APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 721–726 (2000)

Trimethylsilylcyanation of heterocyclic imines catalysed by Lewis acids

Irina Iovel, Lena Golomba, Sergey Belyakov, Juris Popelis, Solveiga Grinberga, Edmunds Lukevics*
Latvian Institute of Organic Synthesis, 21 Aizkraukles St, Riga LV-1006, Latvia

The addition of Me_3SiCN to Shiff bases 1a–8a, synthesized by the reaction of furan and thiophene aldehydes with 3- and 4-aminobenzotrifluorides, has been studied in the presence of various Lewis acids. A series of the corresponding trifluoromethyl derivatives of heterocyclic α-aminonitriles 1–8 was synthesized in 38–80% isolated yields. It was found that 4A molecular sieves (MS) accelerate the addition and increase the yields of the products. The investigated catalysts are ranked by their activity in the following order: $AlBr_3$ + 4AMS > $AlBr_3$ > $AlCl_3$ > $Ti[O(iPr)]_4$. A single crystal of *N*-(5-methyl-2-thienylcyanomethyl)-3-trifluoromethylaniline was obtained and studied by X-ray diffraction. The results showed that it was the crystal of the (*R*) isomer of this compound.

Keywords: trimethylsilylcyanation; catalysis; Lewis acids; Shiff bases; α-aminonitriles

Received 5 April 2000; accepted 9 June 2000

INTRODUCTION

Catalytic cyanation of imines (the Strecker reaction), has been studied intensively in several directions (for recent reviews on this subject, see Refs. 1–3). The products of these additions (α-aminonitriles) are useful intermediates for the synthesis of amino acids[4] and other nitrogen-containing compounds, including precursors of medicines.[5] The addition of hydrocyanic acid to a carbon–nitrogen double bond forms a new chiral centre in the molecule; therefore a large number of studies[6–10] of the synthesis of diastereomeric α-aminonitriles from optically active Shiff bases and catalytic asymmetric cyanation (e.g. Ref. 11) have been reported. The novel catalysts of the Strecker synthesis have also been investigated.[12] Application of trimethylsilyl cyanide (TMSCN) instead of sodium cyanide and hydrocyanic acid as a cyano-anion source provides promising and safer routes to α-aminonitriles.[13,14] In our previous work,[15] the addition of Me_3SiCN to (hetero)aromatic aldehydes was investigated. In the present work, trimethylsilylcyanation of a series of the heterocyclic aldimines is reported. Heterocyclic derivatives containing trifluoromethyl (CF_3) groups were used as substrates that promise high biological activity in the products.[16,17]

* Correspondence to: Edmunds Lukevics, Latvian Institute of Organic Synthesis, 21 Aizkraukles St, Riga LV-1006, Latvia.

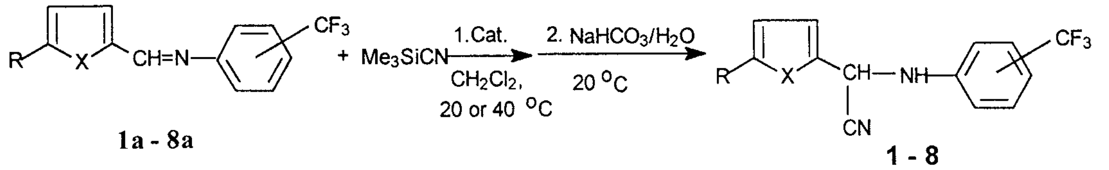
EXPERIMENTAL

General procedure

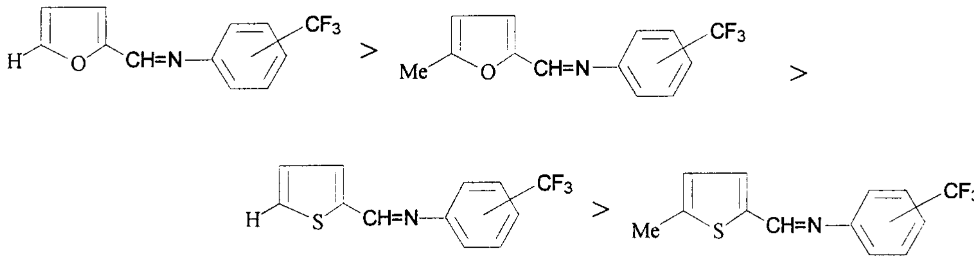
In a typical procedure for trimethylsilylcyanation of imines, in a 5-ml Pierce reaction vial, 1.0 equiv. of imine **1a–8a** in 2 ml dichloromethane reacted with 1.1 equiv. of trimethylsilyl cyanide (**Caution: Toxic!**) in the presence of catalytic amounts of $AlBr_3$ (20 mol%) and 4A molecular sieves (0.5 g) at ambient temperature under argon. When the reaction was complete (monitored by TLC), saturated aqueous $NaHCO_3$ was added, and the product was extracted with diethyl ether. After the organic layer had been dried over $MgSO_4$ and evaporated, the product was isolated by column chromatography on silica gel.

Materials and methods

Dichloromethane was dried over P_2O_5 and distilled prior to use. Trimethylsilyl cyanide (Aldrich) was used without further purification. $AlCl_3$, $AlBr_3$, $Ti[O(iPr)]_4$ and the chemicals for the synthesis of imines were obtained from commercial sources. Molecular sieves 4A (VEB Laborchemie Apolda)



Scheme 1



Scheme 2

and silica gel for column chromatography (Kieselgel 60, 0.063–0.200 mm, Merck) were used.

^{1}H NMR spectra were recorded on Bruker WH-90/DS (90 MHz) and Varian Mercury (200 MHz) spectrometers using $CDCl_3$ as a solvent and Me_4Si as internal standard. Mass spectra were obtained on an MS-50 (70 eV) instrument. Elemental analysis was performed on a Carlo Erba EA-1108 instrument.

X-ray crystallographic study

A four-circle computer-controlled single-crystal

Table 1 The characteristics of the reaction and the products

Product	X	R	CF_3	Catalyst (mol%)	Temp. (°C)	Time (h)	Conversion, (%)[a]	Isolated yield (%)	M.p. (°C)[b]
1	O	H	3-	$AlCl_3$(20)	20	5.5	—	46[d]	Oil
				4A MS[c]	20	6.5	27	—	
2	O	CH_3	3-	$AlCl_3$(20)	20	21	—	40[d]	Oil
				$AlCl_3$(20)	20	5	50	—	
				$AlBr_3$(20)	20	0.5	74	—	
				Ti[O(*i*pr)]$_4$(20)	20	23	68	—	
3	S	H	3-	$AlCl_3$(5)	20	49			
					40	5.5	—	26[d]	—
				$AlBr_3$(20)	20	1	100	80	69–70
4	S	CH_3	3-	$AlCl_3$(5)	20	49			
					40	5.5	30	—	—
				$AlBr_3$(20)	20	5	38	—	—
				$AlBr_3$ (20) + 4A MS	20	26	70	68	84–85
5	O	H	4-	$AlBr_3$(20) + 4A MS	20	2	100	47[d]	143–144
6	O	CH_3	4-	$AlBr_3$(20) + 4A MS	20	1	76	40[d]	95–96
7	S	H	4-	$AlBr_3$(20) + 4A MS	20	6.5	70	38[d]	100–101
8	S	CH_3	4-	$AlBr_3$(20) + 4A MS	20	4	81	40[d]	131–132

[a] Determined by ^{1}H NMR.
[b] After recrystallization from ethyl acetate/hexane or benzene/hexane.
[c] MS, molecular sieves.
[d] The products were isolated by column chromatography.

Table 2 Elemental analysis of the solid α-amino nitriles obtained

Product	Mol. formula	Mol. mass	Found (%)/Calculated (%)			
			C	H	N	S
3	$C_{13}H_9N_2SF_3$	282.29	54.60/55.31	3.21/3.21	9.41/9.92	11.20/11.36
4	$C_{14}H_{11}N_2SF_3$	296.32	56.72/56.75	3.59/3.74	9.42/9.45	10.85/10.82
5	$C_{13}H_9N_2OF_3$	266.22	58.64/58.65	3.50/3.41	10.38/10.52	—
6	$C_{14}H_{11}N_2OF_3$	280.25	60.40/60.00	4.18/3.96	9.86/9.99	—
7	$C_{13}H_9N_2SF_3$	282.29	55.36/55.31	3.12/3.21	10.07/9.92	11.34/11.36
8	$C_{14}H_{11}N_2SF_3$	296.32	56.85/56.75	3.71/3.74	9.46/9.45	10.78/10.82

Table 3 ^{1}H NMR spectra of the α-aminonitriles synthesized

Compound	Chemical shift (ppm), *J* (Hz)				
	J = 0.9–1 CH_3, d	*J* = 8–9 NH, d	CHCN, d	Ring protons	
1	—	4.47	5.46	6.38 (1H, dd, *J*=4, 3.5; FurH-4) 6.53 (1H, dd, *J*=4, 1.5; FurH-3) 7.40 (1H, dd, *J* = 3.5, 1.5; FurH-5)	6.71–7.33 (4H, m; ArH_4)
2	2.29	4.33	5.41	5.97 (1H, dq, *J* = 4, 0.9; FurH-4) 6.44 (1H, d, *J* = 4; FurH-3)	6.78–7.64 (4H, m; ArH_4)
3	—	4.44	5.63	6.78–7.60 (7H, m; ThH_3, ArH_4)	
4	2.49	4.31	5.57	6.69 (1H, dq, *J* = 4, 0.9; ThH-4) 7.13 (1H, d, *J* = 4; ThH-3)	6.82–7.51 (4H, m; ArH_4)
5	—	4.49	5.53	6.47 (1H, dd, *J* = 4, 3.8; FurH-4) 6.62 (1H, m, *J* = 4, 1; FurH-3) 7.49 (1H, dd, *J* = 3.8, 1; FurH-5)	6.80 (2H, d, *J* = 8; ArH-3,5) 7.53 (2H, d, *J* = 8; ArH-2,6)
6	2.31	4.49	5.44	6.00 (1H, dq, *J* = 4.4, 0.9; FurH-4) 6.47 (1H, d, *J* = 4.4; FurH-3)	6.78 (2H, d, *J* = 8; ArH-3,5) 7.51 (2H, d, *J* = 8; ArH-2,6)
7	—	4.58	5.64	7.02 (1H, d, *J* = 5, 4.5; ThH-4) 7.24–7.40 (2H, m, *J* = 5, 4.5, 2; ThH-3,5)	6.78 (2H, d, *J* = 8; ArH-3,5) 7.49 (2H, d, *J* = 8; ArH-2,6)
8	2.49	4.42	5.58	6.64 (1H, dq, *J* = 4, 1; ThH-4) 7.11 (1H, d, *J* = 4; ThH-3)	6.75 (2H, d, *J* = 8; ArH-3,5) 7.47 (2H, d, *J* = 8; ArH-2,6)

Syntex $P2_1$ diffractometer with graphite-monochromatic Mo-K_α ($\lambda = 0.71069$ Å) radiation was used for intensity data collection. A total of 1336 unique reflection intensities were collected at room temperature using the $\theta/2\theta$-scan technique up to $2\theta_{max} = 50°$; one standard reflection showed no significant decay; Lorentz and polarization corrections were applied to the data.

The crystals of **8** are monoclinic, space group $P2_1$; the lattice parameters are as follows: a = 5.337(2), b = 9.978(4), c = 13.334(4) Å, β = 92.44(3)°; V = 709.4(4) Å^3, D_x = 1.378(1) g cm^{-3}, $F(000)$ = 304, μ = 0.252 mm^{-1}, Z = 2.

The crystal structure was solved by the direct method and refined by least squares in block-diagonal approximation with anisotropic temperature factors. The hydrogen atoms were found from differential Fourier synthesis. The final R-factor is 0.0531 for 904 reflections with $I > 2(I)$. All calculations were carried out with the help of the AREN complex of programs.[18]

RESULTS AND DISCUSSION

In this work, the addition of Me_3SiCN to imines **1a–8a** (previously synthesized[19]) was studied in the presence of several Lewis acids (5–20 mol%). The reactions were carried out in dichloromethane at 20 or 40°C. Under these conditions the corresponding novel α-aminonitriles (**1–8**) were obtained in isolated yields up to 80% (Scheme 1). $AlBr_3$ was found to be more active than $AlCl_3$ or

Table 4 Mass spectra of the (α)-aminonitriles synthesized

Compound	MS, *m/z* (I_{rel}, %)
1	266 (8, M^+), 240 (20, $[M - CN]^+$), 239 (100, $[M - HCN]^+$), 238 (52, $[M - HCN - H]^+$), 220 (16, $[M - HCN - F]^+$), 211 (38, $[M - CN - HCO]^+$), 210 (36, $[M - HCN - HCO]^+$), 190 (18), 185 (20), 183 (19), 172 (21, $[M - HCN - Fur]^+$), 170 (25, $[M - HCN - CF_3]^+$), 145 (68, $[C_6H_4—CF_3]^+$), 125 (29), 115 (28), 106 (38, $[Fur—CHCN]^+$), 95 (32), 75 (26), 71 (52), 69 (25, $[CF_3]^+$), 57 (30), 55 (31), 43 (40), 41 (41), 39 (42), 27 (49, $[HCN]^+$)
2	280 (10, M^+), 254 (20, $[M - CN]^+$), 253 (100, $[M - HCN]^+$), 252 (30, $[M - HCN - H]^+$), 238 (25, $[M - HCN - Me]^+$), 211 (22, $[M - CN - Me—CO]^+$), 210 (25, $[M - HCN - Me—CO]^+$), 190 (31), 172 (25), 161 (26), 145 (47, $[C_6H_4—CF_3]^+$), 120 (51, $[Me—C_4H_2O—CHCN]^+$), 95 (18), 69 (12, $[CF_3]^+$), 53 (23), 43 (39, $[H_3CCO]^+$), 39 (17), 27 (30, $[HCN]^+$)
3	282 (2, M^+), 263 (1, $[M - F]^+$), 255 (100, $[M - HCN]^+$), 145 (68, $[C_6H_4—CF_3]^+$), 122 (30, $[C_4H_3S—CHCN]^+$), 112 (28), 111 (31), 95 (44), 84 (46, $[ThH]^+$), 69 (22, $[CF_3]^+$), 43 (30), 39 (42), 27 (38, $[HCN]^+$)
4	296 (3, M^+), 294 (2, $[M - 2H]^+$), 277 (1, $[M - F]^+$), 269 (98, $[M - HCN]^+$), 268 (100, $[M - HCN - H]^+$), 250 (18, $[M - HCN - F]^+$), 200 (17, $[M - HCN - CF_3]^+$), 172 (16), 161 (15), 145 (72, $[C_6H_4—CF_3]^+$), 136 (70, $[Me—C_4H_2S—CHCN]^+$), 125 (12), 97 (60, $[Me—C_4H_2S]^+$), 95 (52), 76 (36), 69 (40, $[CF_3]^+$), 59 (35), 53 (42), 45 (43), 39 (32), 27 (39, $[HCN]^+$)
5	266 (5, M^+), 240 (16, $[M - CN]^+$), 239 (100, $[M - HCN]^+$), 238 (68, $[M - HCN - H]^+$), 220 (13, $[M - HCN - F]^+$), 211 (33, $[M - CN - HCO]^+$), 210 (38, $[M - HCN - HCO]^+$), 190 (8), 185 (19), 183 (14), 172 (9, $[M - HCN - Fur]^+$), 170 (12, $[M - HCN - CF_3]^+$), 145 (85, $[C_6H_4—CF_3]^+$), 125 (18), 115 (17), 106 (62, $[Fur—CHCN]^+$), 95 (22), 78 (12), 75 (15), 73 (10), 69 (5, $[CF_3]^+$), 57 (15), 55 (16), 51 (21), 43 (18), 41 (19), 39 (33), 27 (48, $[HCN]^+$)
6	280 (3, M^+), 278 (2, $[M - 2H]^+$), 254 (15, $[M - CN]^+$), 253 (100, $[M - HCN]^+$), 252 (32, $[M - HCN - H]^+$), 239 (8, $[M - HCN - Me]^+$), 234 (12, $[M - HCN - F]^+$), 211 (40, $[M - CN - Me—CO]^+$), 210 (44, $[M - HCN - Me—CO]^+$), 190 (5), 183 (15), 172 (6), 145 (60, $[C_6H_4—CF_3]^+$), 120 (42, $[Me—C_4H_2O—CHCN]^+$), 95 (33), 81 (18), 79 (16), 75 (15), 73 (16), 69 (22, $[CF_3]^+$), 53 (25), 43 (52, $[H_3CCO]^+$), 41 (15), 39 (26), 27 (38, $[HCN]^+$)
7	282 (6, M^+), 280 (1, $[M - 2H]^+$), 279 (1), 263 (1, $[M - F]^+$), 255 (98, $[M - HCN]^+$), 254 (100, $[M - HCN - H]^+$), 236 (15, $[M - HCN - F]^+$), 234 (12), 186 (14), 145 (62, $[C_6H_4—CF_3]^+$), 122 (58, $[C_4H_3S—CHCN]^+$), 95 (42), 84 (15, $[ThH]^+$), 75 (7), 69 (28, $[CF_3]^+$), 45 (33), 39 (38), 27 (41, $[HCN]^+$)
8	296 (1, M^+), 294 (7, $[M - 2H]^+$), 293 (5), 271 (5), 279 (10), 269 (100, $[M - HCN]^+$), 268 (98, $[M - HCN - H]^+$), 250 (8, $[M - HCN - F]^+$), 200 (12, $[M - HCN - CF_3]^+$), 172 (13), 149 (5), 145 (65, $[C_6H_4 - CF_3]^+$), 136 (28, $[Me—C_4H_2S—CHCN]^+$), 125 (12), 97 (49, $[Me—C_4H_2S]^+$), 94 (41), 69 (31, $[CF_3]^+$), 53 (22), 43 (30), 39 (24), 27 (40, $[HCN]^+$)

[a] Fur, furyl; Th, thienyl.

$Ti[O(iPr)]_4$ (Table 1). To avoid possible hydrolysis problems during the reactions, we carried out the processes in the presence of a dehydration reagent such as 4A molecular sieves (MS). It was found that the addition proceeded sluggishly in the presence of 4A MS without any catalysts. Under the action of the catalyst and 4A MS together, the reactions proceeded most smoothly. The furan derivatives were more active in the addition of Me_3SiCN than the thiophene ones. The order of reactivity of the imines studied was according to Scheme 2.

The products were isolated mainly by column chromatography and identified by ^1H NMR, MS spectra and elemental analysis (Tables 2–4). All the products were thermally very unstable; therefore the GC and GC-MS analyses could not be used for these compounds.

A single crystal of *N*-(5-methyl-2-thienylcyanomethyl)-3-trifluoromethylaniline (**8**) was obtained

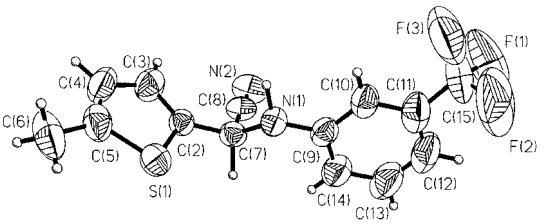


Figure 1 Perspective view of molecule **8** with thermal ellipsoids.

Table 5 Bond lengths and angles for compound **8**

Distance (Å)		Angle (°)	
S(1)–C(5)	1.7077 (0.0076)	C(1)-S(1)-C(5)	92.38 (0.37)
S(1)–C(2)	1.7160 (0.0058)		
C(2)–C(3)	1.3413 (0.0084)	C(3)-C(1)-C(7)	130.19 (0.54)
C(2)–C(7)	1.4793 (0.0071)	C(3)-C(1)-S(1)	110.72 (0.44)
C(2)–S(1)	1.7160 (0.0058)	C(7)-C(1)-S(1)	119.01 (0.40)
C(3)–C(2)	1.3413 (0.0084)	C(1)-C(3)-C(4)	112.51 (0.69)
C(3)–C(4)	1.4118 (0.0104)		
C(4)–C(5)	1.3364 (0.0113)	C(3)-C(4)-C(5)	114.08 (0.64)
C(5)–C(6)	1.5097 (0.0102)	C(4)-C(5)-C(6)	128.68 (0.80)
C(5)–S(1)	1.7077 (0.0076)	C(4)-C(5)-S(1)	110.30 (0.53)
		C(6)-C(5)-S(1)	121.00 (0.76)
C(7)–N(1)	1.4665 (0.0071)	N(1)-C(7)-C(8)	110.78 (0.45)
C(7)–C(8)	1.4807 (0.0097)	C(1)-C(7)-N(1)	110.65 (0.40)
		C(1)-C(7)-C(8)	111.22 (0.47)
C(9)–N(1)	1.4000 (0.0070)	C(7)-N(1)-C(9)	119.98 (0.45)
C(8)–N(2)	1.1511 (0.0072)	C(7)-C(8)-N(1)	175.90 (0.62)
C(9)–C(14)	1.3774 (0.0093)	N(1)-C(9)-C(14)	122.80 (0.60)
C(9)–C(10)	1.4023 (0.0087)	C(10)-C(9)-C(14)	118.88 (0.56)
		C(10)-C(9)-N(1)	118.25 (0.55)
C(10)–C(11)	1.3832 (0.0093)	C(9)-C(10)-C(11)	119.95 (0.68)
C(11)–C(12)	1.3755 (0.0116)	C(10)-C(11)-C(12)	120.64 (0.75)
C(11)–C(15)	1.4806 (0.0135)	C(12)-C(11)-C(15)	119.50 (0.80)
		C(10)-C(11)-C(15)	119.68 (0.92)
C(12)–C(13)	1.3688 (0.0132)	C(11)-C(12)-C(13)	119.70 (0.67)
C(13)–C(14)	1.3945 (0.0101)	C(12)-C(13)-C(14)	120.51 (0.90)
		C(9)-C(14)-C(13)	120.31 (083)
C(15)–F(1)	1.2400 (0.0105)	F(1)-C(15)-F(2)	104.35 (0.86)
		F(1)-C(15)-F(3)	108.91 (1.26)
C(15)–F(2)	1.3544 (0.0135)	F(2)-C(15)-F(3)	99.89 (0.93)
C(15)–F(3)	1.2944 (0.0134)	F(1)-C(15)-C(11)	117.14 (0.94)
		F(2)-C(15)-C(11)	109.23 (1.13)
		F(3)-C(15)-C(11)	115.34 (0.80)

Table 6 Selected torsion angles in molecule **8**

Angle	(°)
C(5)-S(1)-C(2)-C(3)	1.09 (0.50)
C(5)-S(1)-C(2)-C(7)	178.09 (0.45)
C(7)-C(2)-C(3)-C(4)	−177.91 (0.59)
S(1)-C(2)-C(3)-C(4)	−1.36 (0.74)
C(2)-C(3)-C(4)-C(5)	1.00 (0.91)
C(3)-C(4)-C(5)-C(6)	178.21 (0.68)
C(3)-C(4)-C(5)-S(1)	−0.14 (0.80)
C(2)-S(1)-C(5)-C(4)	−0.53 (0.53)
C(2)-S(1)-C(5)-C(6)	−179.04 (0.55)
C(3)-C(2)-C(7)-N(1)	107.39 (0.69)
S(1)-C(2)-C(7)-N(1)	−68.93 (0.57)
C(3)-C(2)-C(7)-C(8)	−16.19 (0.83)
S(1)-C(2)-C(7)-C(8)	167.49 (0.40)
C(8)-C(7)-N(1)-C(9)	−58.69 (0.69)
C(2)-C(7)-N(1)-C(9)	177.47 (0.49)
N(1)-C(7)-C(8)-N(2)	7.23 (8.35)
C(2)-C(7)-C(8)-N(2)	130.74 (8.06)
C(7)-N(1)-C(9)-C(14)	−29.97 (0.86)
C(7)-N(1)-C(9)-C(10)	153.10 (0.54)
C(14)-C(9)-C(10)-C(11)	−0.95 (0.96)
N(1)-C(9)-C(10)-C(11)	176.10 (0.55)
C(9)-C(10)-C(11)-C(12)	0.10 (1.04)
C(9)-C(10)-C(11)-C(15)	175.08 (0.79)
C(10)-C(11)-C(12)-C(13)	0.59 (1.24)
C(15)-C(11)-C(12)-C(13)	−174.40 (1.02)
C(11)-C(12)-C(13)-C(14)	−0.42 (1.50)
N(1)-C(9)-C(14)-C(13)	−175.79 (0.72)
C(10)-C(9)-C(14)-C(13)	1.12 (1.11)
C(12)-C(13)-C(14)-C(9)	−0.44 (1.46)
C(12)-C(11)-C(15)-F(1)	47.44 (1.61)
C(10)-C(11)-C(15)-F(1)	−127.60 (1.13)
C(12)-C(11)-C(15)-F(3)	177.66 (0.96)
C(10)-C(11)-C(15)-F(3)	2.62 (1.50)
C(12)-C(11)-C(15)-F(2)	−70.85 (1.16)
C(10)-C(11)-C(15)-F(2)	114.12 (1.04)

by careful crystallization from ethyl acetate/hexane (1:1) and studied by X-ray diffraction. Figure 1 illustrates the perspective view of molecule **8** with atom labels. Tables 5 and 6 give the bond lengths, valence angles and selected torsion angles. The five- and six-membered rings in structure **8** are planar. The bond lengths in these rings show that there is delocalization of the π-electrons in the system. The bond length N(1)–C(9) 1.400(7) Å indicates conjugation between the six-membered aromatic ring and the lone electron pair on the N(1). However, the nitrogen atom N(1) is not planar, but pyramidal (the sum of the valence angles is 345°). On the whole, the molecule **8** has a normal geometry. The decrease in lengths for the C(11)–C(15) and C–F bonds can be explained[20] by significant thermal vibrations of the F and C(15) atoms (see Fig. 1).

Molecule **8** has a hindered conformation with reference to the C(7)–N(1) bond; the torsion angle C(2)–C(7)–N(1)–C(9) is close to being a flat angle, i.e. both rings have a fully staggered disposition.

There is only one enantiomer (*R*-isomer) in the crystal investigated. An intermolecular hydrogen bond N(1)—H(1)···N(2) was found in the crystal structure. The hydrogen bond length equals 3.207(7) Å: H(1)···N(2) = 2.26 Å, ∠N(1)—H(1)···N(2) = 151°; it is somewhat greater than the mean statistical value (2.98 Å) for the NH···N type of H-bond.[21]

Acknowledgement The authors thank the Latvian Council of Science for support of this work (grant no. 707).

REFERENCES

1. Kobayashi S, Ishitani H. *Chem. Rev.* 1999; **99**: 1069.
2. Mori S. Inone . In: *Comprehensive Asymmetric Synthesis*, Jacobsen EN, Pfaltz A, Yamamoto HH (eds). Springer: Berlin, 1999; 983.
3. Shafran YM, Bakulev VA, Mokrushin VS. *Russian Chem. Rev.* 1989; **58**: 148.
4. March J. *Advanced Organic chemistry. Reactions, Mechanisms, and Structure*, 4th edition. John Wiley: New York, 1992; 874.
5. Matier WL, Owens DA, Comer WT, Deitchman D, Ferguson HC, Seidehamel RJ, Young JR. *J. Med. Chem.* 1973; **16**: 901.
6. Harada K. *Nature* 1963; **200**: 1201.
7. Patel MS, Worsley M. *Can. J. Chem.* 1970; **48**: 1881.
8. Harada K, Okawara T. *J. Org. Chem.* 1973; **38**: 707.
9. Ojima I, Inaba S, Nagai Y. *Chem. Lett.* 1975; 737.
10. Chakrabortu TK, Hussain KA, Venkat Reddy G. *Tetrahedron* 1995; **51**: 9179.
11. Iyer MS, Gigstad KM, Namdev ND, Lipton M. *J. Am. Chem. Soc.* 1996; **118**: 4910.
12. Kobayashi S, Ishitani H, Ueno M. *Synlett* 1997; 115.
13. Ojima I, Inaba S, Nakatsugawa K. *Chem. Lett.* 1975; 331.
14. Mai K, Patil G. *Tetrahedron Lett.* 1984; **25**: 4583.
15. Iovel I, Popelis J, Fleisher M, Lukevics E. *Tetrahedron: Asymmetry* 1997; **8**: 1279.
16. Isikawa N. (ed.). *Compounds of Fluorine. Synthesis and Applications*. Mir: Moscow, 1990. (In Russian, transl. from Japanese.)
17. Welsh JT. *Tetrahedron* 1987; **43**: 3123.
18. Andrianov VI. *Kristallografiya* 1987; **32**: 228.
19. Iovel I, Golomba L, Popelis J, Grinberga S, Lukevics E. *Chem. Heterocycl. Compd.* 2000; 890.
20. Busing WP, Levy HA. *Acta Crystallogr.* 1964; **17**: 142.
21. Kuleshova LN, Zorkii PM. *Acta Crystallogr. Sect. B* 1981; **37**: 1363.

