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*Acta Cryst.* (1976). B32, 2325

## Structural Studies of Pyridine Oximes.

### II. The Crystal and Molecular Structure of *anti*-4-Pyridinecarboxaldehyde Oxime

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(Received 19 January 1976; accepted 16 March 1976)

*anti*-4-Pyridinecarboxaldehyde oxime crystallizes in the monoclinic system, space group  $P2_1/n$ , with four molecules in a cell of dimensions  $a = 9.080$  (1),  $b = 5.4366$  (4),  $c = 12.108$  (1) Å and  $\beta = 90.00$  (1)°. The calculated density is  $1.357$  g cm<sup>-3</sup>. The structure was solved by direct methods and refined by least-squares analysis to an  $R$  index of 0.052. The oxime group is twisted  $7.7^\circ$  from the plane through the pyridine ring. The molecules are connected by single hydrogen bonds to form infinite chains similar to those found in the *syn* configuration of this compound.

#### Introduction

Some derivatives of 4-pyridinecarboxaldehyde oxime and 4-pyrimidinecarboxaldehyde oxime (hereafter abbreviated to 4PYCO and 4PCO, respectively) have been studied (Hagedorn, Stark & Lorenz, 1972) in connexion with the reactivation process of phosphorylated acetylcholine esterase.

The structural investigations of the two configurational isomers of 4PCO have been reported by Martínez-Ripoll & Lorenz (1973, 1974). The *syn* configurational 4PYCO is reported in the preceding paper. We describe here the crystalline and molecular structure of *anti*-4PYCO.

#### Experimental

*anti*-4PYCO was crystallized from an ethanolic solution as transparent, colourless prismatic single crystals. Precise lattice parameters were obtained by least-squares fitting of the  $\theta$  values for 26 reflexions measured on a four-circle diffractometer. Table 1 shows the crystallographic data.

X-ray intensities were obtained on an automatic Philips PW 1100 diffractometer, using graphite-monochromated Mo  $K\alpha$  radiation and pulse-height discrim-

Table 1. *Crystal data for anti-4-pyridinecarboxaldehyde oxime*

Standard deviations, given in parentheses, refer to the least significant digits.			
Formula	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O	$V$	597.7 (1) Å <sup>3</sup>
M.W.	122.127	$Z$	4
Wavelength (Mo $K\alpha$ )	0.7107 Å	$D_{calc}$	1.357 g cm <sup>-3</sup>
$a$	9.080 (1) Å	$\mu$ (Mo $K\alpha$ )	2.29 cm <sup>-1</sup>
$b$	5.4366 (4)	$F(000)$	256
$c$	12.108 (1)	Space	
$\beta$	90.00 (1)°	group	$P2_1/n$

ination. A crystal with dimensions  $0.3 \times 0.3 \times 0.3$  mm was used for collecting the intensities of 1744 independent reflexions ( $2^\circ < \theta < 30^\circ$ ) using the  $\omega/2\theta$  scan mode. Of these, 637 were considered as unobserved according to the criterion  $I < 2\sigma(I)$  and were not used for the refinement. Two reflexions were monitored periodically during the data-collection process, and indicated no crystal decomposition. No correction was made for absorption ( $\mu R \approx 0.07$ ).

#### Determination of the structure

Phases of the 50 highest normalized structure factors ( $E$ 's  $> 1.5$ ) were calculated by the multiresolution tangent formula using *MULTAN* (Main, Woolfson, Declercq & Germain, 1974). The best phased  $E$  map revealed all nine non-hydrogen atoms.

\* Reprints can be obtained from this author.

Structure factors calculated with these coordinates and assuming an overall temperature factor of  $3.6 \text{ \AA}^2$  gave a discrepancy index  $R=0.32$ . Scattering factors for neutral C, O and N atoms were taken from Cromer & Mann (1967), those for H atoms from *International Tables for X-ray Crystallography* (1962).

After four cycles of isotropic full-matrix least-squares refinement for the 1107 observed reflexions and two more cycles with anisotropic temperature factors, the conventional  $R$  value for the observed reflexions was 0.094. A difference synthesis calculated with those observed reflexions within  $\sin \theta/\lambda < 0.5$  showed all the hydrogen atoms as the highest peaks of the map with electron densities ranging from 0.6 to  $0.4 \text{ e \AA}^{-3}$ .

Table 2. Coefficients for the weighting scheme

	$a$	$b$
$0 \leq F_o \leq 1.46$	0.36	0.05
$1.46 < F_o \leq 2.60$	0.75	-0.21
$2.60 < F_o \leq 7.44$	0.20	0.02
$7.44 < F_o \leq 120.00$	0.10	0.03
	$c$	$d$
$0 \leq \sin \theta/\lambda \leq 0.45$	3.44	-6.30
$0.45 < \sin \theta/\lambda \leq 0.71$	-0.01	1.54

Table 3. Final atomic parameters

Standard deviations are given in parentheses.

## (a) Fractional coordinates

	$x$	$y$	$z$
C(1)	0.3235 (2)	1.1880 (4)	0.4953 (2)
C(2)	0.2505 (3)	1.2111 (5)	0.3953 (2)
C(3)	0.1271 (3)	0.8502 (5)	0.4195 (2)
C(4)	0.1946 (3)	0.8106 (4)	0.5207 (2)
C(5)	0.2951 (2)	0.9832 (4)	0.5605 (1)
C(6)	0.3629 (2)	0.9303 (4)	0.6686 (2)
N(1)	0.1534 (2)	1.0471 (4)	0.3576 (1)
N(2)	0.4467 (2)	1.0577 (4)	0.7313 (1)
O	0.4793 (2)	1.2878 (3)	0.6909 (1)
H(1)	0.391 (3)	1.313 (5)	0.517 (2)
H(2)	0.273 (3)	1.348 (6)	0.351 (2)
H(3)	0.060 (4)	0.730 (7)	0.390 (3)
H(4)	0.170 (3)	0.665 (6)	0.563 (2)
H(5)	0.344 (4)	0.770 (6)	0.698 (3)
H(6)	0.536 (4)	1.353 (7)	0.742 (3)

Table 3 (cont.)

(b) Thermal parameters in the form  $\exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{12}hka^*b^* + \dots) \times 10^{-4}]$ 

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	530 (11)	482 (11)	385 (9)	-21 (9)	-130 (8)	20 (8)
C(2)	632 (13)	535 (12)	370 (10)	35 (10)	-122 (8)	60 (9)
C(3)	577 (13)	545 (12)	505 (11)	19 (10)	-218 (9)	-91 (10)
C(4)	573 (12)	435 (11)	431 (10)	-3 (9)	-125 (8)	-17 (9)
C(5)	411 (9)	426 (10)	322 (8)	67 (8)	-88 (6)	-33 (7)
C(6)	532 (11)	466 (11)	386 (9)	36 (9)	-138 (8)	47 (8)
N(1)	583 (10)	567 (11)	375 (8)	126 (9)	-181 (7)	-56 (7)
N(2)	528 (10)	556 (11)	366 (8)	34 (8)	-128 (6)	22 (7)
O	703 (10)	592 (10)	435 (8)	-124 (8)	-263 (7)	34 (7)
	$10^4 U$		$10^4 U$		$10^4 U$	
H(1)	274 (62)	H(3)	534 (94)	H(5)	389 (76)	
H(2)	316 (67)	H(4)	321 (68)	H(6)	516 (91)	

A good weighting scheme was  $w = w_1 w_2$  where  $w_1 = 1/\sigma_1^2$  and  $w_2 = 1/\sigma_2^2$ , and  $\sigma_1 = a + b|F_o|$  and  $\sigma_2 = c + d \sin \theta/\lambda$ , with coefficients given in Table 2. After four cycles of least-squares refinement assuming isotropic temperature factors for the hydrogen atoms, the final unweighted and weighted discrepancy indices were  $R = 0.052$  and  $R_w = 0.070$ , where  $R_w = (\sum w \Delta^2 F / \sum w |F_o|^2)^{1/2}$ . A final difference synthesis had no electron density greater than  $0.2 \text{ e \AA}^{-3}$ . The fractional coordinates of all atoms and their thermal parameters are given in Table 3.\*

## Description and discussion of the structure

## Molecular structure

Fig. 1 shows the shape of the molecule as it exists in the crystal. The bond lengths  $C(5)-C(6) = 1.474$ ,  $C(6)-N(2) = 1.278$  and  $N(2)-O = 1.375$  indicate a structure very predominantly  $>C=N-O-$ . Similar results were found in the structures of *syn*- and *anti*-4PCO and in *syn*-4PYCO (Martínez-Ripoll & Lorenz, 1973, 1974, 1976). The above-mentioned bond lengths for all these compounds are listed below:

	C(5)-C(6)	C(6)-N(2)	N(2)-O
<i>syn</i> -4PCO	1.469 Å	1.273 Å	1.393 Å
<i>syn</i> -4PYCO	1.469	1.275	1.390
<i>anti</i> -4PCO	1.470	1.285	1.378
<i>anti</i> -4PYCO	1.474	1.278	1.375

The averaged values of the C-H (0.96) and O-H (0.87 Å) bond lengths are of the usual order of magnitude. All intramolecular distances and their standard deviations are listed in Table 4.

The molecule of *anti*-4PYCO is almost planar, as can be seen from the deviations of the atoms from the least-squares planes (Table 5). These planes were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959). The oxime group is twisted  $7.7^\circ$  from the plane through the pyridine ring around the C(5)-C(6) bond.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31734 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Bond lengths and bond angles in *anti*-4PYCO

Standard deviations are given in parentheses.

C(5)–C(1)	1.389 (3) Å	C(4)–C(5)–C(1)	117.6 (2)°
C(1)–C(2)	1.386 (3)	C(5)–C(1)–C(2)	118.8 (2)
C(2)–N(1)	1.335 (3)	C(1)–C(2)–N(1)	123.6 (2)
N(1)–C(3)	1.328 (3)	C(2)–N(1)–C(3)	117.7 (2)
C(3)–C(4)	1.386 (3)	N(1)–C(3)–C(4)	123.0 (2)
C(4)–C(5)	1.395 (3)	C(3)–C(4)–C(5)	119.4 (2)
C(5)–C(6)	1.474 (3)	C(1)–C(5)–C(6)	125.7 (2)
C(6)–N(2)	1.278 (3)	C(4)–C(5)–C(6)	116.7 (2)
N(2)–O	1.375 (3)	C(5)–C(6)–N(2)	132.0 (2)
C(1)–H(1)	0.95 (3)	C(6)–N(2)–O	114.2 (2)
C(2)–H(2)	0.94 (3)	C(5)–C(1)–H(1)	122 (2)
C(3)–H(3)	0.96 (4)	H(1)–C(1)–C(2)	119 (2)
C(4)–H(4)	0.97 (3)	C(1)–C(2)–H(2)	118 (2)
C(6)–H(5)	0.96 (3)	H(2)–C(2)–N(1)	119 (2)
O—H(6)	0.87 (4)	C(1)–C(3)–H(3)	117 (2)
		H(3)–C(3)–C(4)	120 (2)
		C(3)–C(4)–H(4)	119 (2)
		H(4)–C(4)–C(5)	121 (2)
		C(5)–C(6)–H(5)	116 (2)
		H(5)–C(6)–N(2)	112 (2)
		N(2)–O—H(6)	104 (2)

## Short intramolecular distances Hydrogen bond

O–C(1)	2.812 (3) Å	O'—N(1)	2.717 (2) Å
O–H(1)	2.25 (3)	H(6')–N(1)	1.85 (4)
		O'—H(6')–N(1)	173 (4)°

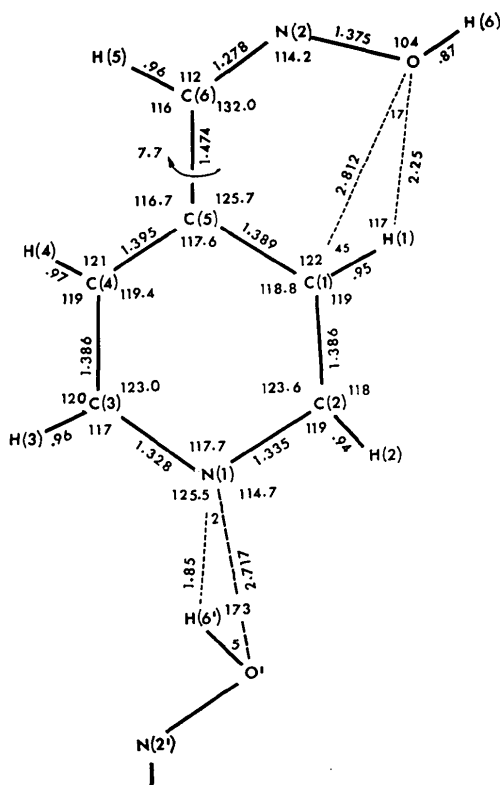
Fig. 1. Bond lengths (Å) and bond angles (°) in *anti*-4PYCO. The hydrogen bond and the intramolecular approach are also shown.

Table 5. Deviations of atoms from least-squares planes

The planes are expressed as  $Ax + By + Cz = D$ , where  $x, y, z$  are the fractional coordinates of the atoms. Asterisks indicate atoms not included in the calculation of the plane.

Plane I	Atom	Deviation
$A = 7.025$	C(1)	0.078 Å
$B = -2.479$	C(2)	0.041
$C = -5.327$	C(3)	-0.061
$D = -3.389$	C(4)	-0.027
	C(5)	0.039
	C(6)	0.071
	N(1)	-0.034
	N(2)	0.010
	O	-0.117
Plane II	Atom	Deviation
$A = 6.730$	C(1)	0.001 Å
$B = -2.672$	C(2)	0.002
$C = -5.538$	C(3)	0.002
$D = -3.741$	C(4)	0.002
	C(5)	-0.004
	N(1)	-0.004
	*C(6)	-0.005
	*N(2)	-0.128
	*O	-0.300
Plane III	Atom	
$A = 7.289$	C(6)	
$B = -2.020$	N(2)	
$C = -5.646$	O	
$D = -3.009$		

Angle between the normals to planes II and III = 7.7°.

An interesting feature of this structure is the close proximity of the OH group to the C(1) atom of the pyridine ring, which contrasts with the expected geometry considering the possible steric hindrance with the H(1) atom. Both distances  $C(1) \cdots O = 2.812$  and  $H(1) \cdots O = 2.25$  Å (Fig. 1), much shorter than the sum of the van der Waals radii (3.22 and 2.72 Å, respectively), imply an opening of the C(5)–C(6)–N(2) angle to 132.0°. Very similar results were found in the structure of *anti*-4PCO (Martínez-Ripoll & Lorenz, 1974), with  $C(1) \cdots O$  and  $H(1) \cdots O$  distances of 2.810 and 2.28 Å, respectively, and an angle of 131.3°. This attractive C–H $\cdots$ O interaction makes the molecule planar. In fact, molecules with *syn* configuration show less planarity than those with the corresponding *anti* configuration:

	Twist angle
<i>syn</i> -4PCO	5°
<i>anti</i> -4PCO	1
<i>syn</i> -4PYCO	14
<i>anti</i> -4PYCO	8.

## Crystal structure

The crystal structure of *anti*-4PYCO viewed along the  $b$  axis is shown in Fig. 2. The molecules are connected by single hydrogen bonds  $O-H(6) \cdots N(1)$ , forming infinite chains as in *syn*- and *anti*-4PCO and *syn*-4PYCO. The geometry of the present hydrogen bond is shown in Fig. 1. All other intermolecular distances have normal values and some of the shortest approaches are shown in Fig. 2.

The general phenomenon that most of the aromatic *syn*-aldoximes have lower melting points than those with *anti*-configuration is also observed for *syn*-4PYCO (m.p. 130–132°C) and *anti*-4PYCO (m.p. 184–185°C). Evidently, in these cases, this is not a consequence of a different type of molecular association (chains or dimers) as was assumed by Jerslev (1957). The explanation of this observation, also found in 4PCO compounds, could be due to a reinforcement of the hydrogen bonds, a situation probably created by the intramolecular C···O interaction present in the isomers with *anti*-configuration.

Most of the computations required in this analysis were performed with the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970) on the 1108 Univac computer of the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid, Spain.

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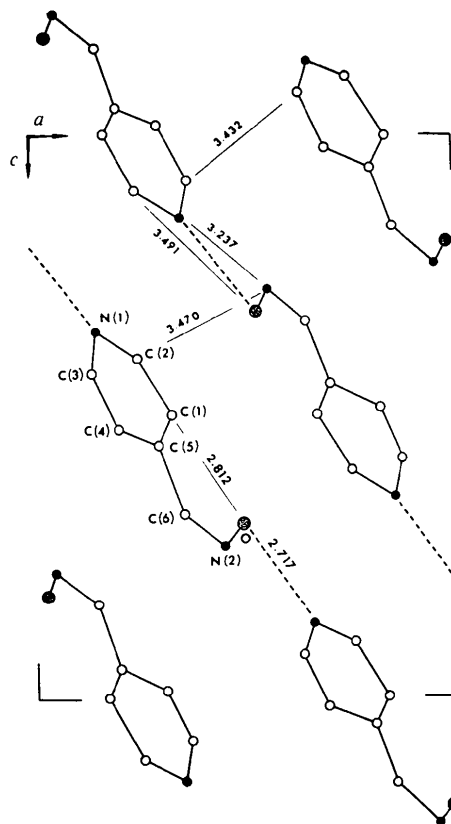


Fig. 2. The crystal structure of *anti*-4PYCO as viewed along the *b* axis. Some of the shortest intermolecular distances (Å) are given. Dashed lines represent the hydrogen bonds.

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