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4-Fluoro-*N*-methyl-*N*-nitroaniline

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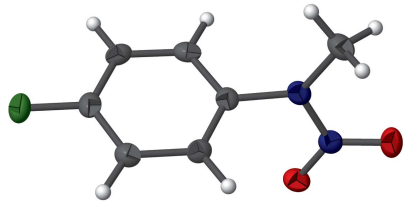
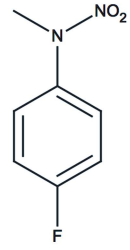
Molecules of the title compound, $C_7H_7FN_2O_2$, are composed of a nitramine group which is twisted with the respect to the aromatic ring, with an N—N—C—C torsion angle of −117.38 (12)°. In the molecule, the N—N bond length [1.3510 (15) Å] indicates some double-bond character, while the angle between the aromatic ring and the nitramine group rules out further delocalization in the molecule. In the crystal, C—H···F hydrogen bonds connect the molecules into $C_1^1(6)$ chains along the *a* axis. C—H···O hydrogen bonds form, which feature $R_2^2(12)$ loops and further connect these chains.

3D view



Chemical scheme



Structure description

Nitroamines find applications in rocket fuels and explosive devices (Williams, 1982). As a result of the unusual properties of the N—N bond, *N*-nitroamines are very active in photochemical reactions (Mialocq & Stephenson, 1986).

In the molecule (Fig. 1), the nitramine group is twisted with the respect to the aromatic ring, with an N1—N2—C1—C2 torsion angle of −117.38 (12)°. The N2—N3 bond length is notably shorter [1.3510 (15) Å] than a typical N—N single bond (1.42 Å; Allen, 2002), but longer than the distance characteristic for an N=N double bond (1.24 Å; Allen, 2002), indicating partial double-bond character. The geometry of the nitroamine group is normal, and corresponds well those in with similar compounds (Ejsmont *et al.*, 1998; Zarychta *et al.*, 2005*a*,*b*, 2011).

In the crystal, weak C6—H6···F1 hydrogen bonds (Fig. 2 and Table 1) connect the molecules into $C_1^1(6)$ chains along the *a* axis. C—H···O contacts further connect the molecules into chains featuring $R_2^2(12)$ loops.

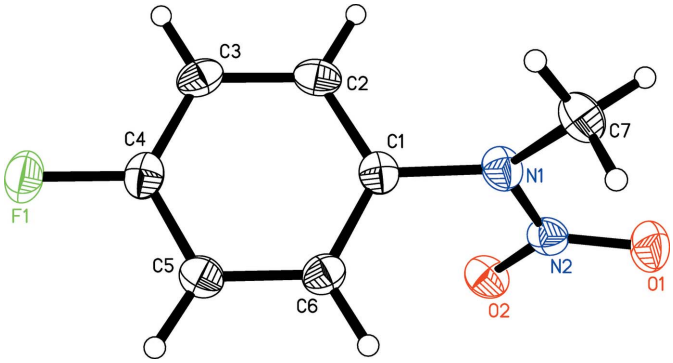


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

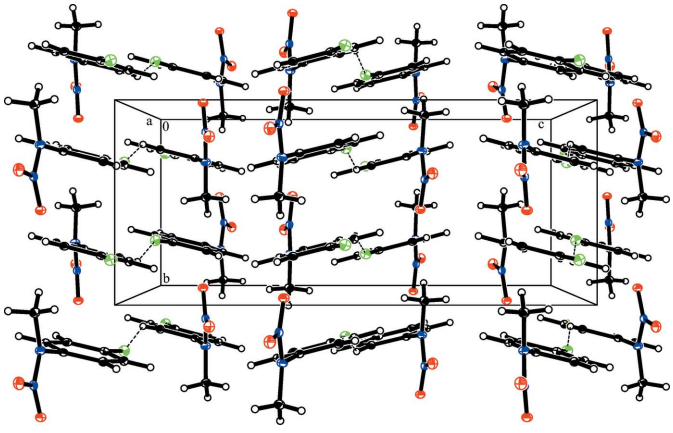


Figure 2
The crystal packing of the title compound, viewed along the *a* axis. The C—H···F hydrogen bonds are shown as dashed lines.

Synthesis and crystallization

The title compound was obtained by a previously reported nitration reaction (Daszkiewicz *et al.*, 1994). The crude product was crystallized from a mixture of diethyl ether with *n*-hexane (1:4) in 79% yield, m.p. 137–138°C.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

References

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Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···F1^{i}	0.958 (15)	2.366 (15)	3.1730 (15)	141.7 (12)
C6—H6···O2^{ii}	0.958 (15)	2.623 (15)	3.3298 (15)	131.0 (11)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_7FN_2O_2$
M_r	170.15
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, b, c (Å)	13.1126 (5), 6.8916 (3), 16.1831 (6)
V (Å^3)	1462.41 (10)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.05 × 0.05 × 0.04
Data collection	
Diffractometer	Oxford Diffraction Xcalibur
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9125, 1434, 1245
R_{int}	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.085, 1.04
No. of reflections	1434
No. of parameters	138
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.16

Computer programs: *CrysAlis CCD* (Oxford Diffraction, 2008), *SHELXS2014/7* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014/7* (Sheldrick, 2015).

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full crystallographic data

IUCrData (2016). **1**, x161446 [doi:10.1107/S2414314616014462]

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4-Fluoro-*N*-methyl-*N*-nitroaniline

Crystal data

$C_7H_7FN_2O_2$
M_r = 170.15
Orthorhombic, *Pbca*
a = 13.1126 (5) Å
b = 6.8916 (3) Å
c = 16.1831 (6) Å
V = 1462.41 (10) Å^3
Z = 8
F(000) = 704
D_x = 1.546 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 9125 reflections
θ = 3.0–26.0°
μ = 0.13 mm^{-1}
T = 100 K
Plate, colourless
0.05 × 0.05 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 1024 x 1024 with blocks 2 x 2 pixels mm^{-1}
ω scans
9125 measured reflections
1434 independent reflections
1245 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 26.0°, θ_{min} = 3.0°
h = −16→16
k = −8→5
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.085
S = 1.04
1434 reflections
138 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.3197P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: SHELXL-2014/7 (Sheldrick 2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0142 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.62328 (5)	0.21268 (11)	0.47654 (5)	0.0324 (2)
O1	1.16296 (7)	0.15293 (15)	0.32855 (6)	0.0335 (3)
O2	1.03374 (7)	−0.03829 (12)	0.35186 (5)	0.0291 (3)
N1	1.01031 (8)	0.28024 (14)	0.34758 (7)	0.0255 (3)
N2	1.07221 (8)	0.12384 (15)	0.34329 (6)	0.0236 (3)
C1	0.90945 (9)	0.25393 (17)	0.38054 (8)	0.0218 (3)
C2	0.82638 (10)	0.28901 (17)	0.33025 (8)	0.0244 (3)
H2	0.8369 (11)	0.324 (2)	0.2744 (10)	0.028 (4)*
C3	0.72915 (10)	0.27567 (17)	0.36275 (9)	0.0244 (3)
H3	0.6743 (12)	0.302 (2)	0.3304 (9)	0.029 (4)*
C4	0.71891 (9)	0.22704 (17)	0.44471 (9)	0.0236 (3)
C5	0.80010 (10)	0.19109 (18)	0.49632 (8)	0.0242 (3)
H5	0.7867 (11)	0.156 (2)	0.5526 (10)	0.030 (4)*
C6	0.89695 (10)	0.20558 (17)	0.46345 (8)	0.0229 (3)
H6	0.9547 (11)	0.181 (2)	0.4981 (10)	0.029 (4)*
C7	1.05729 (12)	0.4711 (2)	0.34364 (9)	0.0294 (3)
H7A	1.0971 (13)	0.483 (2)	0.2957 (12)	0.050 (5)*
H7B	1.0990 (13)	0.491 (3)	0.3897 (12)	0.052 (5)*
H7C	1.0042 (15)	0.562 (3)	0.3432 (10)	0.050 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0206 (4)	0.0365 (5)	0.0401 (5)	0.0010 (3)	0.0042 (3)	0.0017 (3)
O1	0.0247 (5)	0.0407 (6)	0.0351 (6)	0.0014 (4)	0.0086 (4)	−0.0007 (4)
O2	0.0358 (5)	0.0203 (5)	0.0312 (5)	0.0008 (4)	0.0035 (4)	0.0002 (4)
N1	0.0264 (6)	0.0195 (5)	0.0306 (6)	−0.0001 (4)	0.0041 (5)	0.0009 (4)
N2	0.0272 (6)	0.0264 (6)	0.0173 (5)	0.0017 (5)	0.0015 (4)	−0.0011 (4)
C1	0.0237 (6)	0.0161 (5)	0.0256 (7)	−0.0006 (5)	0.0019 (5)	−0.0022 (5)
C2	0.0341 (8)	0.0173 (6)	0.0218 (7)	0.0013 (5)	−0.0019 (5)	0.0007 (5)
C3	0.0260 (7)	0.0184 (6)	0.0287 (7)	0.0021 (5)	−0.0071 (5)	−0.0008 (5)
C4	0.0219 (6)	0.0179 (6)	0.0311 (7)	0.0004 (5)	0.0021 (5)	−0.0036 (5)
C5	0.0281 (7)	0.0226 (6)	0.0219 (7)	−0.0006 (5)	0.0003 (5)	−0.0005 (5)
C6	0.0230 (7)	0.0216 (7)	0.0242 (7)	−0.0003 (5)	−0.0037 (5)	−0.0012 (5)
C7	0.0337 (8)	0.0240 (7)	0.0305 (8)	−0.0052 (6)	0.0047 (6)	0.0013 (5)

Geometric parameters (Å, º)

F1—C4	1.3593 (14)	C3—C4	1.375 (2)
O1—N2	1.2301 (14)	C3—H3	0.908 (15)
O2—N2	1.2337 (14)	C4—C5	1.3756 (18)
N1—N2	1.3510 (15)	C5—C6	1.3805 (18)
N1—C1	1.4376 (16)	C5—H5	0.959 (15)
N1—C7	1.4537 (16)	C6—H6	0.958 (15)
C1—C2	1.3811 (18)	C7—H7A	0.939 (19)

C1—C6	1.3922 (18)	C7—H7B	0.935 (19)
C2—C3	1.3822 (19)	C7—H7C	0.938 (19)
C2—H2	0.944 (16)		

N2—N1—C1	118.11 (10)	F1—C4—C3	118.26 (12)
N2—N1—C7	117.71 (11)	F1—C4—C5	118.09 (12)
C1—N1—C7	121.35 (10)	C3—C4—C5	123.65 (12)
O1—N2—O2	124.40 (11)	C4—C5—C6	117.71 (12)
O1—N2—N1	117.46 (10)	C4—C5—H5	118.7 (9)
O2—N2—N1	118.11 (10)	C6—C5—H5	123.5 (9)
C2—C1—C6	121.14 (12)	C5—C6—C1	119.79 (12)
C2—C1—N1	119.00 (11)	C5—C6—H6	119.2 (9)
C6—C1—N1	119.74 (11)	C1—C6—H6	121.0 (9)
C1—C2—C3	119.44 (12)	N1—C7—H7A	110.6 (10)
C1—C2—H2	119.5 (9)	N1—C7—H7B	110.1 (11)
C3—C2—H2	121.0 (9)	H7A—C7—H7B	108.8 (16)
C4—C3—C2	118.27 (12)	N1—C7—H7C	107.0 (11)
C4—C3—H3	121.8 (9)	H7A—C7—H7C	110.3 (14)
C2—C3—H3	119.9 (9)	H7B—C7—H7C	110.0 (15)

C1—N1—N2—O1	−167.89 (10)	N1—C1—C2—C3	−176.06 (11)
C7—N1—N2—O1	−6.67 (15)	C1—C2—C3—C4	−0.15 (18)
C1—N1—N2—O2	14.26 (15)	C2—C3—C4—F1	−179.58 (10)
C7—N1—N2—O2	175.47 (11)	C2—C3—C4—C5	0.09 (19)
N2—N1—C1—C2	−117.38 (12)	F1—C4—C5—C6	179.86 (10)
C7—N1—C1—C2	82.13 (15)	C3—C4—C5—C6	0.20 (18)
N2—N1—C1—C6	66.58 (15)	C4—C5—C6—C1	−0.42 (18)
C7—N1—C1—C6	−93.91 (15)	C2—C1—C6—C5	0.37 (18)
C6—C1—C2—C3	−0.08 (18)	N1—C1—C6—C5	176.33 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···F1^{i}	0.958 (15)	2.366 (15)	3.1730 (15)	141.7 (12)
C6—H6···O2^{ii}	0.958 (15)	2.623 (15)	3.3298 (15)	131.0 (11)

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