

## 1-(3-Methoxybenzoyl)-3,3-diethylthiourea

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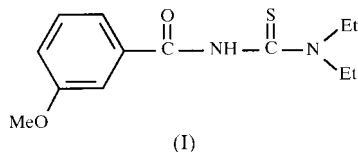
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The title compound, C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, crystallizes in the thioamidic form. The molecules are connected by N—H···S interactions forming dimers with N···S and H···S distances of 3.487 (4) and 2.76 Å, respectively.

## Comment

Among organic sulfur compounds, thioureas and its derivatives are of relevant importance. These compounds have been introduced in almost every branch of chemistry and are commercialized as dyes, photographic films, elastomery plastics and textiles (Chynoweth, 1955). In chemical research work they have been greatly used as intermediates in the synthesis and characterization of organic compounds and in the separation of branched hydro-C atoms in organic mixtures (Gabriele, 1995; Rodríguez *et al.*, 1995). In order to continue these studies we have prepared derivatives of acylthioureas (Rodríguez *et al.*, 1995). The crystal structure of 1-(3-methoxybenzoyl)-3,3-diethylthiourea, (I), has been determined to understand better the role of the geometry of the anions in the reactivity of alkylation reactions with respect to the substitutes present at nitrogen positions 1 and 3.



The title compound crystallizes in the thioamidic form. The S, C2, N1, C1, O1 moiety deviates extensively from planarity. The torsion angles O1—C1—N1—C2 and C1—N1—C2—S are 0.8 (6) and -123.6 (3)°, respectively. The molecule is stabilized in the *s-cisoid*, *s-transoid* conformation with respect

to the imino C1—N1—C2. The bond distance C2—N2 has a double-bond character, but the bonds distances C2—N1 and C1—N1 correspond to a single bond  $Csp^2-Nsp^2$ . This fact indicates that there is  $\pi$  conjugation only along the S—C2—N2 system, but not along O1—C1—N1 and C1—N1—C2 as found in 1-benzoyl-3-*n*-propylthiourea (Dago *et al.*, 1989) and 1-(4-methoxybenzoyl)-3-phenylthiourea (Fajardo *et al.*, 1990). The *p* atomic orbital of the O2 atom in the methoxy group overlaps with the  $\pi$  system of the phenyl ring, as evidenced by the shortening of the O2—C9 bond distance [1.368 (4) Å]. This also results in the coplanarity of the methoxy group with the phenyl ring C8—C9—O2—C13 = 6.4 (5)°. The difference in the values of C10—C9—O2 = 115.5 (3) and C8—C9—O2 = 124.1 (3)° is in agreement with the distortion already observed in anisoles as shown by Domiano *et al.* (1979). The molecules are held together by N—H···S interactions forming dimers with N1···S and H1···S distances of 3.487 (4) and 2.76 Å, respectively.

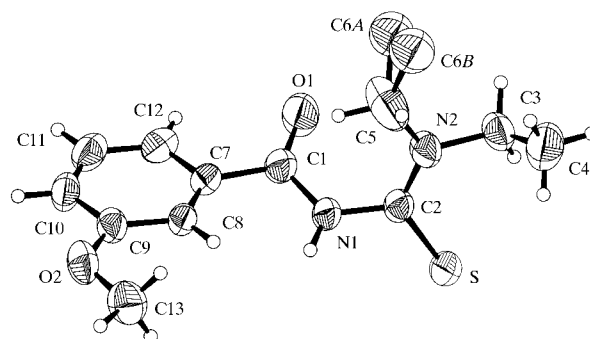


Figure 1

Plot showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for non-H atoms.

## Experimental

The compound was prepared by the reaction of diethylamine with 3-methoxybenzoyl isothiocyanate obtained *in situ* by a method already published (Rodríguez *et al.*, 1995). Recrystallization from ethanol gave suitable crystals for X-ray analysis.

## Crystal data

C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S  
*M<sub>r</sub>* = 266.36  
Triclinic, *P* $\bar{1}$   
*a* = 7.754 (4) Å  
*b* = 8.949 (8) Å  
*c* = 11.251 (7) Å  
 $\alpha$  = 78.48 (6)°  
 $\beta$  = 70.26 (4)°  
 $\gamma$  = 70.06 (6)°  
*V* = 687.6 (8) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.286 Mg m<sup>-3</sup>  
Mo *K* $\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta$  = 2–50°  
 $\mu$  = 0.232 mm<sup>-1</sup>  
*T* = 293 (2) K  
Prism, colourless  
0.61 × 0.57 × 0.34 mm

## Data collection

Stoe Stadi-4 four-circle diffractometer  
 $\omega$  scans  
Absorption correction: empirical (*EMPIR*; Stoe, 1992)  
*T<sub>min</sub>* = 0.833, *T<sub>max</sub>* = 0.924  
3005 measured reflections  
2423 independent reflections  
1803 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.016  
 $\theta_{max}$  = 25°  
*h* = -9 → 1  
*k* = -10 → 10  
*l* = -13 → 13  
2 standard reflections  
frequency: 60 min  
intensity decay: <2.0%

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1092P)^2 + 0.4967P]$
$R(F) = 0.060$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.184$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.030$	$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
2423 reflections	$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
163 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S—C2	1.676 (4)	N1—C2	1.403 (4)
O1—C1	1.212 (4)	N2—C2	1.327 (5)
O2—C9	1.368 (4)	N2—C3	1.471 (5)
O2—C13	1.415 (5)	N2—C5	1.470 (6)
N1—C1	1.388 (4)		
C9—O2—C13	117.8 (3)	S—C2—N1	118.6 (3)
C1—N1—C2	122.3 (3)	N1—C2—N2	117.2 (3)
C2—N2—C3	120.2 (3)	S—C2—N2	124.2 (2)
C2—N2—C5	123.4 (3)	N2—C3—C4	113.6 (4)
C3—N2—C5	116.3 (4)	O2—C9—C10	115.5 (3)
O1—C1—N1	121.5 (3)	O2—C9—C8	124.1 (3)
C13—O2—C9—C8	−6.4 (5)	C2—N1—C1—O1	0.8 (6)
C1—N1—C2—S	−123.6 (3)		

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ S <sup>i</sup>	0.86	2.76	3.487 (4)	143
C3—H3B $\cdots$ S	0.97	2.56	3.024 (5)	109
C5—H5A $\cdots$ O1	0.97	2.49	2.979 (8)	111
C5—H5A $\cdots$ N1	0.97	2.31	2.794 (8)	110

Symmetry code: (i)  $2 - x, -y, 1 - z$ .

H atoms were calculated geometrically and included in the refinement, but were restrained to ride on their parent atoms. The isotropic displacement parameters of the H atoms were fixed to 1.3

times  $U_{\text{eq}}$  of their parent atoms. The C6 atom of the terminal methyl group was located from the  $\Delta F$  map and found to be disordered; it was placed in two positions (C6A and C6B), with 60 and 40% occupancy, respectively. The H atoms of the disordered C6 atom were not located.

Data collection: *DIF4* (Stoe, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 1990), *PARST* (Nardelli, 1983, 1995) and *PARSTCIF* (Nardelli, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1453). Services for accessing these data are described at the back of the journal.

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