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3,5-Difluoro-4-nitropyridine *N*-oxide and 3,5-diamino-4-nitropyridine *N*-oxide monohydrate

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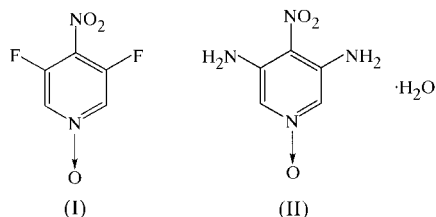
Data validation number: IUC0000136

The molecule of 3,5-difluoro-4-nitropyridine *N*-oxide, $C_5H_2F_2N_2O_3$, is twisted around the C—NO₂ bond by 38.5 (1)°, while the 3,5-diamino analogue, 3,5-diamino-4-nitropyridine *N*-oxide monohydrate, $C_5H_6N_4O_3 \cdot H_2O$, adopts a planar conformation stabilized by intramolecular hydrogen bonds, with a significant redistribution of π electrons.

Comment

The title compounds, (I) and (II), were prepared by Chambers *et al.* (1998) in the course of a study of polyfluorinated nitrogen heterocycles with unusual substitution patterns.

In (I), the difluoropyridine *N*-oxide moiety is essentially planar. The nitro group is not coplanar with it due to a 38.5 (1)° twist around the C4—N4 bond. In (II), this twist is reduced to 4.2 (1)° as repulsive intramolecular O···F interactions are replaced by hydrogen bonds between nitro and amino groups. It is noteworthy that such hydrogen bonds were long supposed to be responsible for directing a nucleophilic attack of NH₃ in the *ortho* position with respect to the nitro group (Chambers *et al.*, 1966).



However, the average deviation of the ring C and N atoms from their mean plane is increased from 0.003 Å in (I) to 0.0135 Å in (II). The O1 and N4 atoms in the latter are tilted out of the ring plane by 0.09 and 0.05 Å in one direction, while N3 and N5 are tilted in the opposite direction by 0.06 and 0.03 Å, respectively. Bond distances in (I) are similar to those in 4-nitropyridine *N*-oxide (Wang *et al.*, 1976) and its 3-methyl

and 3,5-dimethyl derivatives (Shiro *et al.*, 1977). In (II), the N—C bonds in the pyridine ring and the C4—N4 bond are shortened, while the N1—O1 and the pyridine C—C bonds are lengthened. The average alteration amounts to 0.03 Å, indicating a significant shift towards a structure incorporating contributions of *ortho*-quinoidal nature.

In the structure of (I), only the H2···O1 intermolecular contact of 2.33 (2) Å [C2—H2···O1 angle 168 (2)°] can be regarded as a hydrogen bond. Compound (II) crystallizes as a monohydrate with a network of intermolecular hydrogen bonds (Table 3).

The monoclinic unit cell of (I) can be transformed into a pseudo-orthorhombic C-centred one with $a = 5.479$, $b = 21.644$ and $c = 10.840$ Å, but there is neither symmetry, pseudosymmetry, nor twinning associated with this lattice.

Experimental

The preparation of (I) and (II) has been described by Chambers *et al.* (1998). Crystals of (I) were grown from dichloromethane and those of (II) were grown from dimethyl sulfoxide and water.

Compound (I)

Crystal data

$C_5H_2F_2N_2O_3$	$D_x = 1.820$ Mg m ⁻³
$M_r = 176.09$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 449 reflections
$a = 5.479$ (2) Å	$\theta = 10\text{--}23^\circ$
$b = 10.840$ (4) Å	$\mu = 0.186$ mm ⁻¹
$c = 11.159$ (3) Å	$T = 295$ (2) K
$\beta = 104.12$ (1)°	Block, light yellow
$V = 642.7$ (4) Å ³	$0.35 \times 0.25 \times 0.20$ mm
$Z = 4$	

Data collection

SMART 1 K CCD area-detector diffractometer	$R_{int} = 0.032$
ω scans	$\theta_{max} = 27.48^\circ$
4314 measured reflections	$h = -7 \rightarrow 5$
1469 independent reflections	$k = -11 \rightarrow 14$
1086 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 14$
	Intensity decay: 4.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 0.2547P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.143$	$\Delta\rho_{max} = 0.16$ e Å ⁻³
1469 reflections	$\Delta\rho_{min} = -0.15$ e Å ⁻³
118 parameters	Extinction correction: <i>SHELXTL</i>
All H-atom parameters refined	Extinction coefficient: 0.054 (5)

Table 1

Selected geometric parameters (Å) for (I).

N1—O1	1.301 (2)	C4—C5	1.391 (3)
N1—C6	1.359 (3)	C4—N4	1.464 (2)
N1—C2	1.366 (3)	C5—F5	1.334 (2)
C2—C3	1.376 (3)	N4—O42	1.227 (2)
C3—F3	1.336 (2)	N4—O41	1.228 (2)
C3—C4	1.396 (3)		

Compound (II)

Crystal data

C₅H₆N₄O₃·H₂O
M_r = 188.15
 Orthorhombic, *Pna*2₁
a = 7.000 (1) Å
b = 13.123 (1) Å
c = 8.263 (1) Å
V = 759.05 (15) Å³
Z = 4
D_x = 1.646 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 391 reflections
 $\theta = 10.4\text{--}25.5^\circ$
 $\mu = 0.143\text{ mm}^{-1}$
T = 150 (2) K
 Prism, red
 0.40 × 0.15 × 0.08 mm

Data collection

SMART 1K CCD area-detector diffractometer
 ω scans
 5153 measured reflections
 925 independent reflections
 837 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.051
 $\theta_{\text{max}} = 27.48^\circ$
 $h = -9 \rightarrow 9$
 $k = -16 \rightarrow 17$
 $l = -10 \rightarrow 10$
 Intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.035
wR(*F*²) = 0.0933
S = 1.086
 925 reflections
 149 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.3363P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.21\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22\text{ e \AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = 0 (10)

Table 2

Selected geometric parameters (Å) for (II).

N1—O1	1.335 (3)	C4—N4	1.422 (3)
N1—C6	1.342 (4)	C4—C5	1.441 (4)
N1—C2	1.344 (4)	C5—N5	1.339 (4)
C2—C3	1.410 (3)	C5—C6	1.411 (4)
C3—N3	1.334 (4)	O41—N4	1.242 (3)
C3—C4	1.435 (4)	O42—N4	1.258 (3)

Table 3

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H31···O1 ⁱ	0.90 (4)	2.05 (4)	2.922 (3)	162 (3)
N3—H32···O41	0.80 (3)	2.05 (4)	2.599 (3)	125 (4)
N3—H32···O1W ⁱⁱ	0.80 (3)	2.22 (4)	2.915 (3)	145 (4)
N5—H51···O42	0.92 (3)	1.92 (3)	2.609 (3)	130 (3)
N5—H52···O1W ⁱⁱⁱ	0.85 (4)	2.00 (4)	2.845 (3)	172 (4)
O1W—H1W···O42 ^{iv}	0.79 (5)	2.21 (5)	2.994 (3)	175 (5)
O1W—H2W···O1	0.90 (5)	1.87 (5)	2.770 (3)	173 (5)

Symmetry codes: (i) 1 - *x*, 1 - *y*, *z* - ½; (ii) ½ - *x*, *y* - ½, *z* - ½; (iii) -*x*, 1 - *y*, ½ + *z*; (iv) *x* - ½, ½ - *y*, *z*.

The absolute structure (polarity) of (II) could not be determined reliably.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chambers, R. D., Hall, C. W., Hutchinson, J. & Millar, R. W. (1998). *J. Chem. Soc. Perkin Trans. 1*, pp. 1705–1713.
 Chambers, R. D., Hutchinson, J. & Musgrave, W. K. R. (1966). *J. Chem. Soc. C*, pp. 220–224.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Shiro, M., Yamakada, M. & Kubota, T. (1977). *Acta Cryst.* **B33**, 1549–1556.
 Siemens (1995). *SMART* and *SAINT*. Versions 4.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Wang, Y., Blessing, R. H., Ross, F. K. & Coppens, P. (1976). *Acta Cryst.* **B32**, 572–578.