

C14—C15—C16	122.2 (5)	C19—C20—C1	122.7 (5)
N1—C1—C20	121.4 (5)	N1—C4—C5	121.4 (5)
N2—C6—C5	122.5 (5)	N2—C9—C10	122.3 (5)
N3—C11—C10	120.9 (5)	N3—C14—C15	121.2 (5)
N4—C16—C15	121.9 (5)	N4—C19—C20	122.9 (5)

The central H atoms, HN1, HN2, HN3 and HN4, were located from a difference Fourier map using the data with  $\sin\theta/\lambda < 0.5 \text{ \AA}^{-1}$ . The H atoms of the  $\text{CH}_2\text{Cl}_2$  molecule of solvation and the acid protons of the three acetic acid molecules were not included in the model. Scattering factors for the non-H atoms were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), and those for the H atoms from Stewart, Davidson & Simpson (1965). Anomalous terms for the Cl atoms were taken from Cromer (1974). The high final *R* value is attributed to the high thermal motion of some of the atoms of the solvent molecules and the marginal quality of the crystal, which was the only one in the sample.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *CRYSNET* (Berman, Bernstein, Bernstein, Koetzle & Williams, 1976). Structure solution: *SHELXS86* (Sheldrick, 1985). Molecular graphics: *ORTEPII* (Johnson, 1976) and *GENPLOT* (Computer Graphics Service, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and comparison distances and angles in a series of OETPP's, and also a packing diagram and a view of the hydrogen bonding of the acetic acid molecules to the acetates have been deposited with the IUCr (Reference: BK1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 5-Fluoro-8,8-dimethyl-7-oxa-3,9-diazabicyclo[4.3.0]nona-5,9-diene-2,4-dione (C<sub>8</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>3</sub>): a Novel Product from Pyrolysis of *N*-Isopropylidene-*O*-tetrafluoro-4-pyridylhydroxylamine in Glass

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### Abstract

Slight delocalization and strategically placed double bonds have combined to make this unique ring system planar. Pairs of molecules interact across a crys-

tallographic inversion centre to form hydrogen-bonded dimers utilizing a ketonic O atom and an adjacent amine H atom [N···O 2.907 (3), N—H 0.83 (3), H···O 2.08 (3) Å; N—H···O 172 (3)<sup>o</sup>].

### Comment

The structure determination described herein was undertaken to identify the compound as it could not be identified by spectral (<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR, IR and MASS) means. The compound was prepared as part of a general investigation into the synthesis and chemistry of 2- and 4-(diaryl- or dialkylaminoxy)tetrafluoropyridines or -(arylidene-aminoxy)fluoropyridines (Banks, Jondi & Tipping, 1989; Jondi, 1989). It is presumed that it arises *via* homolytic cleavage of the O—N bond in the reactant oxime, *i.e.*

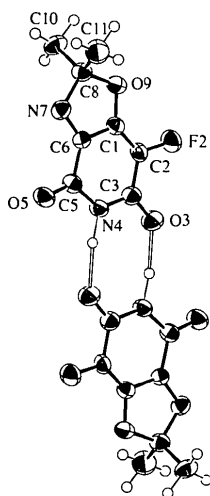
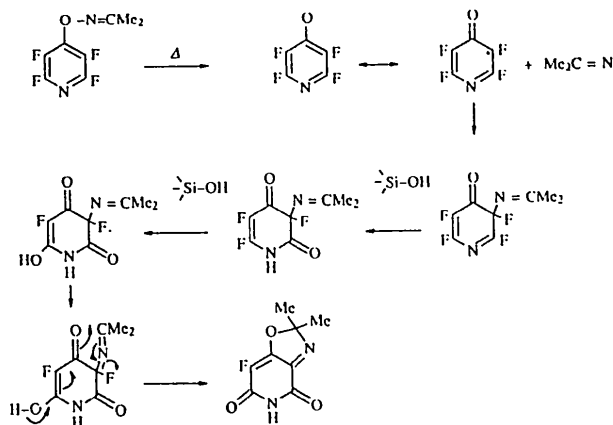


Fig. 1. The title molecule and a hydrogen-bonded symmetry-related neighbour, drawn using ORTEPII (Johnson, 1976). Displacement ellipsoids are plotted at the 50% probability level.

### Experimental

A sample of *N*-isopropylidene-*O*-tetrafluoro-4-pyridylhydroxylamine (2.57 g, 11.6 mmol) was sealed *in vacuo* in a Pyrex ampoule (*ca* 50 ml) and heated at 433 K for 3 h. The resulting material was extracted with dichloromethane (2 × 25 ml) and the solvent removed *in vacuo* to give black material, which showed only one spot on TLC (*R<sub>F</sub>* = 0.20; dichloromethane eluant). Purification by dry column flash chromatography (Merck Kieselgel 60 GF<sub>254</sub> diethyl ether eluant) afforded 5-fluoro-8,8-dimethyl-7-oxa-3,9-diazabicyclo[4.3.0]nona-5,9-diene-2,4-dione (0.22 g, 1.1 mmol, 10%). Analysis: found C 48.6, H 3.2, F 9.8, N 14.2%, *M<sub>r</sub>* 198; C<sub>8</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>3</sub> requires C 8.5, H 3.5, F 9.6, N 14.1%, *M* 198; m.p. 453–456 K. The product was recrystallized from dichloromethane.

### Crystal data

C<sub>8</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>3</sub>

*M<sub>r</sub>* = 198.15

Monoclinic

*C*2/*c*

*a* = 25.171 (3) Å

*b* = 5.245 (1) Å

*c* = 15.557 (2) Å

β = 121.92 (2)<sup>o</sup>

*V* = 1743 (1) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.510 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 14.0–24.0<sup>o</sup>

μ = 0.123 mm<sup>-1</sup>

*T* = 296 K

Needle

0.40 × 0.13 × 0.13 mm

Black

### Data collection

CAD-4 diffractometer

ω/2θ scans

Absorption correction:

none

3258 measured reflections

1729 independent reflections

842 observed reflections

[*I* > 2σ(*I*)]

*R<sub>int</sub>* = 0.0239

θ<sub>max</sub> = 25.0<sup>o</sup>

*h* = 0 → 29

*k* = -6 → 6

*l* = -16 → 14

3 standard reflections

monitored every 200

reflections

intensity decay: not significant

### Refinement

Refinement on *F*

*R* = 0.041

*wR* = 0.027

*S* = 1.947

842 reflections

156 parameters

All H atoms located

from Δ*F* maps and

isotropically refined

Weighting scheme based

on measured e.s.d.'s

(Δ/σ)<sub>max</sub> = 0.0512

Δρ<sub>max</sub> = 0.194 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.162 e Å<sup>-3</sup>

Extinction correction:

Zachariasen (1967) type

2 Gaussian isotropic

Extinction coefficient:

2.1 (1) × 10<sup>-7</sup>

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
F2	0.40884 (9)	1.0681 (4)	0.5073 (1)	0.057 (1)
O3	0.3120 (1)	0.9505 (5)	0.5275 (2)	0.058 (1)
O5	0.25261 (10)	0.2664 (4)	0.3191 (2)	0.053 (1)

O9	0.42552 (9)	0.7240 (4)	0.3740 (2)	0.046 (1)
N4	0.2831 (1)	0.6113 (6)	0.4218 (2)	0.043 (1)
N7	0.3582 (1)	0.3720 (5)	0.2954 (2)	0.041 (1)
C1	0.3811 (1)	0.7164 (6)	0.3964 (2)	0.036 (1)
C2	0.3726 (2)	0.8654 (7)	0.4570 (2)	0.039 (1)
C3	0.3210 (2)	0.8184 (7)	0.4719 (3)	0.041 (1)
C5	0.2877 (2)	0.4414 (7)	0.3581 (2)	0.040 (2)
C6	0.3418 (2)	0.5008 (6)	0.3473 (2)	0.034 (1)
C8	0.4123 (2)	0.5021 (7)	0.3049 (2)	0.042 (1)
C10	0.4693 (2)	0.3342 (9)	0.3556 (4)	0.057 (2)
C11	0.3960 (2)	0.610 (1)	0.2045 (3)	0.065 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

F2—C2	1.349 (3)	N7—C8	1.459 (4)
O3—C3	1.220 (3)	C1—C2	1.326 (4)
O5—C5	1.193 (4)	C1—C6	1.429 (4)
O9—C1	1.337 (3)	C2—C3	1.456 (4)
O9—C8	1.497 (3)	C5—C6	1.491 (4)
N4—C3	1.382 (4)	C8—C10	1.504 (5)
N4—C5	1.382 (4)	C8—C11	1.501 (5)
N7—C6	1.277 (3)		
C1—O9—C8	105.3 (2)	O5—C5—N4	122.8 (3)
C3—N4—C5	128.1 (3)	O5—C5—C6	125.2 (3)
C6—N7—C8	106.6 (3)	N4—C5—C6	111.9 (3)
O9—C1—C2	129.8 (3)	N7—C6—C1	113.1 (3)
O9—C1—C6	108.8 (3)	N7—C6—C5	125.5 (3)
C2—C1—C6	121.4 (3)	C1—C6—C5	121.4 (3)
F2—C2—C1	124.2 (3)	O9—C8—N7	106.2 (2)
F2—C2—C3	115.4 (3)	O9—C8—C10	106.9 (3)
C1—C2—C3	120.4 (3)	O9—C8—C11	106.8 (3)
O3—C3—N4	121.0 (3)	N7—C8—C10	111.1 (3)
O3—C3—C2	122.2 (3)	N7—C8—C11	110.2 (3)
N4—C3—C2	116.8 (3)	C10—C8—C11	115.1 (3)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: LI1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2-Chloro-6-dimethylamino-3,5-pyridine-dicarbaldehyde

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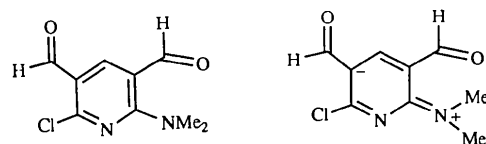
### Abstract

The title compound,  $\text{C}_9\text{H}_9\text{ClN}_2\text{O}_2$ , contains a rather distorted pyridine ring (planar to within  $\pm 0.07 \text{\AA}$ ) with four substituents. The O atoms of the formyl groups at C4 and C2 are displaced from the plane of the pyridine ring by *ca* 1.1 and 0.3  $\text{\AA}$ , respectively. The dimethylamino group at C5, which is planar to within 0.04  $\text{\AA}$ , forms a dihedral angle of  $23.8(1)^\circ$  with the plane of the pyridine ring. The C4—C5 bond in the pyridine ring [1.444 (2)  $\text{\AA}$ ] is much longer than normal in pyridines [1.379  $\text{\AA}$ ], while N1—C1 [1.304 (2)  $\text{\AA}$ ] is shorter and N1—C5 [1.357 (2)  $\text{\AA}$ ] is longer than normal [1.337  $\text{\AA}$ ; Allen, Kennard, Watson, Brammer, Orpen & Taylor (1989). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19]. The C5—N(dimethylamino) bond [1.332 (2)  $\text{\AA}$ ] is shorter than expected.

### Comment

Since we are quite interested in the conformation of highly substituted pyridine derivatives, the determination of the structure of the title compound, which has unsymmetrical substituents, was carried out in order to see how steric and electronic effects in an unsymmetrically substituted pyridine skeleton would be reflected in the bonding geometry, and to compare the structural parameters of the title compound with those of 2,6-bis(dimethylamino)-3,5-pyridinedicarbaldehyde (Lai, Liu, Shiao & Wen, 1994).

The pattern of bond lengths in the title compound indicate that the lone pair of electrons on the N atom of the dimethylamino group is delocalized into the  $\pi$  system of the pyridine ring, as shown by the resonance forms in the scheme below.



The effect of substituents on the conformation of this type of compound is important as aminopyridine derivatives form strong hydrogen bonds with carboxylic acids