Orthorhombic
Pbca
$a = 10.5774(4)$ Å
$b = 7.0688(3)$ Å
$c = 25.620(1)$ Å
$V = 1915.6(1)$ Å^3
$Z = 8$
$D_x = 1.527$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 12.0$–$13.0°$
$\mu = 0.339$ mm^{-1}
$T = 300$ K
Block
$0.43 \times 0.36 \times 0.29$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.874$, $T_{max} = 0.906$
1681 measured reflections
1681 independent reflections

1381 reflections with $I > 2\sigma(I)$
$\theta_{max} = 24.96°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = -30 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R(F) = 0.0393$
$wR(F^2) = 0.1121$
$S = 1.032$
1681 reflections
159 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.7926P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.225$ e Å^{-3}
$\Delta\rho_{min} = -0.320$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O1	1.448 (2)	C1—C7	1.502 (3)
S1—O2	1.441 (2)	O5···O3^{i}	2.661 (3)
S1—O3	1.456 (2)	O6···O1	2.900 (3)
S1—C6	1.779 (2)	O6···O2^{ii}	2.890 (3)
O4—C7	1.200 (3)	O6···O3^{iii}	3.060 (3)
O5—C7	1.312 (3)		
O1—S1—O2	112.4 (1)	C6—C1—C7	123.7 (2)
O1—S1—O3	110.8 (1)	C5—C6—S1	117.8 (2)
O2—S1—O3	113.9 (1)	C1—C6—S1	122.3 (2)
O1—S1—C6	107.0 (1)	O4—C7—O5	124.5 (2)
O2—S1—C6	105.7 (1)	O4—C7—C1	123.1 (2)
O3—S1—C6	106.6 (1)	O5—C7—C1	112.2 (2)
C2—C1—C7	117.6 (2)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (ii) $x, 1 + y, z$; (iii) $-x, 1 - y, 2 - z$.

Data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 VAX/PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1996). Software used to prepare material for publication: *SHELXL93*.

The author thanks the University of Malaya (F102/96 and F677/96) for supporting this work.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Heterocyclic *N*-Acetoxyarylamines, Models for the Putative Ultimate Carcinogens of Aromatic Amines: 2-Acetoxyamino-5-phenylpyridine and 2-Acetoxyaminopyridine

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(*Received 23 September 1996; accepted 9 December 1996*)

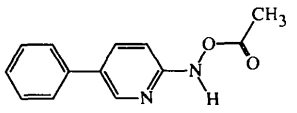
Abstract

The structures of *O*-acetyl-*N*-(5-phenyl-2-pyridyl)-hydroxylamine, $C_{13}H_{12}N_2O_2$, (I), and *O*-acetyl-*N*-(2-pyridyl)hydroxylamine, $C_7H_8N_2O_2$, (II), have been determined in order to confirm earlier structure assignments based on spectroscopic information. Compound (I) is the probable mutagenic metabolite of the phenylalanine pyrolysis product 2-amino-5-phenylpyridine. The crystal structures of (I) and (II) are the first reported for heterocyclic *N*-acetoxyarylamines, the corresponding homocyclic arylamine derivatives being extremely unstable. In the solid state, both (I) and (II) exist as hydrogen-bonded dimers, with the arylamine N atom acting as donor and the pyridine N atom of

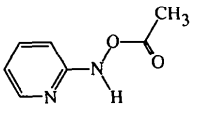
a neighboring inversion-related molecule as acceptor; the distance between donor and acceptor N atoms is 3.007 (2) in (I) and 2.956(2) Å in (II). This orientation of the N—H bond results in the rotation of the acetoxy group out of the plane of the pyridine ring by 22.5 (2) in (I) and 27.4 (2)° in (II).

Comment

The toxicological significance of human and animal exposure to primary arylamines and primary heterocyclic amines is well documented (Hanna, 1996). Of particular current interest are the heterocyclic amine mutagens and carcinogens which are formed as products of amino-acid pyrolysis during the cooking of proteinaceous foods (Sugimura, 1995). Heterocyclic amines undergo metabolic activation in mammalian tissues by the sequential process of hydroxylation of the primary amino group and esterification of the resulting hydroxylamine (Hanna, 1994, 1996). Thus, 2-acetoxyamino-5-phenylpyridine, (I), is a putative ultimate mutagenic metabolite of 2-amino-5-phenylpyridine, a pyrolysis product of phenylalanine (Kato, 1986). The structure of (I) has previously been deduced (Lutgerink *et al.*, 1989) using spectroscopic methods. Although crystals of (I) were described (Lutgerink *et al.*, 1989) as being 'stable for months when stored under argon', no single-crystal X-ray structure for this key member of an important class of compounds has been reported previously. In connection with an investigation of the chemical properties of *N*-acetoxyamine metabolites of arylamines and heterocyclic amines, we have determined the crystal structures of both 2-acetoxyamino-5-phenylpyridine, (I), and 2-acetoxyaminopyridine, (II).



(I)



(II)

The molecular conformations and atom-numbering schemes for (I) and (II) are shown in Figs. 1 and 2, respectively. In (I), the phenyl group is twisted slightly out of the plane of the pyridine ring [C3—C4—C8—C9 7.7 (3)°]. The arylamine H atom is directed towards the pyridine N atom of a neighboring inversion-related molecule, with the result that the molecules pack as hydrogen-bonded dimers located about crystallographic inversion centers, as shown for (I) in Fig. 3. The rotation about the C1—N2 bond that places the N—H bond in a hydrogen-bonding position also rotates the acetoxy groups of both (I) and (II) out of the plane of the pyridine ring, the O1—N2—C1—C2 torsion angle being 22.5 (2) in (I) and 27.4 (2)° in (II). The hydrogen-bonded packing arrangements of (I) and (II) allow some freedom of rotation about the O1—C6 bond, the N2—O1—C6—O2 torsion angle assuming values of −11.0 (3) in (I) and 5.3 (3)° in (II). Details of the hydrogen bonding in both structures are given in Table 3.

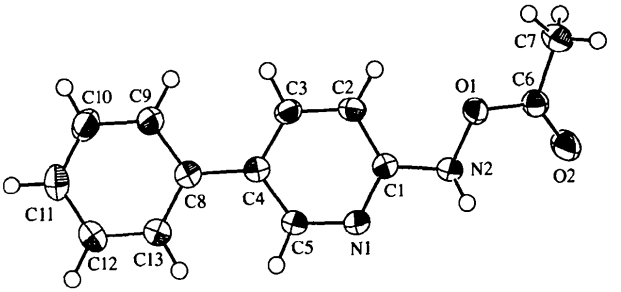


Fig. 1. *ORTEP*II (Johnson, 1976) view of (I) showing the atom numbering. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

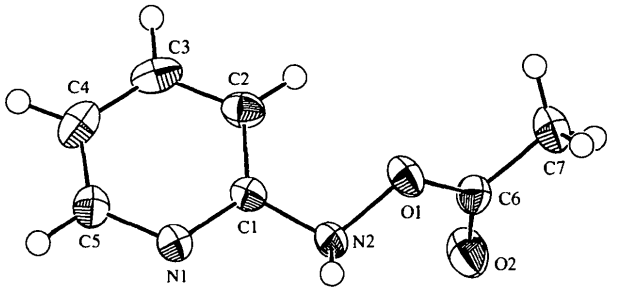


Fig. 2. *ORTEP*II (Johnson, 1976) view of (II) showing the atom numbering. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

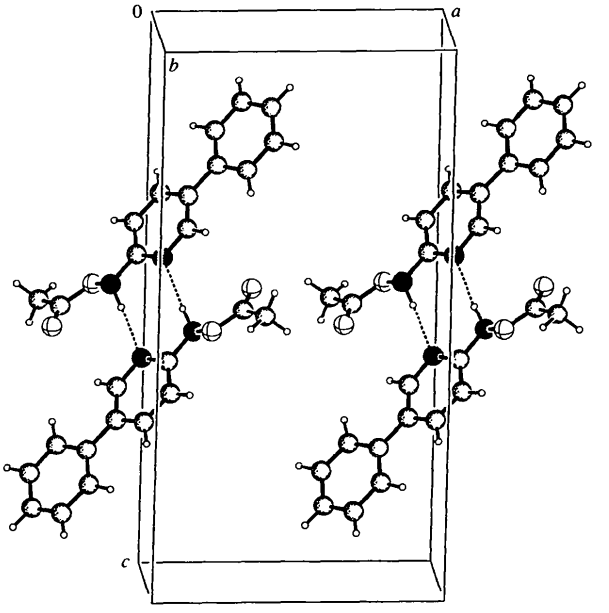


Fig. 3. *PLUTON*92 view (Spek, 1992) of the packing of (I). N atoms are black.

Experimental

2-Nitro-5-phenylpyridine was prepared according to the method of Stavenuiter, Hamzink, van der Hulst, Zomer, Westra & Kriek (1987) and was converted to 2-hydroxyamino-5-phenylpyridine by treatment with hydrazine and Pd/C (Stavenuiter, Verrips-Kroon, Bos & Westra, 1985; Westra, 1981). Reaction of the hydroxyamino intermediate with acetyl cyanide in the presence of triethylamine (Famulok, Bosold & Boche, 1989) afforded (I), which could be crystallized from either dichloromethane/hexane or tetrahydrofuran/hexane. Compound (II) was synthesized from 2-nitropyridine according to the same general procedures used for the preparation of (I), was purified by flash chromatography on silica gel with ether/hexane and crystallized from ethyl acetate/hexane.

Compound (I)

Crystal data

$C_{13}H_{12}N_2O_2$
M_r = 228.25
Monoclinic
$P2_1/c$
a = 10.246 (2) Å
b = 5.524 (2) Å
c = 19.973 (1) Å
β = 90.463 (9)°
V = 1130.3 (3) Å^3
Z = 4
D_x = 1.341 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 24–25°
μ = 0.715 mm^{-1}
T = 173 (2) K
Needle
0.45 × 0.15 × 0.12 mm
Pale yellow

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.880, T_{max} = 0.918
3873 measured reflections
2317 independent reflections
1443 reflections with $I > 3\sigma(I)$
R_{int} = 0.025
θ_{max} = 70.08°
$h = 0 \rightarrow 12$; $-10 \rightarrow 0$
$k = 0 \rightarrow 6$; $-5 \rightarrow 0$
$l = -24 \rightarrow 24$; $-19 \rightarrow 19$
3 standard reflections every 150 reflections
intensity decay: −0.6%

Refinement

Refinement on F
R = 0.037
wR = 0.046
S = 2.17
1443 reflections
191 parameters
H-atom coordinates refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.0320
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 8.58×10^{-6}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—N2	1.437 (2)	C1—C2	1.387 (3)
O1—C6	1.346 (2)	C2—C3	1.377 (3)
O2—C6	1.197 (2)	C3—C4	1.398 (3)
N1—C1	1.334 (2)	C4—C5	1.388 (3)
N1—C5	1.343 (2)	C4—C8	1.487 (2)
N2—C1	1.399 (2)	C6—C7	1.486 (3)
N2—O1—C6	113.0 (1)	C3—C4—C8	122.8 (2)
C1—N1—C5	117.5 (2)	C5—C4—C8	122.0 (2)
O1—N2—C1	108.9 (1)	N1—C5—C4	125.1 (2)
N1—C1—N2	113.7 (2)	O1—C6—O2	122.5 (2)
N1—C1—C2	122.9 (2)	O1—C6—C7	111.3 (2)
N2—C1—C2	123.2 (2)	O2—C6—C7	126.2 (2)
C1—C2—C3	118.0 (2)	C4—C8—C9	121.2 (2)
C2—C3—C4	121.4 (2)	C4—C8—C13	121.8 (2)
C3—C4—C5	115.2 (2)		

Compound (II)

Crystal data

$C_7H_8N_2O_2$
M_r = 152.15
Monoclinic
$P2_1/c$
a = 9.432 (1) Å
b = 5.472 (2) Å
c = 14.9983 (9) Å
β = 101.657 (7)°
V = 758.1 (2) Å^3
Z = 4
D_x = 1.333 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 23–25°
μ = 0.798 mm^{-1}
T = 173 (2) K
Needle
0.32 × 0.12 × 0.12 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.869, T_{max} = 0.909
2610 measured reflections
1558 independent reflections
1013 reflections with $I > 3\sigma(I)$
R_{int} = 0.017
θ_{max} = 70°
$h = 0 \rightarrow 11$; $-9 \rightarrow 0$
$k = 0 \rightarrow 6$; $-5 \rightarrow 0$
$l = -18 \rightarrow 17$; $-14 \rightarrow 14$
3 standard reflections every 150 reflections
intensity decay: −0.3%

Refinement

Refinement on F
R = 0.036
wR = 0.036
S = 2.60
1013 reflections
124 parameters
H-atom coordinates refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.0028
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—N2	1.433 (2)	C1—C2	1.393 (3)
O1—C6	1.361 (2)	C2—C3	1.383 (3)
O2—C6	1.198 (3)	C3—C4	1.383 (4)
N1—C1	1.332 (3)	C4—C5	1.366 (3)
N1—C5	1.346 (3)	C6—C7	1.487 (3)
N2—C1	1.397 (3)		
N2—O1—C6	112.6 (2)	C2—C3—C4	119.5 (2)
C1—N1—C5	116.9 (2)	C3—C4—C5	118.4 (2)
O1—N2—C1	112.1 (2)	N1—C5—C4	123.9 (2)
N1—C1—N2	113.1 (2)	O1—C6—O2	123.5 (2)
N1—C1—C2	123.6 (2)	O1—C6—C7	109.7 (2)
N2—C1—C2	123.1 (2)	O2—C6—C7	126.8 (2)
C1—C2—C3	117.7 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

	D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
(I)	N2—H2N···N1^{i}	2.11 (2)	3.007 (2)	166 (2)
(II)	N2—H2N···N1^{i}	2.09 (2)	2.956 (2)	177 (2)

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

For both structures, the positional parameters of the H atoms were refined: compound (I), C—H range 0.91 (2)–1.00 (2) and N—H distance 0.90 (2) Å; compound (II), C—H range 0.90 (2)–0.99 (2) and N—H distance 0.87 (2) Å.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*, *PLUTON*92 (Spek, 1992) and *ORTEP*II (Johnson, 1976).

This research was supported in part by a grant from the National Cancer Institute (CA 55334).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 637–639

1-Styrylsilatrane

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(*Received 17 October 1996; accepted 8 January 1997*)

Abstract

The structure of (*E*)-1-(2-phenylethenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane, $C_{14}H_{19}NO_3Si$, has been determined by X-ray analysis. The N—Si dative bond length of 2.127 (4) Å is in agreement with structural trends found for such systems. The C atoms linked to the N atom are disordered, an effect which has been observed in other silatrane structures.

Comment

Over the past two decades, silicon atranes or 'silatranes' have attracted considerable attention. In addition to demonstrating unique patterns of chemical reactivity, silatranes also exhibit interesting biological activity, such as the stimulation of hair growth (Voronkov, 1979). However, possibly the most intriguing aspect of these compounds is their nominally pentacoordinate structure. The distorted trigonal bipyramid geometry and short transannular silicon–nitrogen 'bond' possessed by silatranes was first demonstrated by use of single-crystal X-ray diffraction in 1968 (Turley & Boer, 1968). Since then, crystallographic data compiled from numerous other silatrane structures have demonstrated that the length of this silicon–nitrogen transannular interaction in the solid state is dependent primarily upon the substituent bound to the silicon center (Schmidt, Windus & Gordon, 1995, and references therein). This transannular interaction has been extensively studied by a variety of techniques, including multinuclear magnetic resonance spectroscopy (Iwamiya & Maciel, 1993).

The stabilization of β-carbocations is a well documented facet of organosilicon chemistry. It has been demonstrated that the extent of this 'β-effect' can be correlated to the electron-withdrawing ability of the groups on silicon (Brook & Neuy, 1990). This was shown by using the degree of *syn* addition of bromine to (*E*)-β-silylstyrenes as a measure of the stabilizing ability of the silicon center. Recently, these studies have been expanded to include the title compound, (I), a styrene-substituted silatrane.