

## 2-Amino-3-(5-methyl-1,2,4-oxadiazol-3-yl)pyridine

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**Abstract.**  $C_8H_8N_4O$ ,  $M_r = 176.2$ , monoclinic,  $P2_1/c$ ,  $a = 7.297(5)$ ,  $b = 13.882(5)$ ,  $c = 8.997(3)$  Å,  $\beta = 111.55(3)^\circ$ ,  $V = 847.7$  Å<sup>3</sup>,  $D_m = 1.41(5)$  (floatation),  $D_x = 1.381$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.106$  mm<sup>-1</sup>,  $Z = 4$ , at 293(1) K. The structure consists of discrete pairs of molecules connected by two intermolecular hydrogen bonds. The molecule is essentially planar due to a rather strong intramolecular hydrogen bond.

**Introduction.** Crystals suitable for X-ray analysis were obtained by cooling a warm solution to room temperature. Transparent needles elongated along  $a$  were obtained. The systematically absent reflexions  $(0k0)$ ,  $k = 2n + 1$  and  $h0l$ ,  $l = 2n + 1$  on Weissenberg photographs and the centrosymmetric distribution of  $|E|$  values ( $\langle E^2 \rangle = 1.000$ ,  $\langle |E^2 - 1| \rangle = 0.982$ ,  $\langle |E| \rangle = 0.761$ ) indicated space group  $P2_1/c$ . Cell dimensions were obtained by least squares from the  $2\theta$  values of 30 reflexions measured on the diffractometer [Mo  $K\alpha_1$  radiation,  $\lambda = 0.70926$  Å,  $T = 293(1)$  K]. A crystal  $0.4 \times 0.2 \times 0.1$  mm was used for data collection on the diffractometer. Details of the data collection and

reduction are given in Table 1. The data were corrected for variation in reference reflexions and Lorentz-polarization effects, but not for absorption.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An  $E$  map with the highest combined figure of merit CFOM (2.991) obtained with the unit weighting of ABSFOM (1.167),  $\psi_o$  (295) and RESID (29.89), computed with 250 phases ( $|E| > 1.35$ ) gave sites for all the heavy atoms. Refinement was by full-matrix least squares, minimizing  $\sum w(F_o - kF_c)^2$ , where the weighting function was determined empirically:  $w = w_F \times w_S$  where

$$w_F(|F_o| < 5.1) = (|F_o|/5.1)^4,$$

$$w_F(|F_o| > 15.0) = (15.0/F_o)^3,$$

$$w_F(5.1 < |F_o| < 15.0) = 1.0$$

and

$$w_S(\sin \theta < 0.20) = (\sin \theta/0.20)^5,$$

$$w_S(\sin \theta > 0.37) = (0.37/\sin \theta)^2,$$

$$w_S(0.20 < \sin \theta < 0.37) = 1.0.$$

All the H atoms were located in a difference map after anisotropic refinement. However, the positions of the H atoms were recalculated with C–H = 1.08 Å except for those of the amino and methyl groups which were included with the coordinates obtained from the difference map. An isotropic temperature factor  $B$  of 3.5 Å<sup>2</sup> was assumed for all the H atoms and was kept fixed throughout the refinement. A final difference map was featureless. Final refinement parameters are given in Table 2. Scattering factors for C, N and O were those

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Table 1. Data-collection summary

Temperature (K)	293 (1)
Diffractometer	CAD-4, automatic, four-circle
X-radiation (Å)	Mo $K\alpha$ ( $\lambda = 0.71069$ )
Monochromator	Graphite
Scan method	$\omega$ - $2\theta$ (moving-crystal-moving-counter)
$2\theta$ scan width ( $^\circ$ )	$0.7 + 0.2 \tan \theta$
Scan rate ( $^\circ \text{ min}^{-1}$ )	Minimum: 2.0; maximum: 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\text{max}}$ ( $^\circ$ )	50
Maximum scan time (s)	30
Aperture (mm)	$2.5 + 0.9 \tan \theta$
Reference reflexions	113, 251, 232
Intensity decrease (%)	2
Measured reflexions	1488
Observed reflexions	834
Unobserved reflexions	654 [ $I < 1.5 \sigma(I)$ ]
$\sigma(I)$ base	Counting statistics
Linear absorption coefficient (mm <sup>-1</sup> )	0.106 for Mo $K\alpha$

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Table 2. Refinement summary

Final refinement cycle	
Scale factor ( $k$ )	1.006
$R = \sum  AF  / \sum  F_o $	0.064
$R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$	0.068
Average shift/error	0.012
Maximum shift/error	0.041
Data ( $m$ )-to-variable ( $n$ ) ratio	7.01
$[\sum w(\Delta F)^2 / (m - n)]^{1/2}$	0.561
Final difference map	
Maximum $\Delta\rho$ (e Å <sup>-3</sup> )	0.25

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Table 3. Final fractional coordinates ( $\times 10^4$ ; for  $H \times 10^3$ ) with e.s.d.'s in parentheses

	x	y	z
N(1)	5271 (5)	899 (3)	1614 (4)
N(2)	6472 (7)	-643 (3)	1973 (4)
C(2)	6241 (7)	199 (3)	2640 (5)
C(3)	6937 (6)	342 (3)	4316 (5)
C(4)	6628 (7)	1235 (3)	4865 (5)
C(5)	5636 (8)	1952 (3)	3810 (5)
C(6)	4975 (8)	1743 (3)	2197 (5)
O(1')	9336 (5)	-1701 (2)	6595 (4)
N(2')	8368 (6)	-1255 (3)	5091 (4)
C(3')	7977 (7)	-395 (3)	5474 (5)
N(4')	8604 (6)	-235 (3)	7099 (4)
C(5')	9394 (7)	-1045 (3)	7692 (5)
C(6')	10362 (9)	-1324 (4)	9408 (6)
H(2A)	597	-73	80
H(2B)	712	-115	274
H(4)	717	138	614
H(5)	536	266	423
H(6)	419	230	136
H(7A)	1027	-202	954
H(7B)	966	-93	1005
H(7C)	1190	-113	984

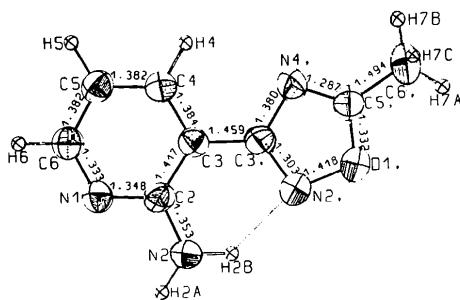


Fig. 1. A molecule viewed along the normal to the mean plane. The atoms are represented by thermal ellipsoids drawn at the 50% probability level (Johnson, 1965).

of Cromer & Mann (1968) and for H of Stewart, Davidson & Simpson (1965). All calculations were carried out on the CDC Cyber 172 computer at RRC Ljubljana with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Table 3 lists the final coordinates.\*

**Discussion.** From several transformations of 2-amino-3-cyanopyridine a compound with m.p. 418 K was obtained which analyzed as  $C_8H_8N_4O$ . Also 4-amino-pyrido[2,3-d]pyridine 3-oxide when treated with acetic anhydride gives the formyl derivative of the above compound and upon deacylation with aqueous sodium bicarbonate the compound under investigation was

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34469 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

obtained again (Verček, Leban, Stanovnik & Tišler, 1978). Chemical, analytical and spectroscopic evidence gave several possible structures for the title compound and an X-ray study was undertaken to choose between them.

Fig. 1 shows a view of the molecule with the bond lengths. Bond distances and angles are given in Table 4. The molecule exists as 2-amino-3-(5-methyl-1,2,4-oxadiazol-3-yl)pyridine. The aminopyridine and oxadiazole parts of the molecule are planar and are described by the equations

$$0.8674X + 0.3312Y - 0.3715Z = 3.4990 \text{ \AA}$$

and

$$0.8811X + 0.3248Y = 0.3438Z = 3.6346 \text{ \AA},$$

Table 4. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Hydrogen bonds			
N(2)—H(2B)	0.98	N(2)—H(2A)	0.98
N(2')...H(2B)	1.97	N(1')...H(2A)	2.04
N(2)...N(2')	2.766 (5)	N(2)...N(1')	3.024 (5)
N(2)—H(2B)...N(2')	135.9	N(2)—H(2A)...N(1')	175.5
N(1)—C(2)	1.348 (5)	C(2)—N(1)—C(6)	118.9 (4)
N(1)—C(6)	1.333 (6)	N(1)—C(2)—N(2)	116.0 (4)
N(2)—C(2)	1.353 (6)	N(1)—C(2)—C(3)	121.4 (4)
C(2)—C(3)	1.417 (6)	N(2)—C(2)—C(3)	122.6 (4)
C(3)—C(4)	1.384 (6)	C(2)—C(3)—C(4)	117.6 (4)
C(3)—C(3')	1.459 (6)	C(2)—C(3)—C(3')	123.4 (4)
C(4)—C(5)	1.382 (6)	C(4)—C(3)—C(3')	118.9 (4)
C(5)—C(6)	1.382 (6)	C(3)—C(4)—C(5)	120.9 (4)
O(1')—N(2')	1.419 (5)	C(4)—C(5)—C(6)	117.6 (4)
O(1')—C(5')	1.332 (6)	N(1)—C(6)—C(5)	123.6 (4)
N(2')—C(3')	1.303 (6)	N(2')—O(1')—C(5')	106.1 (3)
C(3')—N(4')	1.380 (6)	O(1')—N(2')—C(3')	103.2 (3)
N(4')—C(5')	1.287 (6)	C(3)—C(3')—N(2')	124.1 (4)
C(5')—C(6')	1.494 (7)	C(3)—C(3')—N(4')	121.7 (4)
		N(2')—C(3')—N(4')	114.2 (4)
		C(3')—N(4')—C(5')	102.8 (4)
		O(1')—C(5')—N(4')	113.8 (4)
		O(1')—C(5')—C(6')	117.6 (4)
		N(4')—C(5')—C(6')	128.6 (5)

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

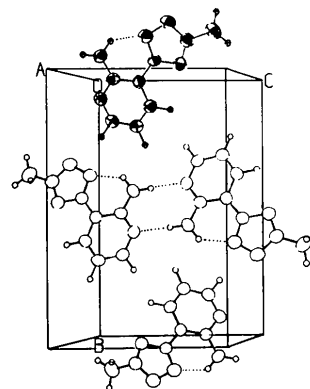


Fig. 2. A view of the unit cell along [100]. Dotted lines represent hydrogen bonds.

where

$$X = ax \sin \beta, Y = by$$

and

$$Z = ax \cos \beta + cz.$$

The largest deviations from the planes are  $-0.009 \text{ \AA}$  for C(3) and  $-0.005 \text{ \AA}$  for C(5') respectively. The dihedral angle between the six- and five-membered rings is  $1.8^\circ$ ; thus the molecule as a whole is planar to within  $0.025 \text{ \AA}$ . The planarity is the consequence of the rather strong intramolecular hydrogen bond N(2)—H(2B)···N(2'). Details of the hydrogen bonding are given in Table 4. The mean plane through N(2), C(2), C(3), C(3'), N(2'), H(2B) is  $0.8720X + 0.3204Y - 0.3701Z = 3.5162 \text{ \AA}$  and the largest deviation from the plane is  $0.021 \text{ \AA}$  for H(2B).

Table 4 shows that N(4')—C(5') and C(3')—N(2') in the oxadiazole ring exhibit double-bond character whereas the bond lengths in the aminopyridine unit suggest aromatic character. The methyl group attached to the oxadiazole ring does not appear to be disordered. H(7C) is nearly perpendicular to the oxadiazole ring and the torsion angles are N(4')—C(5')—C(6')—H(7C)  $+87.1^\circ$ , N(4')—C(5')—C(6')—H(7A)  $-153.3^\circ$ , N(4')—C(5')—C(6')—H(7B)  $-30.9^\circ$ . Torsion angles are taken as positive if the bond in front has to be turned clockwise in order to eclipse the rear bond.

A view of the molecular packing is in Fig. 2. Discrete pairs of molecules exist which are held together by

hydrogen bonds. H(2A) is involved in the intermolecular hydrogen bonds N(2)—H(2A)···N(1') and N(2')—H(2A')···N(1), of  $3.024(5) \text{ \AA}$  [symmetry code: (i)  $1 - x, -y, -z$ ]. All contacts between the pairs of molecules correspond to normal van der Waals distances.

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## Octa(phenylsilasesquioxane)\* Acetone Solvate

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**Abstract.**  $C_{48}H_{40}O_{12}Si_8 \cdot C_3H_6O$ ,  $M_r = 1091.7$ , tetragonal,  $P4/n$ ,  $a = b = 14.608(4)$ ,  $c = 12.918(4) \text{ \AA}$ ,  $U = 2759.5 \text{ \AA}^3$ ,  $D_m = 1.30$ ,  $D_c = 1.314 \text{ Mg m}^{-3}$ ,  $Z = 2$ ,  $F(000) = 1136$ ,  $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$ ,  $\mu(\text{Cu K}\alpha) = 2.2 \text{ mm}^{-1}$ . The structure was refined to  $R = 0.0617$  for 1509 unique reflections. The  $Ph_8Si_8O_{12}$  molecule is formed by linking six eight-membered rings and has fourfold crystallographic symmetry.

**Introduction.** Earlier reports suggested that octa-(phenylsilasesquioxane) crystallizes in several forms: monoclinic, triclinic (Larsson, 1960a) and rhombohedral (Brown, Vogt & Prescott, 1964). As part of our general study of the structure and conformation of cyclosiloxanes, many of which seem to show polymorphism, we have begun an investigation of this system.

The compound was prepared by allowing phenyltrichlorosilane, acetone and water to stand for a few days (Brown, 1965) and recrystallized from dichloromethane and acetone as colourless plates. The pre-

\* 1,3,5,7,9,11,13,15-Octaphenylpentacyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]-octasiloxane.