 6$
$l = -13 \rightarrow 8$

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.753 (2)	N1—N2	1.406 (3)
S1—C7	1.816 (3)		
C8—S1—C7	103.4 (1)	C8—N1—N2	121.0 (2)
C8—S1—C7—C1	−169.7 (2)	N2—N1—C8—S2	179.5 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*A*···S1	0.86	2.35	2.772 (2)	110
N1—H1*A*···S2^{i}	0.86	2.58	3.345 (2)	149

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.113
S = 0.976
2398 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1096P)^2 + 0.5240P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms (N—H = 0.86 Å, C—H = 0.93 and 0.97 Å)

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government, Universiti Kebangsaan Malaysia and Universiti Sains Malaysia for research grant R & D Nos. 03-02-02-005 and 305/pfizik/610942. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1480). Services for accessing these data are described at the back of the journal.

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