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2,3,4,5,6-Pentafluoroaniline

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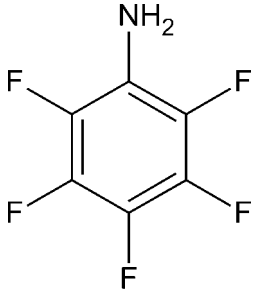
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.025; wR factor = 0.065; data-to-parameter ratio = 5.8.

In the title compound, $C_6H_2F_5N$, the N atom of the amino group deviates by 0.19 (2) Å from the plane of its bonded atoms and thus has slightly pyramidal sp^2 hybridization. The crystal packing is governed largely by N—H···F interactions and interaction of F atoms with the perfluorophenyl ring (C—F···π_F = 3.21 and 3.25 Å). Intermolecular N—H···F hydrogen bonds link molecules into polar sheets parallel to the (100) plane.

Related literature

For related literature on the structure of the pentafluoroaniline cocrystal and of some other fluorinated anilines, see: Gdaniec (2007), Chopra *et al.* (2006), Grzegorczyk & Gdaniec (2006); for a review of fluorine-atom interactions, see Reichenbächer *et al.* (2005).



Experimental

Crystal data

$C_6H_2F_5N$
M_r = 183.09
Monoclinic, *Cc*
a = 7.591 (2) Å
b = 13.311 (2) Å
c = 6.4023 (14) Å
β = 110.90 (2)°
V = 604.3 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 100.0 (3) K
0.4 × 0.4 × 0.4 mm

Data collection

Kuma KM4 CCD κ-geometry diffractometer
Absorption correction: none
2423 measured reflections
688 independent reflections
682 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.065
S = 1.08
688 reflections
118 parameters
2 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···F3^{i}	0.91 (4)	2.20 (4)	3.086 (3)	162 (4)
N1—H1···F4^{ii}	0.83 (4)	2.40 (4)	3.146 (2)	151 (3)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *Mercury* (Version 1.4; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2169).

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supplementary materials

Acta Cryst. (2007). E**63**, o2954 [**doi:10.1107/S1600536807023197**]

2,3,4,5,6-Pentafluoroaniline

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Comment

Structural study of pentafluoroaniline, (I), originates from our interest in diverse interaction observed in fluorinated compounds [*e.g.* *X*(O,*N*,*C*)—H···F, *F*···perfluorophenyl, phenyl-perfluorophenyl] that can be exploited for crystal engineering. The crystal structure of two monofluorinated anilines have been reported recently (Chopra *et al.*, 2006) showing no intermolecular N—H···N and N—H···F interactions as cohesive force of the crystal. No hydrogen bonds were also found in decafluorodiphenylamine structure (Grzegorczyk & Gdaniec, 2006). Hydrogen bonding to covalently bound fluorine was a subject of several reports and nowadays low propensity of 'organic' fluorine to participate in classical hydrogen bonding is well recognized (Reichenbächer *et al.*, 2005).

The molecule of (I) is shown in Fig. 1. A l l C—F distances are within the range 1.338 (2)–1.342 (2) Å. The amino group is slightly piramidalized, N atom of the amino group deviates by 0.19 (2) Å from the plane of its substituents, and thus the N atom hybridization is intermediate between sp^2 and sp^3. The C1—N1 bond of 1.376 (3) Å is substantially shorter than that observed in the 1:2 pentafluoroaniline - pentafluorophenol cocrystal [1.410 (5) Å; Gdaniec, 2007]. In the latter case the amino nitrogen, which acted as an acceptor of hydrogen bonding from the phenolic OH group, had the sp^3 hybridization.

The crystal packing of (I) is governed largely by N—H···F interactions and interaction of fluorine atoms with perfluorophenyl rings. The N—H···F interactions correspond to relatively strong bonding as indicated by the H···F distances and N—H···F angles (Table 1). These hydrogen bonds assemble molecules of (I) into polar sheets parallel to the (001) plane (Fig. 2a). The F···F intermolecular contacts are all longer than 3.084 (2) Å. The pentafluorophenyl rings of molecules related by an n-glide plane are arranged into stacks parallel to the [101] direction·These stacks exhibit large offset which brings atoms F2 and F6 directly above and below the centroid of the electron-defficient phenyl ring, with F···centroid distances of 3.21 and 3.25 Å, respectively (Fig. 2 b). Similar *F*···pentafluorophenyl ring interactions were observed in decafluorodiphenylamine (Grzegorczyk & Gdaniec, 2006).

Experimental

Pentafluoroaniline was purchased from Alfa Aesar. Single crystal used for this study was obtained by recrystallization from n-heptane at 277 K. It was mounted in a cryoloop and flash-cooled to 100 K

Refinement

The H atoms of the amino group were located in electron-density difference maps and were freely refined. In the absence of significant anomalous scattering effects, Friedel pairs were averaged.

Figures

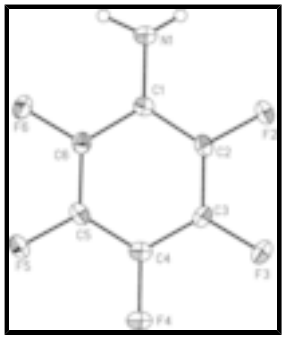


Fig. 1. : Molecular structure of (I) with displacement ellipsoids shown at the 50% probability level.

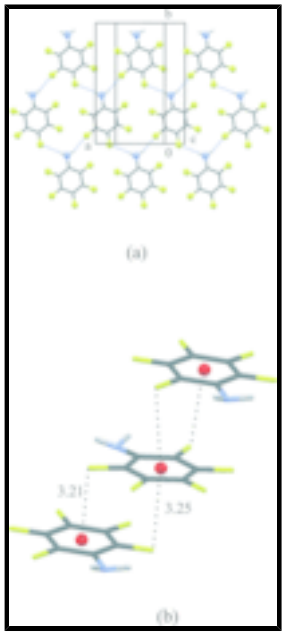


Fig. 2. : Crystal structure of (I): (*a*) (001) sheet of molecules viewed down the *z* axis with N—H···F hydrogen bonds shown as dashed lines and (*b*) *F*···pentafluorophenyl ring interactions (F···ring centroid distances are given in Å)

2,3,4,5,6-Pentafluoroaniline

Crystal data

$C_6H_2F_5N$	F_{000} = 360
M_r = 183.09	D_x = 2.012 Mg m^{-3}
Monoclinic, *Cc*	Melting point: 306 K
Hall symbol: C -2yc	Mo *K*α radiation λ = 0.71073 Å
a = 7.591 (2) Å	Cell parameters from 1580 reflections
b = 13.311 (2) Å	θ = 4–25º
c = 6.4023 (14) Å	μ = 0.23 mm^{-1}
β = 110.90 (2)º	*T* = 100.0 (3) K
V = 604.3 (2) Å^3	Block, colorless
Z = 4	0.4 × 0.4 × 0.4 mm

Data collection

Kuma KM4CCD κ geometry diffractometer	682 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.014$
Monochromator: graphite	$\theta_{max} = 27.5°$
$T = 100.0(3)$ K	$\theta_{min} = 4.6°$
ω scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -14 \rightarrow 17$
2423 measured reflections	$l = -6 \rightarrow 8$
688 independent reflections	

Refinement

Refinement on F^2	All H-atom parameters refined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.2882P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.065$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
688 reflections	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
118 parameters	Extinction coefficient: 0.023 (3)
2 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: difference Fourier map	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.4464 (3)	0.90222 (15)	0.6239 (4)	0.0201 (5)
F2	0.70684 (17)	0.76715 (11)	0.5825 (2)	0.0194 (3)
F3	0.6465 (2)	0.56639 (11)	0.5710 (2)	0.0235 (4)

F4	0.3236 (2)	0.49224 (11)	0.6051 (3)	0.0236 (4)
F5	0.06082 (18)	0.62247 (10)	0.6494 (2)	0.0213 (3)
F6	0.1169 (2)	0.82310 (11)	0.6457 (2)	0.0206 (3)
C1	0.4132 (3)	0.80038 (18)	0.6127 (4)	0.0142 (5)
C2	0.5454 (3)	0.73180 (18)	0.5952 (4)	0.0149 (4)
C3	0.5158 (3)	0.62946 (17)	0.5912 (4)	0.0156 (5)
C4	0.3526 (3)	0.59154 (18)	0.6096 (4)	0.0164 (5)
C5	0.2195 (3)	0.6579 (2)	0.6307 (4)	0.0161 (5)
C6	0.2493 (3)	0.75991 (17)	0.6305 (4)	0.0154 (5)
H2	0.341 (7)	0.939 (3)	0.608 (7)	0.047 (11)*
H1	0.522 (5)	0.924 (3)	0.568 (6)	0.025 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0221 (10)	0.0125 (10)	0.0274 (11)	−0.0006 (8)	0.0110 (10)	0.0010 (8)
F2	0.0139 (6)	0.0219 (7)	0.0240 (7)	−0.0031 (6)	0.0087 (6)	0.0001 (6)
F3	0.0205 (7)	0.0192 (7)	0.0333 (9)	0.0070 (6)	0.0127 (6)	0.0011 (6)
F4	0.0276 (9)	0.0126 (7)	0.0329 (8)	−0.0017 (6)	0.0136 (7)	0.0000 (6)
F5	0.0170 (7)	0.0224 (7)	0.0275 (8)	−0.0047 (6)	0.0115 (6)	−0.0005 (6)
F6	0.0184 (7)	0.0200 (7)	0.0260 (7)	0.0049 (6)	0.0112 (6)	0.0005 (6)
C1	0.0151 (13)	0.0140 (10)	0.0128 (8)	−0.0006 (9)	0.0043 (9)	0.0003 (8)
C2	0.0118 (9)	0.0190 (12)	0.0135 (10)	−0.0014 (9)	0.0041 (8)	0.0009 (8)
C3	0.0151 (11)	0.0158 (11)	0.0160 (10)	0.0039 (8)	0.0056 (9)	0.0001 (8)
C4	0.0188 (12)	0.0140 (10)	0.0151 (9)	−0.0014 (9)	0.0046 (9)	0.0004 (8)
C5	0.0140 (10)	0.0196 (11)	0.0146 (11)	−0.0036 (9)	0.0052 (8)	−0.0004 (9)
C6	0.0140 (11)	0.0173 (11)	0.0146 (10)	0.0018 (10)	0.0049 (8)	0.0012 (9)

Geometric parameters (Å, °)

N1—C1	1.376 (3)	F6—C6	1.341 (3)
N1—H2	0.91 (4)	C1—C2	1.390 (3)
N1—H1	0.83 (4)	C1—C6	1.397 (3)
F2—C2	1.342 (3)	C2—C3	1.379 (3)
F3—C3	1.341 (3)	C3—C4	1.381 (3)
F4—C4	1.339 (3)	C4—C5	1.384 (3)
F5—C5	1.338 (3)	C5—C6	1.377 (3)
C1—N1—H2	113 (3)	C2—C3—C4	120.3 (2)
C1—N1—H1	118 (2)	F4—C4—C3	120.3 (2)
H2—N1—H1	118 (3)	F4—C4—C5	120.8 (2)
N1—C1—C2	121.8 (2)	C3—C4—C5	118.9 (2)
N1—C1—C6	121.8 (2)	F5—C5—C6	120.1 (2)
C2—C1—C6	116.3 (2)	F5—C5—C4	119.7 (2)
F2—C2—C3	119.4 (2)	C6—C5—C4	120.2 (2)
F2—C2—C1	118.4 (2)	F6—C6—C5	119.4 (2)
C3—C2—C1	122.2 (2)	F6—C6—C1	118.47 (19)
F3—C3—C2	119.9 (2)	C5—C6—C1	122.1 (2)
F3—C3—C4	119.8 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···F3^{i}	0.91 (4)	2.20 (4)	3.086 (3)	162 (4)
N1—H1···F4^{ii}	0.83 (4)	2.40 (4)	3.146 (2)	151 (3)

Symmetry codes: (i) *x*−1/2, *y*+1/2, *z*; (ii) *x*+1/2, *y*+1/2, *z*.

Fig. 1

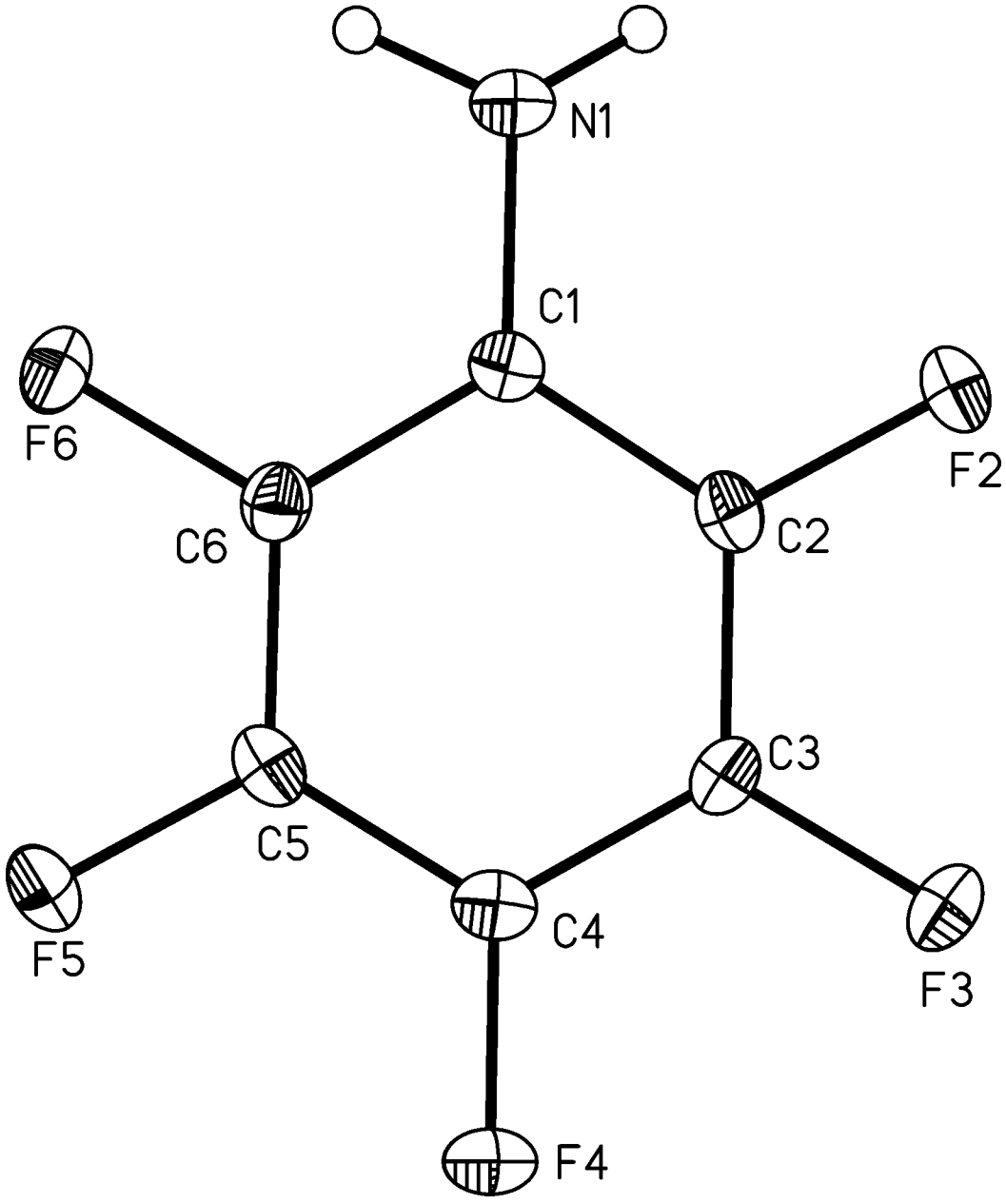
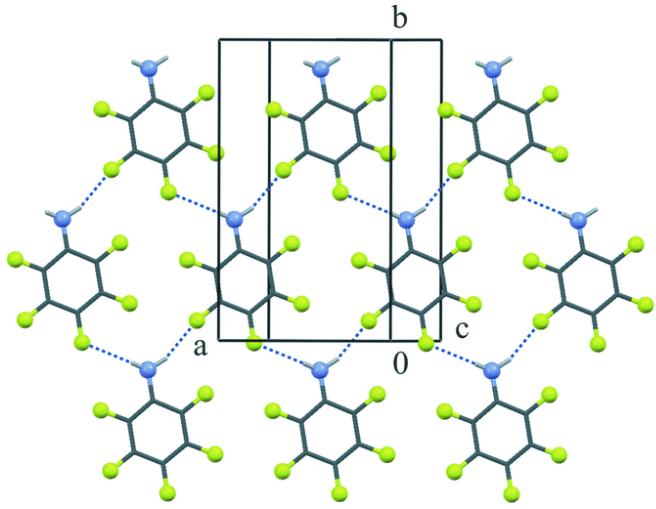
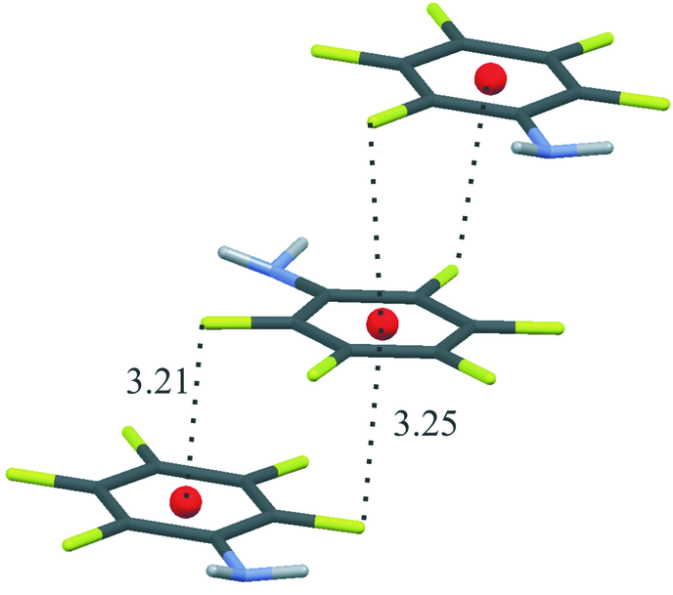


Fig. 2



(a)



(b)