Monoclinic
$P2_1/n$
$a = 6.5453\ (6)$ Å
$b = 7.5995\ (8)$ Å
$c = 24.855\ (3)$ Å
$\beta = 95.46\ (2)°$
$V = 1230.7\ (2)$ Å^3
$Z = 4$
$D_x = 1.502$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 9.9–18.2°$
$\mu = 0.12$ mm^{-1}
$T = 293$ K
Prism
$0.15 \times 0.12 \times 0.10$ mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2719 measured reflections
2495 independent reflections
1613 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 26.29°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 0$
$l = -30 \rightarrow 30$
3 standard reflections
frequency: 120 min
intensity decay: 0.70%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.117$
$S = 1.114$
2493 reflections
188 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.6014P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.221$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.167$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.054 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—N1	1.310 (2)	O6—C6	1.291 (2)
N1—C5	1.353 (3)	O6—HO6	1.01 (3)
N1—C1	1.354 (3)	C6—C7	1.478 (3)
N2—C3	1.467 (3)	C7—C12	1.389 (3)
O4—C11	1.359 (2)	C7—C8	1.390 (3)
O4—HO4	0.95 (3)	C10—C11	1.391 (3)
O5—C6	1.246 (3)	C11—C12	1.383 (3)
O1—N1—C5	119.8 (2)	C12—C7—C8	120.3 (2)
O1—N1—C1	119.8 (2)	C12—C7—C6	119.0 (2)
C5—N1—C1	120.4 (2)	C8—C7—C6	120.7 (2)
C6—O6—HO6	113.7 (15)	O4—C11—C12	117.6 (2)
O5—C6—O6	122.6 (2)	O4—C11—C10	122.4 (2)
O5—C6—C7	120.9 (2)	C12—C11—C10	119.9 (2)
O6—C6—C7	116.5 (2)		

The ring H atoms were added at calculated positions and refined using a riding model with *SHELXL*93 (Sheldrick, 1993) defaults (C—H 0.93 Å). A $B_{\rm iso}$ value of 6.0 Å^2 was assigned to all H atoms. Atom HO4 was located from a difference Fourier map and its coordinates were refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SDP*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1126). Services for accessing these data are described at the back of the journal.

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1-(*tert*-Butyl)-3-(2-pyridyl)thiourea

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Abstract

In the title compound, $(CH_3)_3CNHCSNH(C_5H_4N)$ (or $C_{10}H_{15}N_3S$), the *endo*-N···imino-N distance of 2.668 (2) Å is indicative of intramolecular hydrogen bonding. The pyridyl ring and the thiourea plane are inclined at an angle of 13.29 (9)°. The molecules are dimerized through a pair of hydrogen bonds of the type C=S···H—N.

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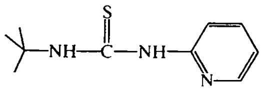
Comment

Recently, we started a project on the synthesis and structure determination of unsymmetrically substituted urea and thiourea derivatives with potential applications in non-linear optics. *N*-Pyridylurea (Velikova, Angelova & Kossev, 1997) and its addition compounds to some inorganic acids (Velikova, Petrova & Angelova, 1997; Velikova, Angelova, Petrova & Kossev, 1997) were found to crystallize in centrosymmetric space groups. The title compound, (I), is an intermediate in the synthesis of *N*-(2-pyridyl)thiourea (Nair, 1963, 1966) and its structure was determined for comparative purposes.


(I)

The S—C bond length of 1.683 (2) Å corresponds well with the values in non-coordinated thioureas [1.68 (2) (Allen *et al.*, 1987) and 1.69 (2) Å (Teslya *et al.*, 1987)]. When coordinated, the C—S bond becomes longer, as, for example, in the complexes $3Pb(ReO_4)_2.2tu.3H_2O$, where tu = thiourea [1.742 (16) Å; Macíček & Angelova, 1995], $Cd(ReO_4)_2.4tu$ [1.711 (4) and 1.726 (4) Å; Petrova *et al.*, 1996], tetra[1-allyl-3-(2-pyridyl)thiourea-*S*]di-μ-chloro-tetrachlorodibismuth(III) [1.71 (1) and 1.72 (2) Å; Battaglia & Corradi, 1981], and chloro(triphenylphosphine)-[1-phenyl-3-(2-pyridyl)thiourea]copper(I) and chlorobis-[1-phenyl-3-(2-pyridyl)thiourea]copper(I) [1.70 (2) and 1.72 (1) Å; Ferrari *et al.*, 1985]. A variation of the ureido C—N bonds occurs in the title compound: the presence of the electron-withdrawing pyridyl group leads to elongation of the C1—N2 bond with respect to the shorter C1—N3 bond, which is affected by the electron-donating *tert*-butyl group.

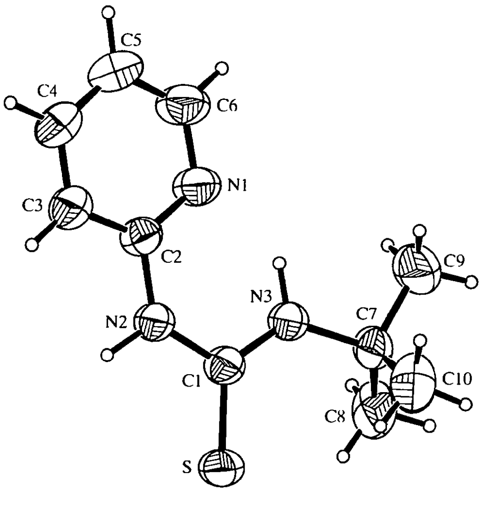


Fig. 1. A view of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are circles of an arbitrary radius.

The molecule is stabilized in the *s-cisoid,s-transoid* conformation by an intramolecular *endo*-N1···H—N3 hydrogen bond, which has also been found in previously reported pyridylthiourea derivatives (Ferrari *et al.*, 1985; Battaglia & Corradi, 1981, 1983; Teslya *et al.*, 1987) as well as in pyridylurea (Velikova, Angelova & Kossev, 1997). The six-membered hydrogen-bonded ring and the pyridyl ring are close to coplanarity, the dihedral angle being 10.43 (4)°.

An intermolecular hydrogen bond occurs between the imino-N2 atom and the S atom of the centrosymmetrically related molecule at $(-x, -y, 1 - z)$ (Table 2). The other intermolecular contacts correspond to typical van der Waals interactions.

Experimental

tert-Butyl isothiocyanate (14 g, 0.124 mol) was reacted with 2-aminopyridine (12.2 g, 0.13 mol) in benzene (5 ml) at 378–383 K for 2 h. After cooling and washing with *n*-hexane, 1-(*tert*-butyl)-3-(2-pyridyl)thiourea (29 g; 79% yield) was obtained.

Crystal data

$C_{10}H_{15}N_3S$
$M_r = 209.31$
Monoclinic
$P2_1/n$
$a = 10.118$ (2) Å
$b = 9.705$ (3) Å
$c = 11.919$ (3) Å
$\beta = 97.32$ (1)°
$V = 1160.9$ (9) Å^3
$Z = 4$
$D_x = 1.1976$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 9.4$–11.3°
$\mu = 0.246$ mm^{-1}
$T = 292$ K
Prismatic
0.43 × 0.40 × 0.37 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
6265 measured reflections
2792 independent reflections
2059 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 27.97$°
$h = -13 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections frequency: 120 min intensity decay: 1.9%

Refinement

Refinement on F^2
$R(F) = 0.043$
$wR(F^2) = 0.128$
$S = 1.020$
2792 reflections
127 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.1606P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.256$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.135$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S—C1	1.683 (2)	C2—C3	1.394 (2)
N1—C2	1.329 (2)	C3—C4	1.374 (2)
N1—C6	1.345 (2)	C4—C5	1.375 (3)
N2—C1	1.380 (2)	C5—C6	1.366 (3)
N2—C2	1.396 (2)	C7—C8	1.515 (2)
N3—C1	1.324 (2)	C7—C9	1.524 (2)
N3—C7	1.484 (2)	C7—C10	1.515 (3)
C1—N2—C2	130.00 (12)	N3—C7—C9	104.65 (13)
C1—N3—C7	130.05 (13)	N3—C7—C10	110.39 (14)
N3—C1—N2	116.46 (13)	C8—C7—C9	109.04 (16)
N3—C1—S	126.36 (11)	C10—C7—C8	111.13 (16)
N2—C1—S	117.19 (10)	C10—C7—C9	110.10 (16)
N3—C7—C8	111.32 (14)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—HN2···S^i	0.86	2.62	3.454 (1)	163
N3—HN3···N1	0.86	1.94	2.668 (2)	142

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

The structure was solved by direct methods. All non-H atoms were refined anisotropically and H atoms were geometrically constrained with isotropic displacement parameters.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Data reduction: *SDP*/*PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1341). Services for accessing these data are described at the back of the journal.

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Three 3-arylsulfonyl-1,3-oxazolidines

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Abstract

The structure determinations of (1*S*,2*R*)-2-[(2*S*,4*R*)-2-ethyl-4-phenyl-3-tosyl-1,3-oxazolidin-2-yl]-1-methyl-1-phenylpropanol, $C_{28}H_{33}NO_4S$, (I), ethyl (3*R*)-3-[(2*S*,4*R*)-2-ethyl-4-phenyl-3-tosyl-1,3-oxazolidin-2-yl]-3-hydroxy-3-phenylpropanoate, $C_{29}H_{33}NO_6S$, (II), and (1*R*)-2,3,4,5-tetrahydro-5-[(2*S*,4*R*)-2-methyl-4-phenyl-3-tosyl-1,3-oxazolidin-2-yl]-3-methylene-5-phenylfuran-2-one, $C_{28}H_{27}NO_5S$, (III), were undertaken in order to determine the absolute configuration of the chiral centres. The oxazolidine rings of (I) and (II) exhibit a twist, whereas the oxazolidine ring of (III) adopts an envelope conformation. The hydroxyl groups of (I) and (II) form intramolecular hydrogen bonds.

Comment

Various methods for asymmetric synthesis are based on the utilization of chiral 1,3-oxazolidines. Stereochemically homogeneous 3-arenesulfonyl-1,3-oxazolidines, readily available from enantiomerically pure β-amino-alkanols, are powerful chiral templates for auxiliary-directed asymmetric synthesis (Hoppe *et al.*, 1989, 1990; Hoffmann *et al.*, 1993). They readily add nucleophiles to the carbonyl group, and the attack can be directed selectively from either of its diastereotopic faces (Conde Frieboes *et al.*, 1993; Harder *et al.*, 1994). We have determined the crystal structures of three arylsulfonyl-oxazolidines, in order to establish unambiguously the absolute configuration of the reaction products. In all three cases, the newly formed chiral centre [C22 in (I), C21 in (II) and (III)] shows the *R* configuration.

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