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1-Chloro-1,1-difluoro-*N*-(4-methoxyphenyl)-3-(pyrrolidin-2-ylidene)-propan-2-imine

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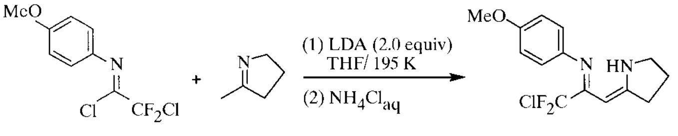
In the title compound, $C_{14}H_{15}ClF_2N_2O$, the *Z* configuration has been confirmed. The molecular structure shows an intramolecular N—H···N hydrogen bond [H···N 2.04 (6), N···N 2.709 (6) Å and N—H···N 124 (5)°]. This interaction could be responsible for the *Z* configuration.

Comment

Fluorine-containing amino compounds have found a wide range of synthetic and biochemical applications due to the unique biological properties imparted by fluorine (Soloshonok *et al.*, 1997, 1998; Bégué & Bonnet-Delpon, 1996). Due to the increasing interest in the synthesis and reactivity of 1,3-difunctionalized fluorine-containing organic compounds (Uneyama *et al.*, 1993; Fustero *et al.*, 1996), we have focused our attention on the fluorinated vinylogous amidines.

We have recently developed the reaction of fluorinated imidoyl chlorides with ketimines to afford the first reported fluorinated vinylogous amidines (Fustero *et al.*, 1999). Although, several tautomeric α–γ structures were possible, the β enaminic structure was determined by NMR analyses. However, the sterochemical assignment (*Z* or *E*) was not fully confirmed. Two-dimensional HOESY NMR ^1H–^{19}F experiments suggest the *Z* configuration for the β enamino tautomer (Fustero *et al.*, 1999). We have now determined the first crystal structure of a fluorinated vinylogous amidine which confirms the assigned geometry.

In the molecular structure of the title compound, (I), the pyrrolidine ring is planar (mean deviation 0.028 Å), with the N1—C1 bond length [1.326 (7) Å] shorter than N1—C4 [1.451 (7) Å]. This suggests an electronic elocalization along the imino–enamino group with bond lengths C1—C5, C5—C6 and C6—N2 of 1.380 (8), 1.417 (7) and 1.312 (7) Å, respectively. The pyrrolidine ring NH group acts as a hydrogen-bond donor to the iminic N atom in the same molecule. The resulting intramolecular hydrogen bond N1—H1···N2 [H1···N2 2.04 (6), N1···N2 2.709 (6) Å and N1—H1···N2 124 (5)°] makes a planar six-membered ring N2—C6—C5—C1—N1—H1 (mean deviation 0.014 Å). The pyrrolidine ring and the hydrogen-bonded ring adopt a nearly coplanar conformation (dihedral angle 3.6°); this plane is almost perpendicular to the aromatic ring (83.5°).



(I)

Experimental

n-Butyllithium (2.5 *M* in hexane, 2.8 ml, 7 mmol) was added dropwise to a solution of diisopropylamine (1 ml, 7 mmol) in THF (10 ml) at 273 K under argon. After being stirred for 10 min, 2-methyl-1-pyrroline (3.5 mmol) in THF (7 ml) was added. The resulting mixture was stirred at 273 K for 30 min, and then cooled to 195 K. *N*-(*p*-Anisidino)-2-chloro-2,2-difluoroacetimidoyl chloride (3.5 mmol) in THF (7 ml) was added and stirred at 195 K. After 1 h, the reaction was quenched by addition of saturated ammonium chloride solution. The aqueous layer was extracted with dichloromethane (3 × 25 ml). The combined organic extracts were washed with brine, then dried (Na_2SO_4), and evaporated under reduced pressure to furnish the crude product. Flash chromatography [*n*-hexane–EtOAc (3:1)] on silica gel gave a yellow solid (79%, m.p. 361–363 K). Single crystals of (I) suitable for X-ray diffraction were grown by cooling a hexane solution.

Crystal data

$C_{14}H_{15}ClF_2N_2O$
$M_r = 300.73$
Monoclinic, $P2_1/c$
$a = 7.6548\ (15)$ Å
$b = 10.436\ (2)$ Å
$c = 17.543\ (4)$ Å
$\beta = 91.34\ (3)^\circ$
$V = 1401.0\ (5)$ Å^3
$Z = 4$
$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.5$–12.2°
$\mu = 0.292$ mm^{-1}
$T = 293\ (2)$ K
Prism, yellow
0.78 × 0.46 × 0.42 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
3826 measured reflections
2453 independent reflections
1774 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 24.97^\circ$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 5$
$l = 0 \rightarrow 20$
3 standard reflections every 247 reflections intensity decay: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.208$
$S = 1.038$
2453 reflections
185 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1017P)^2 + 1.8583P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.59$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.326 (7)	C1—C2	1.457 (7)
N1—C4	1.451 (7)	C2—C3	1.429 (8)
N2—C6	1.312 (7)	C3—C4	1.537 (8)
N2—C11	1.419 (6)	C5—C6	1.417 (7)
C1—C5	1.380 (8)		
C1—N1—C4	113.6 (4)	C2—C3—C4	105.5 (5)
C6—N2—C11	126.1 (4)	N1—C4—C3	103.1 (5)
N1—C1—C5	123.9 (4)	C1—C5—C6	124.6 (5)
N1—C1—C2	108.2 (5)	N2—C6—C5	121.5 (5)
C5—C1—C2	127.6 (5)	N2—C6—C7	122.0 (4)
C3—C2—C1	109.1 (5)	C5—C6—C7	116.5 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$N2	0.97 (4)	2.04 (6)	2.709 (6)	124 (5)

The amino-group H atom was found in a difference Fourier synthesis and refined with a restrained N—H bond length. Other H atoms were refined using a riding model (C—H 0.93–0.98 Å).

Data collection: *CAD*-4–96 *Software* (Enraf–Nonius, 1996); cell refinement: *CAD*-4–96 *Software*; data reduction: *MolEN* (Fair, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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