$S = 1.114$
1290 reflections
128 parameters
H atoms refined using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*93
Extinction coefficient: 0.013 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C2—O2	1.233 (3)	C7—C8	1.502 (4)
C2—N1	1.373 (3)	C7—C12	1.514 (3)
C2—C3	1.442 (3)	C8—C9	1.505 (4)
C3—C4	1.336 (4)	C9—C10	1.523 (4)
C4—C5	1.387 (4)	C10—C11	1.517 (4)
C5—C6	1.362 (3)	C11—C12	1.501 (4)
C6—N1	1.362 (3)	N1—O1	1.404 (2)
C7—O1	1.479 (3)		
O2—C2—N1	121.8 (2)	N1—C6—C5	118.4 (2)
O2—C2—C3	125.8 (2)	C6—N1—C2	126.4 (2)
N1—C2—C3	112.4 (2)	C6—N1—O1	116.4 (2)
C4—C3—C2	122.4 (3)	C2—N1—O1	117.1 (2)
C3—C4—C5	121.2 (2)	N1—O1—C7	110.15 (14)
C6—C5—C4	119.1 (2)		
O2—C2—C3—C4	−177.3 (3)	C8—C9—C10—C11	−56.3 (3)
N1—C2—C3—C4	0.7 (3)	C9—C10—C11—C12	55.6 (3)
C2—C3—C4—C5	−1.5 (4)	C8—C7—C12—C11	49.1 (3)
C3—C4—C5—C6	0.0 (4)	C5—C6—N1—C2	−3.1 (3)
C4—C5—C6—N1	2.1 (3)	C5—C6—N1—O1	−179.7 (2)
C12—C7—C8—C9	−50.5 (3)	O2—C2—N1—O1	−3.6 (3)
C7—C8—C9—C10	54.5 (3)	C2—N1—O1—C7	79.0 (2)

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Express*. Data reduction: *CAD*-4*red* (Geselle, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal*3.2 (Hall, Flack & Stewart, 1992).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1240). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1631-1634

Hydrogen Bonding in 1-Hydroxy-4(1*H*)-pyridinethione

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(*Received 11 February 1997; accepted 13 June 1997*)

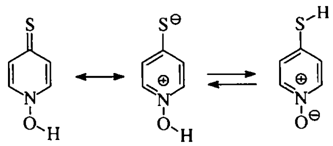
Abstract

The crystal lattice of the title compound, C_5H_5NOS, a vinylogous cyclic thiohydroxamic acid, comprises a network of hydrogen bonds [O—H 1.16(3), O···S 2.971(2), H···S 1.82(3) Å and O—H···S 171(1)°], with the hydroxyl moiety as hydrogen-bond donor and the S atom as acceptor. According to the observed C—S distance of 1.718(2) Å, the sulfur–carbon bond in the title compound is closer to a single than a double bond. The sum of bond angles at N1 is 360.8° which suggests a planar arrangement of the N—O group with respect to the carbon framework of the heterocycle.

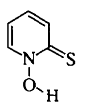
Comment

The interest in thiohydroxamic acids and their derived *O*-esters has been renewed as a result of their fascinating properties as precursors of free alkoxyl radicals in synthetic organic chemistry and medicine (Hartung & Gallou, 1995; Adam, Ballmeier, Epe, Grimm & Saha-Möller, 1995). These transformations generally involve the 2-isomer, (2), of the title compound 1-hydroxy-4(1*H*)-pyridinethione, (1). The pyridinethiones (1) and (2) have been known for almost 40 years and have been studied extensively in solution with respect to their tautomeric equilibria between the thiol [*e.g.* (1*c*)] and the OH forms [*e.g.* (1*a*) and (1*b*)]. It is interesting to note that although (2) is a commercial product and its zinc salt is widely used as the active ingredient in antidandruff shampoos (Barnett, Kretschmar & Hartman, 1977), nothing has been reported to date on the structure of cyclic thiohydroxamic acids. This is presumably because thiohydroxamic acids are light sensitive compounds and usually decompose in the X-ray beam during data collection. However, we wished to determine the basic geometric features of cyclic thiohydroxamic acids in the solid state for use in the future design of new alkoxyl radical precursors in organic synthesis. Thus, an attempt was made to study compound (1) by X-ray diffraction on a Turbo-CAD-4 diffractometer.

(1)



(1*a*) (1*b*) (1*c*)



(2)

The title pyridinethione, (1), is depicted in Fig. 1 and shows a slight distortion due to the C—N bonds [N1—C2 1.343 (3) and N1—C6 1.350 (3) Å] which are shorter than the distances C3—C4 1.408 (3) and C4—C5 1.399 (3) Å. The C4—S1 bond is significantly longer than the corresponding values for carbon–sulfur double bonds of 1.666 (4) Å in *O*-alkyl and 1.662 (6) Å in *O*-acyl derivatives of 1-hydroxy-2(1*H*)-pyridinethione, (2) (Hartung, Hiller, Schwarz, Svoboda & Fuess, 1996). Taking into account the unusual low chemical shift of the C—S carbon at $\delta = 129$ p.p.m. in the ^{13}C NMR spectrum of (1) in D_2O (Hartung, Hiller & Schmidt, 1996; Barton, Crich & Kretzschmar, 1986), the observed C4—S1 distance suggests a significant contribution of the mesomeric structure (1*b*) to the ground-state

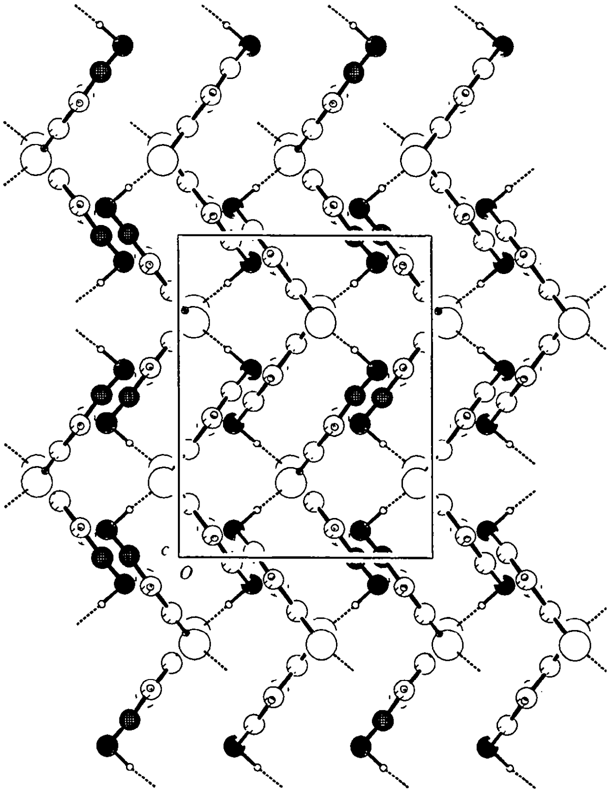


Fig. 2. Hydrogen bonds between molecules of pyridinethiones (1) in adjacent layers in the unit cell (*z* orthogonal view)

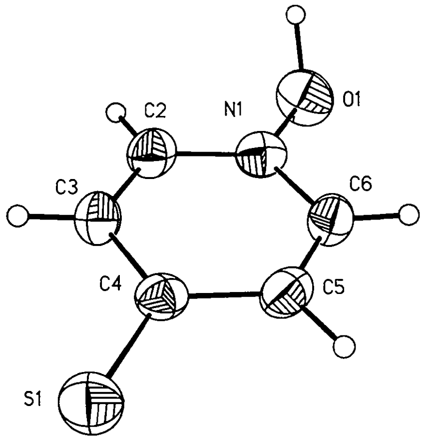


Fig. 1. Molecular structure of compound (1). Displacement ellipsoids are plotted at the 50% probability level.

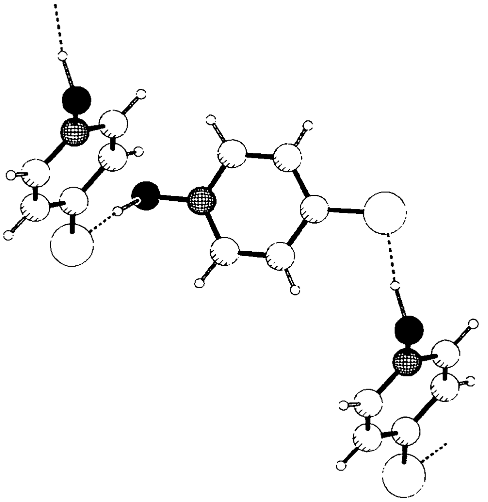


Fig. 3. Arrangement of hydrogen-bonded molecules of compound (1) in the solid state.

description of the title compound. The N1—O1 group in (1) is situated in the plane of the heterocycle [C3—C2—N1—O1 177.3 (2)°]. The hydroxyl H atom was located from the Fourier map [O1—H1O 1.16 (3) Å and N1···O1—H1O 107 (1)°]. It resides between O1 and S1 of adjacent molecules [H1O···S1 1.82 (3) Å, O1—H1O···S1 171 (1)° and S1···O1 2.971 (2) Å] and is part of a hydrogen bond which contributes efficiently to the packing of single molecules of (1) in the solid state to afford the beautifully stacked network of 1-hydroxy-4(1*H*)-pyridinethione, (1) (Figs. 2 and 3).

Experimental

1-Hydroxy-4(1*H*)-pyridinethione was prepared as reported previously from 4-chloropyridine 1-oxide and thiourea, and subsequent saponification of the isothiorunium salt (Jones & Katritzky, 1960). Colourless prisms [m.p. 418–419 K (decomp.); 413 K (decomp.)] of (1) were grown by slow cooling of a concentrated solution of (1) in ethanol.

Crystal data

C_5H_5NOS
$M_r = 127.17$
Orthorhombic
Pbca
$a = 8.352\,(1)$ Å
$b = 10.664\,(1)$ Å
$c = 12.650\,(1)$ Å
$V = 1126.7\,(2)$ Å^3
$Z = 8$
$D_x = 1.499$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71093$ Å
Cell parameters from 25 reflections
$\theta = 4.03\text{–}12.18°$
$\mu = 0.439$ mm^{-1}
$T = 295\,(2)$ K
Prism
0.20 × 0.10 × 0.08 mm
Colourless

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.952$, $T_{\max} = 0.999$
1385 measured reflections
780 independent reflections

634 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.013$
$\theta_{\max} = 22.97°$
$h = -9 \rightarrow 3$
$k = -1 \rightarrow 11$
$l = -1 \rightarrow 13$
3 standard reflections frequency: 90 min intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.083$
780 reflections
94 parameters
H atoms located from a difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.1819P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.152$ e Å^{-3}
$\Delta\rho_{\min} = -0.177$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0008 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C2	−0.1117 (3)	0.9102 (2)	0.8025 (2)	0.0383 (6)
C3	−0.0306 (3)	0.8277 (2)	0.7404 (2)	0.0369 (6)
C4	−0.0377 (2)	0.8346 (2)	0.6294 (2)	0.0325 (5)
C5	−0.1304 (3)	0.9327 (2)	0.5886 (2)	0.0378 (6)
C6	−0.2072 (3)	1.0157 (2)	0.6515 (2)	0.0382 (6)
N1	−0.1966 (2)	1.0029 (2)	0.75747 (13)	0.0361 (5)
O1	−0.2845 (2)	1.0837 (2)	0.81990 (13)	0.0497 (5)
S1	0.05955 (8)	0.73127 (6)	0.54729 (5)	0.0475 (3)

Table 2. *Selected geometric parameters (Å, °)*

C2—N1	1.343 (3)	C5—C6	1.352 (3)
C2—C3	1.360 (3)	C6—N1	1.350 (3)
C3—C4	1.408 (3)	N1—O1	1.380 (2)
C4—C5	1.399 (3)	O1—H1O	1.16 (3)
C4—S1	1.718 (2)		
N1—C2—C3	119.6 (2)	N1—C6—C5	119.2 (2)
C2—C3—C4	121.4 (2)	C2—N1—C6	122.0 (2)
C5—C4—C3	115.5 (2)	C2—N1—O1	119.8 (2)
C5—C4—S1	121.2 (2)	C6—N1—O1	118.0 (2)
C3—C4—S1	123.3 (2)	N1—O1—H1O	107 (1)
C6—C5—C4	122.3 (2)		
N1—C2—C3—C4	−2.1 (3)	S1—C4—C5—C6	−179.5 (2)
C2—C3—C4—C5	1.2 (3)	C3—C2—N1—O1	177.3 (2)
C3—C4—C5—C6	0.4 (3)		

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Express*. Data reduction: *REDU*4 (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal*3.2 (Hall, Flack & Stewart, 1992) and *PLUTON*93 (Spek, 1993).

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Deutscher Akademischer Austauschdienst (DAAD) within the Accoes-Integradas-Program.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1236). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1634–1635

The 1:1 Complex Formed by 3-Picoline *N*-Oxide and *p*-Toluic Acid

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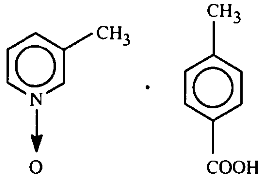
(Received 14 February 1997; accepted 27 May 1997)

Abstract

The title complex, $C_6H_7NO.C_8H_8O_2$, is held together by a hydrogen bond [O···O 2.528 (2) Å] between the carboxyl OH and the O atom of the *N*-oxide. The complex shows a dihedral angle of 33.31 (9)° between the plane of the rings of the molecules.

Comment

The 3-picoline *N*-oxide molecule (MPNO) is an interesting compound and forms molecular complexes with different hydrogen-bond donors. The study of similar molecular complexes has increased in recent years due to the non-linear optical properties that they may exhibit in the solid state (Prasad & Williams, 1991; Moreno-Fuquen, De Almeida Santos & Lechat, 1996, and references therein). In order to complement the crystallographic information and to analyse its behaviour in similar systems, the crystal molecular structure determination of MPNO and *p*-toluic acid (PTOL) was undertaken.



MPNO PTOL

Since satisfactory structural information about MPNO is not available in the literature, other similar systems have been analysed, *e.g.* the picolinic acid *N*-oxide (Laing & Nicholson, 1971). The intramolecular distances and angles of MPNO are in fair agreement with those reported for the picolinic acid *N*-oxide system. The parameter which is affected in the formation of the molecular complex is the C=O bond length of the PTOL molecule which changes from 1.292 (Takwale & Pant, 1971) to 1.206 (2) Å in the present structure. This change may be related to the more accurate values reported in this work. Other intramolecular distances and angles of the PTOL molecule in the present complex appear to be consistent with those reported previously for the free molecule (Takwale & Pant, 1971). An *ORTEP*II (Johnson, 1976) representation of the molecular complex with its numbering scheme is presented in Fig. 1.

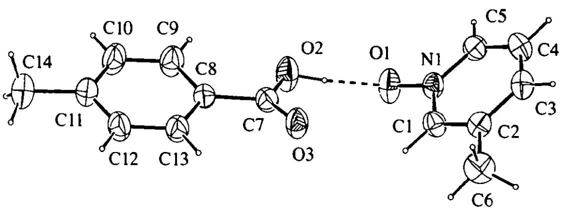


Fig. 1. A perspective view of the molecular complex with the atomic numbering scheme. The displacement ellipsoids are plotted at the 30% probability level.

The title complex owes its formation to an intermolecular hydrogen bond between O2 of the carboxylic group of PTOL and the nitroxide O1 atom of the MPNO molecule. The O···O distance is 2.528 (2) Å and the angle O2—HO2···O1 is 164 (2)°. The dihedral angle formed by the planes of the rings of these molecules is 33.31 (9)°. Formation of infinite chains parallel to the [111] direction was observed. This is due to the occurrence of π–π interactions (Hunter & Sanders, 1990) between the aromatic rings of the molecular complexes related by the centre of inversion (a diagram of this is with the supplementary material). The overlapping rings of the MPNO molecules (symmetry operator $2-x$, $1-y$, $1-z$) have a mean interplanar distance of 3.446 (3) Å and the overlapping rings of the PTOL molecules (symmetry operator $1-x$, $-y$, $-z$) have a mean interplanar distance of 3.288 (8) Å.

Experimental

Crystals of this molecular complex were obtained by slow evaporation from an equimolecular solution of MPNO and PTOL in acetonitrile. Initial reagents were purchased (Aldrich) and were used without additional purification.