

***N*-Ethoxycarbonyl-*N'*-(2-methylphenyl)thiourea**

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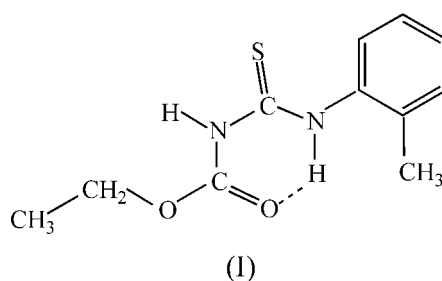
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Key indicatorsSingle-crystal X-ray study
 $T = 296\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.042
 wR factor = 0.115
Data-to-parameter ratio = 15.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$, has been determined by X-ray analysis. An intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond forms a six-membered ring in the central part of the molecule. In the crystal structure, the molecules are connected into infinite zigzag chains by intermolecular $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds along the c axis.

Comment

Thiourea derivatives have found extensive applications in the fields of medicine, agriculture and analytical chemistry. The wide spectrum of biological activities associated with such compounds has been fully reviewed (Schroeder, 1955; Antholine & Taketa, 1982). Recently, some *N*-substituted *N'*-ethoxycarbonyl thiourea compounds have been found with high antibacterial activity (Huang *et al.*, 1995). In addition, *N*-substituted *N'*-ethoxycarbonyl thiourea compounds have attracted considerable attention in recent years due to their coordination ability with transition metal ions (Shen *et al.*, 1999). Owing to their strong coordination ability, many *N*-substituted *N'*-alkoxycarbonyl thioureas are extensively utilized as the sequestering agent for copper sulfides and precious metals (Fairthorne *et al.*, 1997). We have now synthesized the title thiourea derivative, (I), and obtained its structure by X-ray analysis.



Compound (I) adopts a *cis-trans* configuration (Fig. 1), where the benzene ring and the ethoxycarbonyl moiety lie, respectively, *cis* and *trans* relative to the S atom across the thiourea C–N bonds. There is an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond, which forms a six-membered ring involving atoms C9, N2 and C8. In the crystal structure of (I), intermolecular $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Fig. 2 and Table 1) connect the molecules into chains along the c axis.

The spectroscopic data for (I) are in agreement with the crystal structure. The IR spectrum of (I) exhibits $\text{N}-\text{H}$ stretching vibration absorption at 3217.0 and 3159.8 cm^{-1} ,

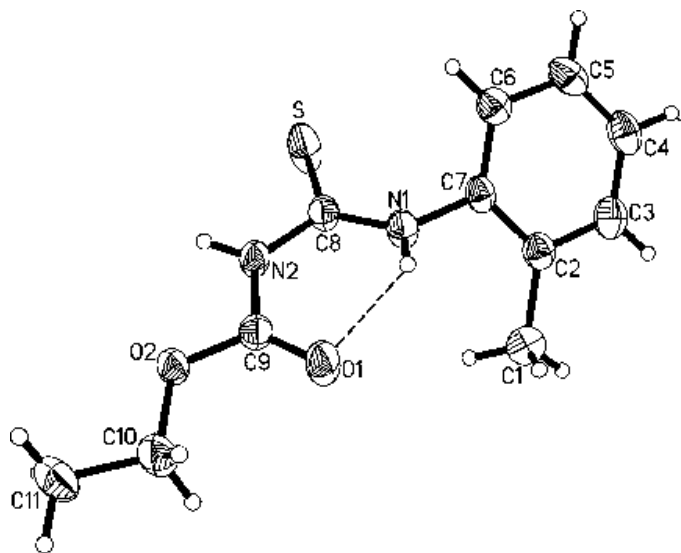


Figure 1

A view of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

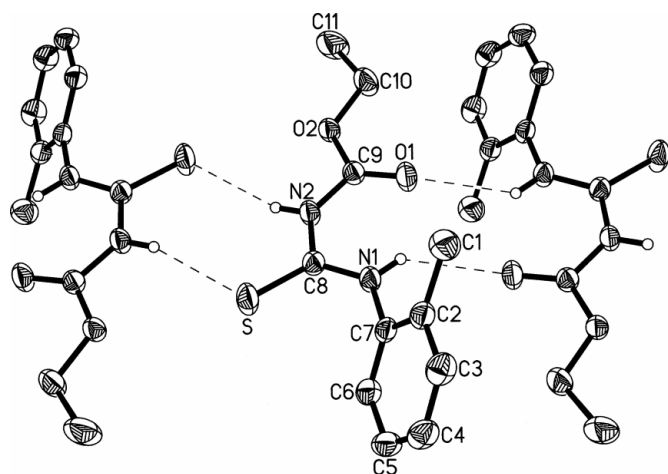


Figure 2

A view of the molecular arrangement and intermolecular hydrogen-bonding interactions (dashed lines) in the crystal structure of (I).

which is in accord with the intra- and intermolecular N—H...O and N—H...S hydrogen bonds. As far as thiol–thione tautomerism is concerned, we observed the S—H stretching vibration absorption at 2581.7 cm^{-1} . The ^1H NMR spectrum of the title compound exhibits two peaks in the low-field region (11.18 and 8.33 p.p.m.). These signals are assigned to the NH H atoms in the N—H...O and N—H...S hydrogen bonds.

Experimental

The synthesis of (I) was carried out by adding KSCN (12 mmol) and polyethyleneglycol-400 (0.1 ml) as phase-transfer catalyst to a solution of ethyl chloroformate (10 mmol) in dry ethyl acetate (10 ml), followed by stirring at room temperature for 5 h. After filtration to

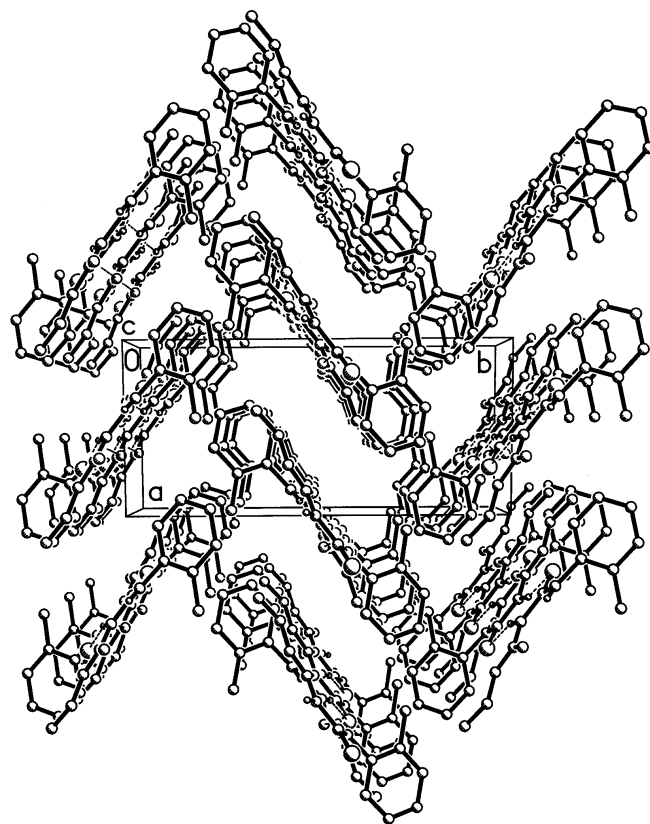


Figure 3

The packing diagram of (I) projected down the *c* axis. H atoms have been omitted for clarity.

remove the inorganic solid, 2-methylphenylamine (10 mmol) was slowly added to the reaction mixture with constant stirring. The reaction mixture was then again stirred at room temperature for 5 h. On completion, the ethyl acetate had evaporated and the crude product was obtained. Recrystallization from ethanol gave the pure product. Colourless single crystals of (I) were obtained by slow evaporation of an EtOAc solution of compound (I) for about one week.

Crystal data

$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$
 $M_r = 238.30$
 Monoclinic, $P2_1/n$
 $a = 7.360$ (1) Å
 $b = 15.811$ (3) Å
 $c = 10.789$ (2) Å
 $\beta = 103.82$ (1)°
 $V = 1219.2$ (4) Å³
 $Z = 4$

$D_x = 1.298\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 28 reflections
 $\theta = 3.3\text{--}15.1^\circ$
 $\mu = 0.25\text{ mm}^{-1}$
 $T = 296$ (2) K
 Block, colourless
 $0.58 \times 0.58 \times 0.50\text{ mm}$

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: empirical (*SHELXTL*; Bruker, 1998)
 $T_{\min} = 0.871$, $T_{\max} = 0.902$
 2625 measured reflections
 2257 independent reflections
 1734 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 25.5^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 19$
 $l = -13 \rightarrow 12$
 3 standard reflections every 97 reflections
 intensity decay: 4.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.2368P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.115$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.08$	$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
2257 reflections	$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$
148 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.042 (4)

Table 1

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1N \cdots O1^i$	0.86	2.55	3.244 (2)	139
$N2-H2N \cdots S^{ii}$	0.86	2.52	3.3505 (18)	162
$N1-H1N \cdots O1$	0.86	2.04	2.709 (2)	134

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, 2-z$.

The positions of all H atoms were constrained geometrically, with C—H distances in the range 0.93–0.97 \AA and N—H distances of 0.86 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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