

(E)-O-Ethyl N-(4-nitrophenyl)thiocarbamate

Ronald E. Benson,^a Grant A. Broker,^b Lee M. Daniels,^a Edward R. T. Tiekink,^{b*} James L. Wardell^b and David J. Young^c

^aRigaku Americas Corporation, 9009 New Trails Drive, The Woodlands, TX 77381, USA,

^bDepartment of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA, and ^cEskitis Institute for Cell and Molecular Therapies, Griffith University, Nathan, Queensland 4111, Australia

Correspondence e-mail: edward.tiekink@utsa.edu

Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.052
wR factor = 0.162
Data-to-parameter ratio = 25.2

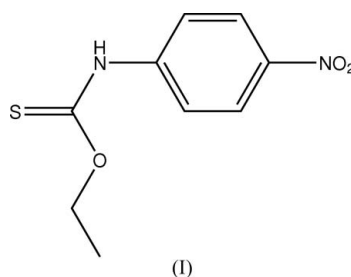
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_3\text{S}$, is effectively planar, adopts an *E* conformation about the central C—N bond and exists in the thione form. N—H \cdots S and C—H \cdots O hydrogen bonds link the molecules into ribbons. Layers of ribbons are connected to adjacent layers *via* C—H \cdots O interactions. The crystal is a non-merohedral twin, with the twin law describing a rotation of 180° around the $[\bar{1}00]$ direction.

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Comment

Compounds related to the title compound, (I), with general formula $\text{ROC}(=\text{S})\text{N}(\text{H})\text{R}'$, have been shown in theory to prefer the *E* conformation about the central C—N bond, which has substantial double-bond character (Ho *et al.*, 2005). Such a conformation allows for the formation of an $\{\cdots\text{H}-\text{N}-\text{C}=\text{S}\}_2$ synthon. In structures where there are no competing functional groups for hydrogen bonding, this synthon is invariably observed (*e.g.* Taylor & Tiekink, 1994; Abraham *et al.*, 1995; Ho *et al.*, 2003, 2005; Kuan *et al.*, 2005; Tadbuppa & Tiekink, 2005; Jian *et al.*, 2006). In cases where competing functionality is present, other synthons are observed in the solid state (*e.g.* Morales *et al.*, 2000), but with retention of the *E* conformation. In contrast, competing synthons can force the energetically unstable *Z* conformation in the structures of formula $\text{ROC}(=\text{S})\text{N}(\text{H})\text{R}'$, where $R = \text{Me}$ and Et , and R' is 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl (Zhang *et al.*, 2001), and $\text{MeOC}(=\text{S})\text{N}(\text{H})\text{R}'$, where R' is 2-(2-methyl-5-nitro-1*H*-imidazol-1-yl) (Bernardinelli *et al.*, 1995).



Compound (I) (Fig. 1) adopts an *E* conformation. The molecule, including the pendant groups, is essentially planar, as seen from the torsion angle data (Table 1). The geometric data collected in Table 1 show that the molecule exists in the thione form shown in the scheme. The thioamide $\{\cdots\text{H}-\text{N}-\text{C}=\text{S}\}_2$ synthon is formed between centrosymmetric molecules, $\text{N1}-\text{H1}\cdots\text{S1}^i$ (details in Table 2). Both nitro-O atoms are involved in C—H \cdots O interactions, the first of these occurring between C4—H4 and O2ⁱⁱ (Table 2).

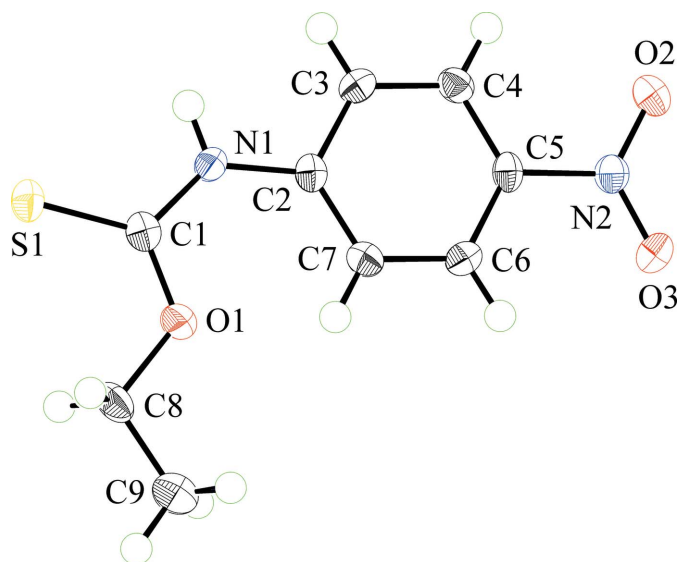


Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 50% probability level.

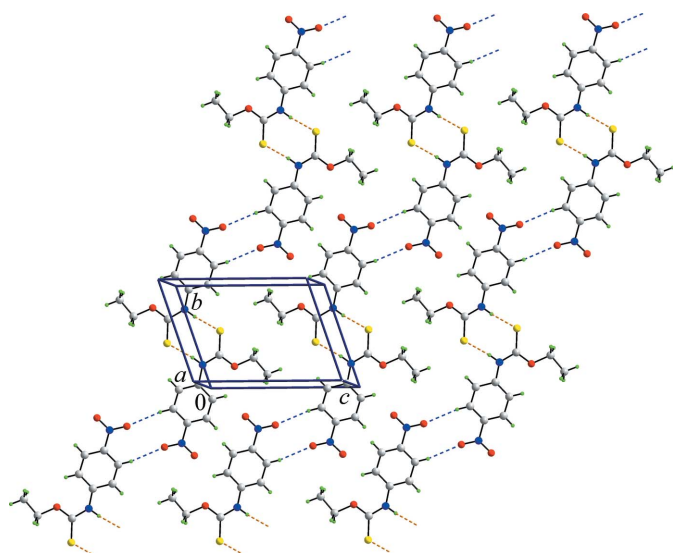


Figure 2
The unit-cell contents for (I), showing the formation of chains mediated by N—H...S (orange dashed lines) and C—H...O (blue dashed lines) hydrogen bonding.

The result of these hydrogen-bonding interactions is the formation of ribbons, as highlighted in Fig. 2. Layers of such ribbons are connected to other layers *via* C—H...O interactions involving both O2 and O3 atoms (Table 2).

Experimental

The title compound was prepared by refluxing 4-nitrophenylisothiocyanate (Aldrich) with absolute ethanol using the literature procedure of Bost & Andrews (1943). The white precipitate, which was obtained upon concentration of the reaction solution, was dissolved in hot chloroform and layered with hot hexane. Upon cooling, this resulted in the formation of colorless crystals of (I), which were isolated by vacuum filtration (m.p. 451–452 K). Spectroscopic

analysis: $^1\text{H NMR}$ (CDCl_3 , δ , p.p.m.): 1.48 (3 H, *t*, $J = 7.0$ Hz, CH_3), 4.67 (2 H, *q*, $J = 7.0$ Hz, CH_2), 7.57 (2 H, *br*, aryl-H), 8.23 (2 H, *m*, aryl-H), 8.42 (1 H, *br*, NH); IR (crystals, cm^{-1}): $\nu(\text{N—H})$ 3284 (*br*), $\nu(\text{N—O}_2)$ 1548 (*s*), $\nu(\text{CN})$ 1494 (*s*), $\nu(\text{N—O}_2)$ 1376 (*m*), $\nu(\text{CS})$ 1032 (*s*).

Crystal data

$\text{C}_9\text{H}_{10}\text{N}_2\text{O}_3\text{S}$
 $M_r = 226.25$
Triclinic, $P\bar{1}$
 $a = 6.9247$ (12) Å
 $b = 7.6430$ (14) Å
 $c = 10.4772$ (19) Å
 $\alpha = 105.782$ (8)°
 $\beta = 90.136$ (8)°
 $\gamma = 107.769$ (7)°

$V = 505.94$ (16) Å³
 $Z = 2$
 $D_x = 1.485$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 150$ (2) K
Block, colorless
0.22 × 0.13 × 0.13 mm

Data collection

Rigaku AFC12 κ /SATURN 724
diffractometer
 ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.935$, $T_{\max} = 0.961$

14293 measured reflections
3481 independent reflections
3295 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 26.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.162$
 $S = 1.10$
3481 reflections
138 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2 + 0.4757P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.75$ e Å⁻³
 $\Delta\rho_{\min} = -0.31$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—C1	1.672 (2)	N1—C1	1.354 (3)
O1—C1	1.322 (3)	N1—C2	1.412 (3)
C1—O1—C8	119.59 (16)	S1—C1—N1	121.58 (16)
C1—N1—C2	131.38 (18)	O1—C1—N1	113.49 (17)
S1—C1—O1	124.93 (15)		
C1—N1—C2—C3	177.19 (19)	C1—O1—C8—C9	179.11 (18)
O2—N2—C5—C4	5.3 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
N1—H1 \cdots S1 ⁱ	0.88	2.70	3.4435 (19)	142
C4—H4 \cdots O2 ⁱⁱ	0.95	2.57	3.481 (3)	162
C8—H8A \cdots O2 ⁱⁱⁱ	0.99	2.57	3.345 (3)	135
C3—H3 \cdots O3 ^{iv}	0.95	2.54	3.275 (3)	135

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

All H atoms were included in the riding-model approximation, with C—H = 0.95–0.99 Å and N—H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl-C})$ or $1.2U_{\text{eq}}(\text{N and remaining C})$.

Initial indexing of the unit cell provided evidence that the crystal was a non-merohedral twin, as the predicted reflection positions fit poorly to the actual positions and a large number of reflections were

not predicted by the initial indexing result. Indexing with the *TwinSolve* program (Rigaku/MSK & Prekat, 2006) clearly indicated two triclinic twin components. The twin law describes a rotation of 180° around the $[\bar{1}00]$ direction, given by the matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -0.674 & -1 \\ 0 & -0.016 & 0 \end{pmatrix}$. Integration of the intensities produces a reflection file with three types of reflections, namely component 1, component 2, and overlaps of 1 and 2. An absorption correction based on the measurement of equivalent reflections [multi-scan; *ABSCOR* (Higashi, 1995)] was applied; three constrained absorption surfaces were used, based on each of the three types of reflections.

Data collection: *CrystalClear* (Rigaku/MSK, 2005); cell refinement: *TwinSolve* (Rigaku Americas Corporation & Prekat, 2006); data reduction: *TwinSolve*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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