electronic reprint

Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368
Editors: **W. Clegg and D. G. Watson**

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

Ronald E. Benson, Grant A. Broker, Lee M. Daniels, Edward R. T. Tiekink, James L. Wardell and David J. Young

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*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]

[a]Rigaku Americas Corporation, 9009 New Trails Drive, The Woodlands, TX 77381, USA, [b]Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA, and [c]Eskitis 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 σ(C–C) = 0.003 Å
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.

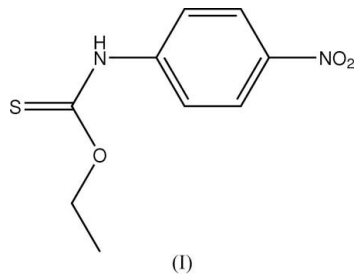
© 2006 International Union of Crystallography
All rights reserved

The title compound, $C_9H_{10}N_2O_3S$, is effectively planar, adopts an *E* conformation about the central C—N bond and exists in the thione form. N—H···S and C—H···O hydrogen bonds link the molecules into ribbons. Layers of ribbons are connected to adjacent layers *via* C—H···O interactions. The crystal is a non-merohedral twin, with the twin law describing a rotation of 180° around the [$\bar{1}$00] direction.

Received 15 August 2006
Accepted 17 August 2006

Comment

Compounds related to the title compound, (I), with general formula *R*OC(═S)N(H)*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 {···H—N—C═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 *R*OC(═S)N(H)*R*′, where *R* = Me and Et, and *R*′ is 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl (Zhang *et al.*, 2001), and MeOC(═S)N(H)*R*′, where *R*′ is 2-(2-methyl-5-nitro-1*H*-imidazol-1-yl) (Bernardinelli *et al.*, 1995).



(I)

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 {···H—N—C═S}$_2$ synthon is formed between centrosymmetric molecules, N1—H1···S1^{i} (details in Table 2). Both nitro-O atoms are involved in C—H···O interactions, the first of these occurring between C4—H4 and O2^{ii} (Table 2).

electronic reprint

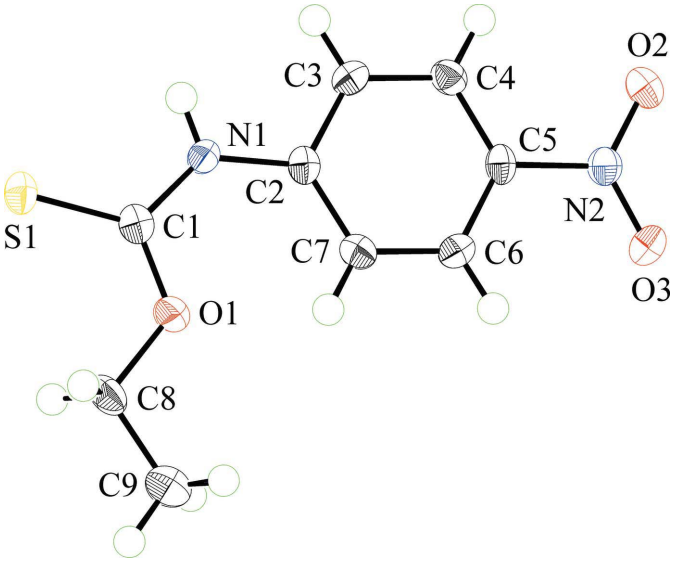


Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 50% probability level.

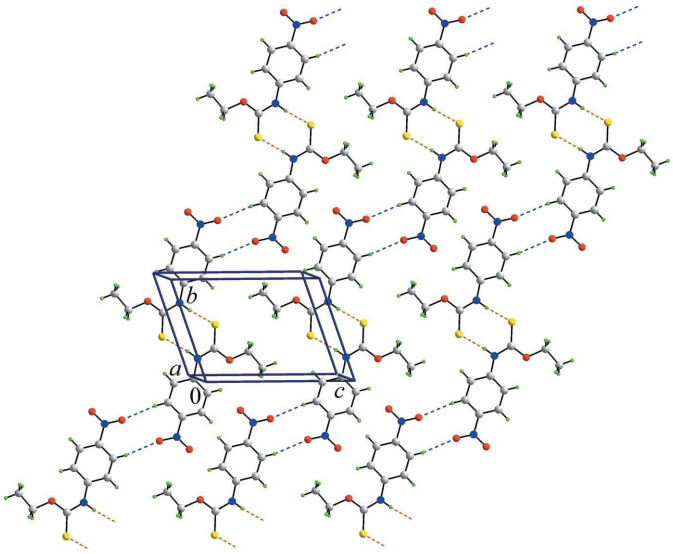


Figure 2
The unit-cell contents for (I), showing the formation of chains mediated by N—H···S (orange dashed lines) and C—H···O (blue dashed lines) hydrogen bonding.

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}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}): ν(N—H) 3284 (*br*), ν(N—O_2) 1548 (*s*), ν(CN) 1494 (*s*), ν(N—O_2) 1376 (*m*), ν(CS) 1032 (*s*).

Crystal data

$C_9H_{10}N_2O_3S$
M_r = 226.25
Triclinic, $P\overline{1}$
a = 6.9247 (12) Å
b = 7.6430 (14) Å
c = 10.4772 (19) Å
α = 105.782 (8)°
β = 90.136 (8)°
γ = 107.769 (7)°
V = 505.94 (16) Å^3
Z = 2
D_x = 1.485 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 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_{int} = 0.035
θ_{max} = 26.5°

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—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S1^{i}	0.88	2.70	3.4435 (19)	142
C4—H4···O2^{ii}	0.95	2.57	3.481 (3)	162
C8—H8*A*···O2^{iii}	0.99	2.57	3.345 (3)	135
C3—H3···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_{iso}(H) = 1.5U_{eq}(methyl-C) or 1.2U_{eq}(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

electronic reprint

not predicted by the initial indexing result. Indexing with the *TwinSolve* program (Rigaku/MSC & 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 (1 0 0, −0.674 −1 0, −0.016 0 −1). 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/MSC, 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*.

The authors thank the Australian Academy of Science for funding to allow DJY to visit UTSA.

References

Abraham, S. P., Samuelson, A. G. & Nethaji, M. (1995). *Proc. Indian Acad. Sci. Chem. Sci.* **107**, 255–271.
Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Bernardinelli, G., Berclaz, T., Geoffroy, M. & Rajalakshmi, N. (1995). *Acta Cryst.* C**51**, 1390–1392.
Bost, R. W. & Andrews, E. R. (1943). *J. Am. Chem. Soc.* **65**, 900–901.
Brandenburg, K. (2006). *DIAMOND*. Release 3.1. Crystal Impact GbR, Bonn, Germany.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Ho, S. Y., Bettens, R. P. A., Dakternieks, D., Duthie, A. & Tiekink, E. R. T. (2005). *CrystEngComm*, **7**, 682–689.
Ho, S. Y., Lai, C. S. & Tiekink, E. R. T. (2003). *Acta Cryst.* E**59**, o1155–o1156.
Jian, F.-F., Yu, H.-Q., Qiao, Y.-B. & Liang, T.-L. (2006). *Acta Cryst.* E**62**, o3416–o3417.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kuan, F. S., Tadbuppa, P. & Tiekink, E. R. T. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 393–394.
Morales, A. D., Novoa de Armas, H., Blaton, N. M., Peeters, O. M., De Ranter, C. J., Márquez, H. & Pomés Hernández, R. (2000). *Acta Cryst.* C**56**, 1042–1043.
Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.
Rigaku Americas Corporation & Prekat (2006). *TwinSolve*. Rigaku/MSC, The Woodlands, Texas, USA, and Prekat AB, Lund, Sweden.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Tadbuppa, P. & Tiekink, E. R. T. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 395–396.
Taylor, R. & Tiekink, E. R. T. (1994). *Z. Kristallogr.* **209**, 64–67.
Zhang, S.-S., Wang, Z.-W., Li, M., Jiao, K., Razak, I. A., Shanmuga Sundara Raj, S. & Fun, H.-K. (2001). *Acta Cryst.* C**57**, 566–568.

electronic reprint