

The first bipodal thiocarbamic acid ester, *O,O'*-diethyl *N,N'*-(*p*-phenylene-dicarbonyl)bis(thiocarbamate)

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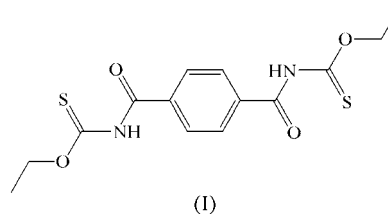
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The title compound, $C_{14}H_{16}N_2O_4S_2$, is the first reported X-ray crystallographic structure determination of a bipodal *O*-alkyl *N*-benzoylthiocarbamate. This compound crystallizes in a *cis-S,O* orientation (*Z,Z'* configuration), with the two *S/O* moieties *anti* relative to one another, as indicated by the twofold rotation axis located at the center of the benzene ring.

Comment

N,N-Dialkyl- and *N*-alkyl-*N'*-aroylthioureas have been studied extensively, as has the complexation of these ligands with several transition metals (Koch, 2001). Moreover, the bipodal ligands 3,3,3',3'-tetraalkyl-1,1'-isophthaloylbis(thioureas) and 3,3,3',3'-tetraalkyl-1,1'-terephthaloylbis(thioureas) (*L*) have been shown to readily form 2:2 and 3:3 metallomacrocyclic complexes in high yield with the general structure $cis-[M(L-S,O)]_n$ [$n = 2$ and 3, and $M = Pt^{II}$ (Koch *et al.*, 1999); $n = 2$, and $M = Pd^{II}$ and Ni^{II} (Koch *et al.*, 2001); $n = 2$ and $M = Ni^{II}$ (Bourne *et al.*, 2004)]. The latter nickel(II) metallomacrocyclic complexes also show some interesting host-guest chemistry. In this context, the bipodal *O*-alkyl-*N*-benzoylthiocarbamic acid esters are of interest as potential structural analogues to the well studied bipodal *N,N,N''',N''''*-tetraalkyl-*N,N'''*-aroylbis(thioureas). In recent years, *O*-alkyl-*N*-benzoylthiocarbamic acid esters have also been proposed as intermediates for regio- and chemoselective deoxygenation of primary and secondary alcohols (Oba & Nishiyama, 1994). The similarities between the bipodal *N,N*-dialkyl- and *N*-alkyl-*N'*-aroylthioureas and the bipodal *O*-alkyl-*N*-benzoylthiocarbamic acid esters stimulated an investigation into the synthesis and characterization of this class of ligands, in order to better understand their potential coordination to transition metals. A survey of the literature yields few detailed structural studies of these *O*-alkyl-*N*-benzoylthiocarbamic acid esters. To date, only one crystal structure similar to that of the title compound, (I), has been reported in the literature, *viz.* that of *O*-isopropyl *N*-(2-furoyl)thiocarbamate (Morales *et al.*, 2000).

The observed *cis-S,O* orientation (*Z,Z'* configuration) of (I) (Fig. 1) differs from the reported *trans-S,O* orientation of the



analogous monopodal and bipodal *N,N*-dialkyl- and *N*-alkyl-*N'*-aroyl(acyl)thioureas, as well as from the configuration observed for *O*-isopropyl *N*-(2-furoyl)thiocarbamate (Koch, 2001; Koch *et al.*, 1995; Köning *et al.*, 1985; Morales *et al.*, 2000). Compound (I) has a twofold rotation axis located at the center of the benzoyl ring and crystallizes in an *s-cisoid s-cisoid* conformation with respect to the C6–N7–C3 system. The two *S/O* groups are thus *anti* relative to one another, as indicated by the twofold rotation axis. The *cis-S,O* configuration of the title compound results in a 1–4 H7···O2 interaction, as indicated by the H7···O2 distance of 2.21 Å [$N7···O2 = 2.181(3)$ Å]. Atom H7 participates in a clear intermolecular hydrogen bond ($N7-H7···O1$), as shown in Fig. 2 and Table 2. Atom O1 of one molecule in turn forms a hydrogen bond with atom H7 of the adjacent molecule, resulting in each molecule being linked to four other molecules within the crystal structure. Atoms S1, C6, N7, C3 and O1 adopt an essentially planar arrangement, the S1–C6–N7–C3 and C6–N7–C3–O1 torsion angles being $-1.6(4)$ and $-5.8(4)^\circ$, respectively. As a result, the entire molecule is effectively planar, in contrast to what is usually observed in the related 3,3,3',3'-tetraalkyl-1,1'-terephthaloylbis(thioureas) (Koch *et al.*, 2001) and 3,3,3',3'-tetraethyl-1,1'-terephthaloylbis(thiourea) (Ugur *et al.*, 2003).

In (I), the C6–N7 bond distance (Table 1) is shorter than that observed for the corresponding bipodal compounds 3,3,3',3'-tetraethyl-1,1'-terephthaloylbis(thiourea)

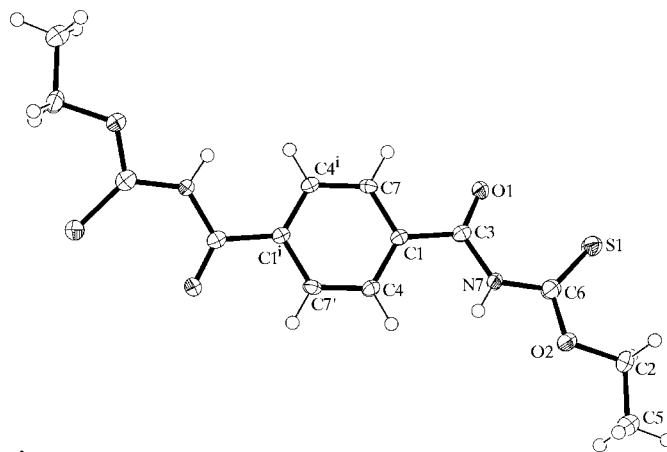


Figure 1

The molecular structure of the title compound, showing the atomic numbering scheme. There is a twofold axis passing through the center of the benzene ring. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $1 + y, x - 1, -z$.]

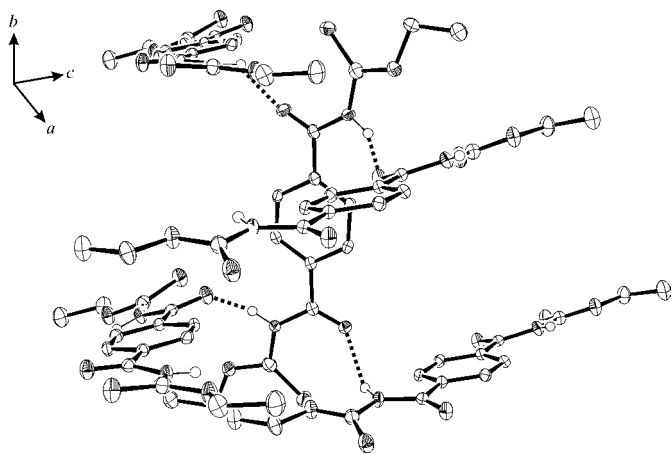


Figure 2

A view of the structure of the title compound, showing the N—H...O intermolecular hydrogen bonds (dashed lines). All H atoms, apart from atom H7, have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

[1.4173 (16) Å; Ugur *et al.*, 2003] and 3,3,3',3'-tetraethyl-1,1'-isophthaloylbis(thiourea) [1.428 (4) Å; Koch *et al.*, 2001], suggesting a greater degree of double-bond character in the C—N bond in question for (I). Moreover, the C3—N7 bond length in the title compound is comparable in length to the corresponding bonds in the aforementioned bipodal *N',N',N''',N''''*-tetraalkyl-*N,N''*-aroylbis(thioureas). The partial double-bond character of the C—N bonds observed here is consistent with that suggested by Schröder *et al.* (1995) on the basis of spectroscopic studies.

The asymmetry of the C7—C1—C3 and C4—C1—C3 angles (Table 1) may be caused by a repulsion between the N7—H7...H4—C4 system [N7...C4 = 2.923 (3) Å] and an attraction between the C7—H7A...O1 system [C7...O1 = 2.749 (3) Å and H7A...O1 = 2.43 Å]. A similar asymmetry of bond angles around the carbonyl group relative to the furoyl group within the monopodal *O*-isopropyl *N*-(2-furoyl)thiocarbamate has been reported (Morales *et al.*, 2000).

Experimental

All reactions were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. The title compound was synthesized using a modification of the procedure initially reported for the preparation of thioureas by Douglas & Dains (1934). The reagents, *viz.* terephthaloyl dichloride and KSCN, were used as supplied without further purification. Acetone (calcium carbonate) and ethanol (Mg, I₂) were rendered anhydrous and distilled prior to use. Terephthaloyl dichloride (2.5 mmol) in acetone (25 ml) was added to KSCN (5 mmol) in acetone (25 ml) under an inert atmosphere. The mixture was heated under reflux for 1 h and then cooled to room temperature, after which ethanol (5 mmol) in acetone (25 ml) was added dropwise with stirring and the mixture was further warmed to 333 K for 2 h. Water (50 ml) was added, followed by extraction of the product into chloroform. Removal of the solvent *in vacuo* resulted in a pale-yellow amorphous residue containing a mixture of products (thin-layer chromatography). The title compound was crystallized from a 1:1 mixture of chloroform and ethanol, yielding crystals suitable for single-crystal diffraction analysis [yield 84.8%

(based on terephthaloyl dichloride), m.p. 410.3–411.2 K]. ¹H NMR (CDCl₃): δ 9.29 (*br, s*, 2H), 7.93 (*s*, 4H, Ph), 4.65 (*qu*, 4H, CH₂), 1.44 (*tr*, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 188.9 (CO), 161.9 (CS), 136.9 (*ipso*-Ph), 128.3 (*ortho*-Ph), 69.6 (CH₂), 13.7 (CH₃). FT-IR (KBr disks): 3260 (*s*), 1697 (*s*), 1542 (*s*), 1281 (*s*), 1186 (*m*) cm⁻¹. Analysis calculated for C₁₄H₁₆N₂O₄S₂ (340.41 g mol⁻¹): C 50.58, H 4.50, N 8.23, S 18.84%; found C 50.40, H 4.74, N 8.60, S 17.64%.

Crystal data

C₁₄H₁₆N₂O₄S₂
M_r = 340.41
 Tetragonal, *P*4₃2₁2
a = 10.5794 (4) Å
c = 14.0773 (12) Å
V = 1575.58 (16) Å³
Z = 4
D_x = 1.435 Mg m⁻³

Mo Kα radiation
 Cell parameters from 1547 reflections
 θ = 2.4–26.0°
 μ = 0.36 mm⁻¹
T = 100 (2) K
 Needle, colorless
 0.43 × 0.06 × 0.06 mm

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
 T_{\min} = 0.975, T_{\max} = 0.979
 16 377 measured reflections
 1547 independent reflections

1448 reflections with $I > 2\sigma(I)$
 R_{int} = 0.050
 θ_{max} = 26.0°
 h = -13 → 13
 k = -13 → 13
 l = -17 → 17

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.041
 $wR(F^2)$ = 0.104
 S = 1.09
 1547 reflections
 96 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.9712P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.002
 $\Delta\rho_{\text{max}}$ = 0.35 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.22 e Å⁻³
 Absolute structure: Flack (1983),
 598 Friedel pairs
 Flack parameter = 0.08 (15)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-----------|--------------------|-----------|
| S1—C6 | 1.638 (3) | C1—C4 | 1.392 (3) |
| O1—C3 | 1.213 (3) | C1—C7 | 1.401 (3) |
| N7—C6 | 1.383 (3) | C1—C3 | 1.503 (4) |
| N7—C3 | 1.384 (3) | C4—C7 ⁱ | 1.377 (4) |
| O2—C6 | 1.340 (3) | | |
| C4—C1—C3 | 124.6 (2) | C7—C1—C3 | 116.1 (2) |
| S1—C6—N7—C3 | -1.6 (4) | C6—N7—C3—O1 | -5.8 (4) |

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

Table 2

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| N7—H7...O1 ⁱⁱ | 0.88 | 2.17 | 2.895 (3) | 140 |

Symmetry code: (ii) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{4} + z$.

H atoms were placed in calculated positions, with C—H distances of 0.99 (for CH₂ H atoms), 0.98 (for CH₃ H atoms) and 0.95 Å (for phenyl H atoms), and were refined using a riding model, with *U*_{iso}(H) values of 1.2*U*_{eq}(C) (for CH₂ and phenyl) and 1.5*U*_{eq}(C) (for CH₃).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1474). Services for accessing these data are described at the back of the journal.

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