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SYNTHESIS AND STRUCTURE OF SOME 2-TRIFLUOROMETHYL-SUBSTITUTED HETARYLMETHYLIDENE(OR PROPYLIDENE)ANILINES

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The reaction of furan, thiophene, pyridine, and also furylacryloyl aldehydes with 2-trifluoromethylanilines has been studied in the presence of molecular sieves and a series of new heterocyclic aldimines has been synthesized. The molecular and crystalline structure of some of them were determined by X-ray structural analysis.

Keywords: heterocyclic Schiff's bases, 2-trifluoromethylaniline, molecular sieves.

Previously we developed an efficient method [1-4] for the synthesis of a broad range of azomethines by the condensation of heterocyclic aldehydes with amines in the presence of molecular sieves. In these processes the latter plays the role not only of a dehydrating agent but also of an optimal acid catalyst, which does not lead (unlike in the majority of homogeneous systems) to the resinification of the acidophobic furan and thiophene substrates and does not form salts at the ring nitrogen atom of pyridine compounds, which usually prevents further conversion. Using this method a series of syntheses has been carried out in the present work (Scheme 1) and the corresponding heterocyclic aldimines with a trifluoromethyl substituent have been obtained. These are potentially biologically active compounds.

By reacting furfural, thiophene aldehyde, and their 5-methyl derivatives **1a-d**, 2-, 3-, and 4-pyridine aldehydes **2a-c**, and also furylacroleins **3a-c** with 2-trifluoromethylaniline in the presence of molecular sieve 4A, the corresponding products N-(hetarylmethylidene or hetarylpropylidene)-2-trifluoromethylanilines **4a-d**, **5a-c**, and **6a-c** (Table 1) were synthesized. Benzene was used as solvent. In difference to 3- and 4-trifluoromethylanilines studied previously in [1-4] (the condensation of which with aldehydes occurs even at room temperature), 2-trifluoromethylaniline reacts with all the carbonyl compounds studied only on heating (80°C). Probably the CF_3 group in a position close to the nitrogen atom of the aromatic amine impedes condensation. The reactivity of the aldehydes, which are derivatives of five-membered O and S heterocycles (except for 5-methylfurylacrolein), is greater than that of the pyridine aldehydes. All the compounds obtained were yellow crystalline or liquid substances, their ^1H NMR spectra, mass spectra, and elemental analyses corresponded to the structure of the desired aldimines.

Monocrystals of the new compounds **4d** and **6c** were obtained and were investigated by X-ray diffraction with the aim of establishing their molecular and crystal structure (Fig. 1). The principal crystallographic data, coordinates of non-hydrogen atoms, and some geometric characteristics of the studied aldimines are given in Tables 2-6. The molecules of the compounds have the *trans* (**4d**) and *trans-E* configuration (**6c**). The planes of the phenyl and heterocyclic fragments are mutually inclined in the molecules at 40.0(3)° (**4d**) and 29.1(5)° (**6c**).

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TABLE 1. Characteristics of the Compounds Synthesized

Aldimine	Reaction time, h	Empirical formula	Found, % Calculated, %				mp, °C* [bp, °C]	Yield, %
			C	H	N	S		
4a	6	$C_{12}H_8F_3NO$	60.16 60.26	3.30 3.37	5.76 5.86		55-56 [80° (0.5 mm Hg), subl.]	70
4b	6	$C_{13}H_{10}F_3NO$	61.41 61.66	3.76 3.98	5.48 5.53		27	56
4c	6	$C_{12}H_8F_3NS$	56.70 56.47	3.08 3.16	5.37 5.49	12.51 12.56	75-76	73
4d	6	$C_{13}H_{10}F_3NS$	57.91 57.98	3.73 3.74	5.20 5.20	11.88 11.91	62-63 [70° (0.1 mm Hg), subl.]	61
5a*2	8	$C_{13}H_9F_3N_2$						98
5b*2	8	$C_{13}H_9F_3N_2$						98
5c	8	$C_{13}H_9F_3N_2$	62.28 62.40	3.58 3.63	11.12 11.19		45-46	51
6a	6	$C_{14}H_{10}F_3NO$	63.41 63.40	3.71 3.80	5.10 5.28		65-66	74
6b*2	15	$C_{15}H_{12}F_3NO$	64.02 64.52	4.73 4.33	4.46 5.02			75
6c	6	$C_{14}H_9F_3N_2O_3$	54.23 54.20	2.79 2.92	8.91 9.03		102-103	72

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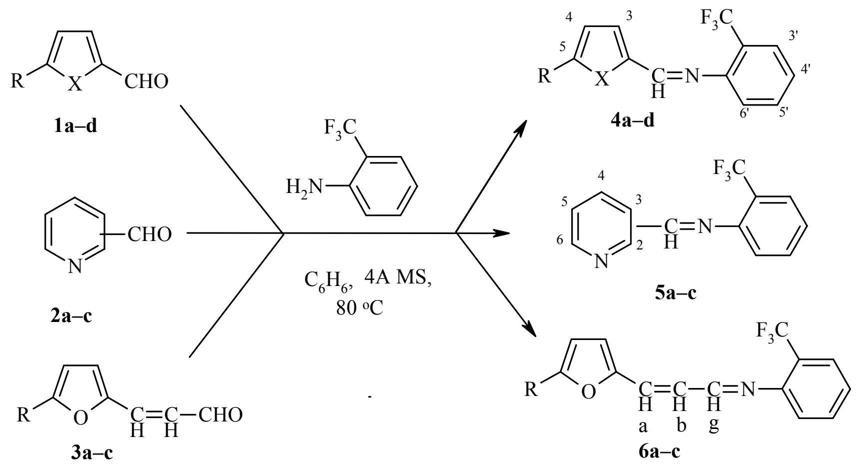
* Recrystallization solvent: **4c**, **6c** ethyl acetate–hexane and **4d**, **5c**, and **6a** hexane.

*2 Oily liquid.

Scheme 1



1, **4** **a** X = O, R = H, **b** X = O, R = Me; **c** X = S, R = H; **d** X = S, R = Me;
3, **6** **a** R = H, **b** R = Me, **c** R = NO_2; position of substituent **2**, **5** **a** 2-, **b** 3-, **c** 4-

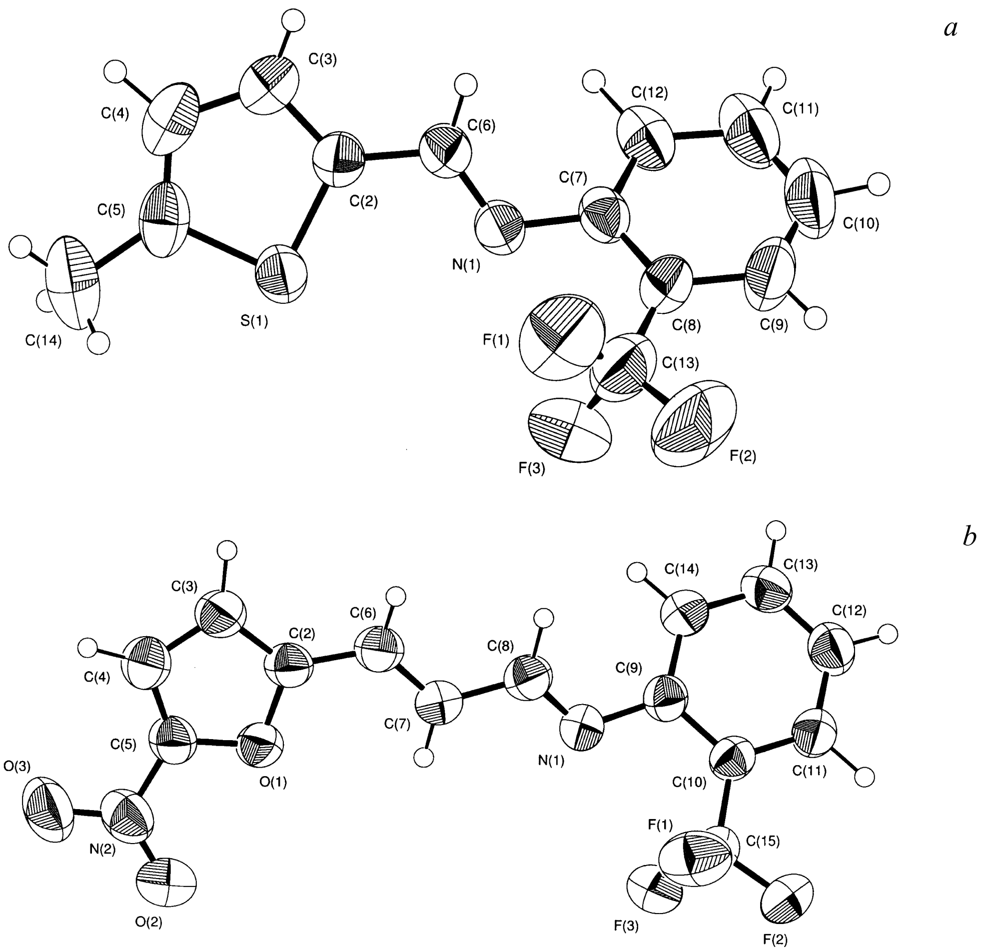


Fig. 1. Spatial models of the molecules of compounds **4d** (*a*) and **6c** (*b*) with numbering of atoms and ellipsoids of thermal vibrations.

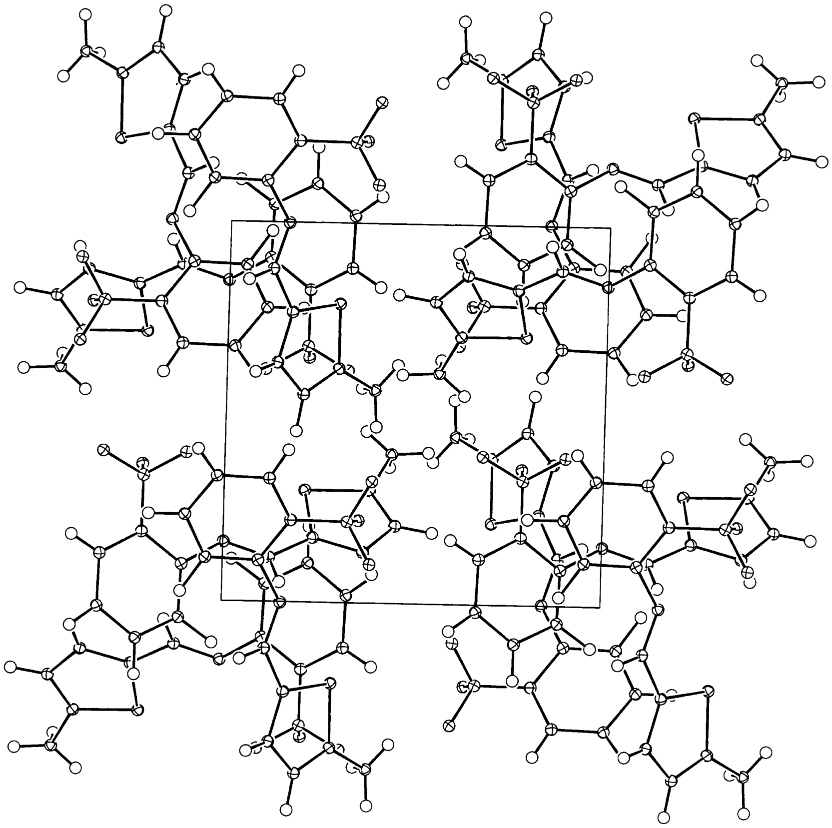


Fig. 2. Projection of the crystal structure of compound **4d** along the *z* axis.

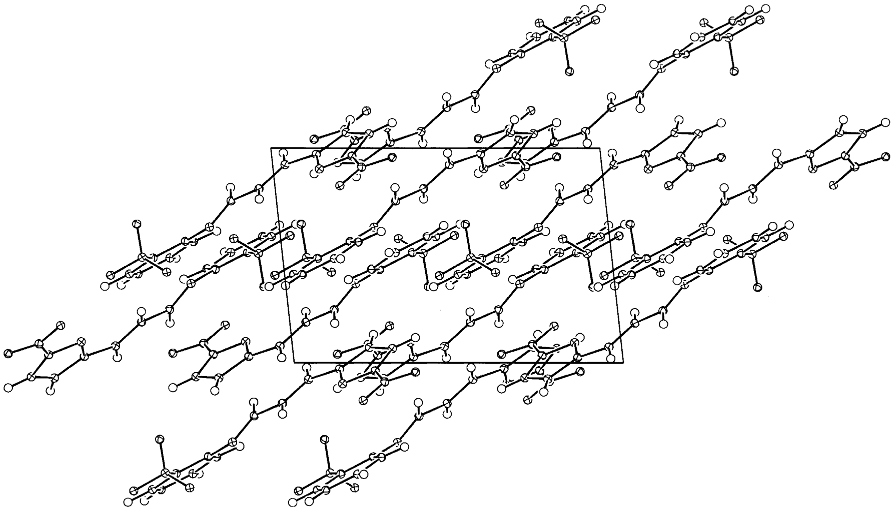


Fig. 3. Projection of the crystal structure of compound **6c** along the *y* axis.

The more flattened **6c** molecules are packed in the crystal parallel to the crystal (1 0 1) plane. In the highly symmetrical crystal structure of **4d** the packing of the molecules is more loose and plane-parallel stacks of molecules were not observed (Figs. 2 and 3).

TABLE 2. Crystallographic Data for Compounds **4d** and **6c**

Characteristic	**4d**	**6c**
Empirical formula	$C_{13}H_{10}F_3NS$	$C_{14}H_9F_3N_2O_3$
Molecular weight	269.29	310.23
Color	Yellow	Orange
Crystal size, mm	0.15×0.27×0.27	0.08×0.15×0.37
Crystal system	Tetragonal	Monoclinic
Space group	$P\,4_3$	$P\,2_1/c$
Lattice parameters		
a, Å	9.7828(3)	7.9451(4)
b, Å	—	14.4700(7)
c, Å	13.8724(5)	11.9143(5)
β, deg	—	96.305(3)
Unit cell volume, *V*, $Å^3$	1327.63(7)	1361.45(11)
Number of molecules in unit cell, *Z*	4	4
Density, *d*, g/cm^3	1.347(1)	1.514(1)
Absorption coefficient, μ, mm^{-1}	0.26	0.13
Number		
Independent reflections	1615	3540
reflections with $I > 3\sigma(I)$	1266	1523
refinement parameters	203	220
Final reliability factor, *R*	0.035	0.046

TABLE 3. Coordinates of Non-hydrogen Atoms and Their Equivalent Isotropic Thermal Parameters in Structure **4d**

Atom	*x*	*y*	*z*	U_{eq}
S(1)	0.29288(8)	0.21221(8)	0.24790(6)	0.0605(4)
N(1)	0.1548(3)	0.0014(3)	0.12345(18)	0.0558(11)
C(7)	0.0942(3)	-0.1076(3)	0.0711(2)	0.0558(14)
C(2)	0.1686(3)	0.2355(3)	0.1621(2)	0.0573(14)
C(5)	0.2943(4)	0.3837(4)	0.2756(3)	0.0690(17)
C(6)	0.1154(3)	0.1224(3)	0.1071(2)	0.0582(14)
C(8)	0.1774(4)	-0.2141(3)	0.0394(3)	0.0689(17)
F(1)	0.3877(3)	-0.1011(4)	0.0248(4)	0.132(2)
C(3)	0.1324(5)	0.3695(4)	0.1576(4)	0.081(2)
F(3)	0.3556(4)	-0.2154(4)	0.1524(3)	0.130(2)
C(4)	0.2026(5)	0.4528(4)	0.2222(4)	0.084(2)
C(11)	-0.1012(6)	-0.2249(5)	0.0059(4)	0.092(3)
C(13)	0.3259(6)	-0.2117(5)	0.0584(5)	0.097(3)
C(12)	-0.0457(4)	-0.1132(4)	0.0545(3)	0.0712(18)
C(10)	-0.0189(7)	-0.3281(5)	-0.0263(4)	0.101(3)
C(14)	0.3912(7)	0.4392(9)	0.3497(5)	0.105(4)
F(2)	0.3890(4)	-0.3189(5)	0.0200(5)	0.169(3)
C(9)	0.1190(6)	-0.3232(4)	-0.0105(4)	0.091(3)

TABLE 4. Coordinates of Non-hydrogen Atoms and Their Equivalent Isotropic Thermal Parameters in Structure **6c**

Atom	*x*	*y*	*z*	U_{eq}
O(1)	0.9051(2)	0.02621(14)	0.14033(14)	0.0584(10)
F(2)	0.4074(3)	0.11147(14)	-0.52929(14)	0.0888(12)
F(3)	0.4220(3)	0.07046(13)	-0.35771(15)	0.0867(12)
N(1)	0.6329(3)	0.18929(16)	-0.21239(18)	0.0608(13)
C(10)	0.4874(3)	0.2268(2)	-0.3953(2)	0.0539(14)
C(2)	0.9732(4)	0.11319(19)	0.1358(2)	0.0567(15)
C(6)	0.9241(4)	0.1681(2)	0.0380(3)	0.0615(16)
C(11)	0.4127(4)	0.2904(2)	-0.4720(2)	0.0602(15)
N(2)	0.9138(4)	-0.0975(2)	0.2692(3)	0.0754(17)
C(5)	0.9648(4)	-0.0066(2)	0.2437(3)	0.0624(16)
C(8)	0.7554(4)	0.2096(2)	-0.1378(2)	0.0602(16)
O(2)	0.8283(4)	-0.14221(18)	0.1975(2)	0.0919(17)
C(7)	0.8126(4)	0.1454(2)	-0.0488(2)	0.0579(16)
C(15)	0.4908(4)	0.1274(2)	-0.4276(2)	0.0620(16)
C(12)	0.4122(4)	0.3832(2)	-0.4463(3)	0.0683(18)
C(9)	0.5664(4)	0.2569(2)	-0.29038(19)	0.0553(14)
C(13)	0.4871(5)	0.4134(2)	-0.3435(3)	0.0675(17)
C(14)	0.5640(4)	0.3515(2)	-0.2662(3)	0.0622(16)
C(3)	1.0726(4)	0.1316(2)	0.2339(3)	0.0709(19)
O(3)	0.9591(4)	-0.1243(2)	0.3663(2)	0.1050(18)
F(1)	0.6468(3)	0.09652(14)	-0.4334(2)	0.0988(14)
C(4)	1.0672(4)	0.0537(2)	0.3031(3)	0.075(2)

TABLE 5. Main Bond Lengths (*d*) and Values of Valence Angles (θ) in Molecules of Compound **4d**

Bond	*d*, Å	Angle	θ, deg
1	2	3	4
S(1)–C(2)	1.716(4)	C(2)–S(1)–C(5)	91.8(2)
S(1)–C(5)	1.721(4)	C(7)–N(1)–C(6)	118.9(3)
N(1)–C(7)	1.420(4)	N(1)–C(7)–C(8)	118.6(3)
N(1)–C(6)	1.265(5)	N(1)–C(7)–C(12)	121.7(4)
C(7)–C(8)	1.393(6)	C(8)–C(7)–C(12)	119.6(4)
C(7)–C(12)	1.389(6)	S(1)–C(2)–C(6)	121.4(3)
C(2)–C(6)	1.442(5)	S(1)–C(2)–C(3)	110.2(3)
C(2)–C(3)	1.359(6)	C(6)–C(2)–C(3)	111.2(3)
C(5)–C(4)	1.346(8)	S(1)–C(5)–C(4)	128.4(4)
C(5)–C(14)	1.501(8)	S(1)–C(5)–C14	120.7(6)
C(8)–C(13)	1.477(8)	C(4)–C(5)–C14	128.1(6)
C(8)–C(9)	1.395(6)	N(1)–C(6)–C(2)	120.8(3)
F(1)–C(13)	1.324(8)	C(7)–C(8)–C(13)	120.4(4)
C(3)–C(4)	1.391(8)	C(7)–C(8)–C(9)	119.3(4)
F(3)–C(13)	1.336(10)	C(13)–C(8)–C(9)	120.2(5)
C(11)–C(12)	1.394(7)	C(2)–C(3)–C(4)	114.0(5)
C(11)–C(10)	1.366(10)	C(5)–C(4)–C(3)	112.9(4)
C(13)–F(2)	1.329(7)	C(12)–C(11)–C(10)	120.6(5)
C(10)–C(9)	1.368(10)	C(8)–C(13)–F(1)	113.6(5)
C(6)–H(6)	0.93(5)	C(8)–C(13)–F(3)	112.8(6)
C(3)–H(3)	0.94(8)	C(8)–C(13)–F(2)	111.9(5)

TABLE 5 (continued)

1	2	3	4
C(4)–H(4)	0.98(6)	F(1)–C(13)–F(3)	105.4(6)
C(11)–H(11)	0.94(6)	F(1)–C(13)–F(2)	107.0(6)
C(12)–H(12)	1.12(6)	F(3)–C(13)–F(2)	105.6(6)
C(10)–H(10)	0.97(8)	C(7)–C(12)–C(11)	119.7(5)
C(14)–H(14A)	0.88(12)	C(11)–C(10)–C(9)	120.2(5)
C(14)–H(14B)	1.01(13)	C(8)–C(9)–C(10)	120.7(5)
C(14)–H(14C)	0.96(13)		
C(9)–H(9)	0.93(6)		

TABLE 6. Main Bond Lengths (*d*) and Valence Angles (θ) in Molecules of Compound **6c**

Bond	*d,* Å	Angle	θ, deg
O(1)–C(2)	1.373(3)	C(2)–O(1)–C(5)	104.9(2)
O(1)–C(5)	1.357(3)	C(8)–N(1)–C(9)	120.0(2)
F(2)–C(15)	1.337(3)	C(11)–C(10)–C(15)	119.4(2)
F(3)–C(15)	1.330(3)	C(11)–C(10)–C(9)	119.9(3)
N(1)–C(8)	1.278(3)	C(15)–C(10)–C(9)	120.6(2)
N(1)–C(9)	1.411(3)	O(1)–C(2)–C(6)	117.9(2)
C(10)–C(11)	1.383(4)	O(1)–C(2)–C(3)	109.8(2)
C(10)–C(15)	1.489(4)	C(6)–C(2)–C(3)	132.2(3)
C(10)–C(9)	1.405(3)	C(2)–C(6)–C(7)	126.7(3)
C(2)–C(6)	1.429(4)	C(10)–C(11)–C(12)	121.0(3)
C(2)–C(3)	1.364(4)	C(5)–N(2)–O(2)	119.5(2)
C(6)–C(7)	1.326(4)	C(5)–N(2)–O(3)	115.5(3)
C(11)–C(12)	1.378(4)	O(2)–N(2)–O(3)	124.9(3)
N(2)–C(5)	1.419(4)	O(1)–C(5)–N(2)	116.0(2)
N(2)–O(2)	1.218(3)	O(1)–C(5)–C(4)	112.5(3)
N(2)–O(3)	1.235(3)	N(2)–C(5)–C(4)	131.5(3)
C(5)–C(4)	1.339(4)	N(1)–C(8)–C(7)	121.1(3)
C(8)–C(7)	1.444(4)	C(6)–C(7)–C(8)	122.8(3)
C(15)–F(1)	1.328(3)	F(2)–C15–F(3)	105.3(2)
C(12)–C(13)	1.373(4)	F(2)–C(15)–C(10)	112.3(2)
C(9)–C(14)	1.401(4)	F(2)–C(15)–F(1)	105.5(2)
C(13)–C(14)	1.378(4)	F(3)–C(15)–C(10)	114.7(2)
C(3)–C(4)	1.399(4)	F(3)–C(15)–F(1)	105.9(2)
C(6)–H(6)	0.90(4)	C(10)–C(15)–F(1)	112.5(2)
C(11)–H(11)	1.01(3)	C(11)–C(12)–C(13)	119.7(3)
C(8)–H(8)	1.01(3)	N(1)–C(9)–C(10)	118.0(2)
C(7)–H(7)	0.92(3)	N(1)–C(9)–C(14)	123.7(2)
C(12)–H(12)	0.94(3)	C(10)–C(9)–C(14)	118.1(2)
C(13)–H(13)	0.95(3)	C(12)–C(13)–C(14)	120.5(3)
C(14)–H(14)	0.97(3)	C(9)–C(14)–C(13)	120.9(3)
C(3)–H(3)	1.01(4)	C(2)–C(3)–C(4)	107.1(3)
C(4)–H(4)	0.93(3)	C(5)–C(4)–C(3)	105.7(3)

EXPERIMENTAL

The ^{1}H NMR spectra were investigated on a Varian Mercury (200 MHz) spectrometer for solutions in $CDCl_3$, internal standard was TMS. The mass spectra were obtained on an HP 6890 GC/MS chromato-mass spectrometer fitted with an HP 5 MS capillary column (30.0 m × 250 μm × 0.25 μm), with temperature programing from 70 to 260°C (10°C/min).

Before use benzene was distilled over CaH_2. 5-Methyl-2-thiophenecarbaldehyde was synthesized by the method of [5]. The remaining reagents used in the work were obtained from Fluka, Merck, and Acros. Aldehyde **3c** was recrystallized from benzene, and other aldehydes were purified by vacuum distillation, after which their properties corresponded to literature data. 2-Trifluoromethylaniline was used without additional purification. Molecular sieves 4A (VEB Laborchemie Apolda) were used in the work.

General Procedure for the Synthesis of Aldimines 4a-d, 5a-c, and 6a-c. Dry benzene (10 ml) and the initial aldehyde and amine (about 5 mmol) were placed in a round-bottomed flask with a reflux condenser, then freshly calcined molecular sieve (5 g) was added and the mixture was heated on a water bath at 80°C in an atmosphere of argon, taking samples periodically and analyzing them by TLC and GLC-MS. Practically complete conversion into the appropriate products occurred during a definite time depending on the substrates (Table 1). At the end of the reaction the sieve was filtered off, washed with benzene, and the filtrate was evaporated at reduced pressure (40°C, 15 mm Hg). The insignificant quantity of starting materials was removed in vacuum (45-50°C, 0.1 mm Hg). The products were oily substances or crystalline compounds. The solid substances were purified by vacuum sublimation or by recrystallization and their ^{1}H NMR spectra were recorded.

X-Ray Structural Investigation. Monocrystals of aldimines **4d** and **6c** were obtained by slow crystallization from a hexane–ethyl acetate, 1:1 mixture. The analysis was carried out at 25°C on a Nonius Kappa CCD automatic diffractometer (MoKα radiation, $2\theta_{max}$ = 55°C). The structures of the indicated compounds were solved by the direct method of [6] and refined by the least squares method in a full matrix anisotropic approach. All the hydrogen atoms were found from a difference synthesis and were refined isotropically. All the calculations were carried out using the set of programs from [7].

N-(2-Furylmethylidene)-2-trifluoromethylaniline (4a). Mass spectrum, *m/z* (I_{rel}, %): 240 (12, $[M + H]^+$), 239 (100, M^+), 238 (68 $[M-H]^+$), 220 (7,$[M-F]^+$), 210 (14, $[M-HCO]^+$), 191 (9), 183 (5), 172 (10, $[M-Fur]^+$), 170 (19, $[M-CF_3]^+$), 145 (59, $[C_6H_4CF_3]^+$), 125 (14), 115 (7), 95 (19), 75 (18), 68 (10, $FurH^+$), 51 (18). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.56 (1H, dd, *J* = 5.0, *J* = 2.0, H-4); 7.00 (1H, d, *J* = 7.6, H-3'); 7.04 (1H, d, *J* = 5.0, H-3); 7.24 (1H, dd, *J* = 5.0, *J* = 2.0, H-5); 7.28 (1H, t, *J* = 7.6, H-5'); 7.52 (1H, t, *J* = 7.6, H-4'); 7.66 (1H, d, *J* = 7.6, H-6'); 8.15 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-2-trifluoromethylaniline (4b). Mass spectrum, *m/z* (I_{rel}, %): 254 (14, $[M+H]^+$), 253 (100, M^+), 252 (47, $M-H]^+$), 238 (9, $[M-Me]^+$), 234 (6, $[M-F]^+$). 218 (18), 211 (6), 210 (22, $[M-MeCO]^+$), 191 (20), 190 (12), 184 (14), 183 (5), 172 (10), 145 (58, $[C_6H_4CF_3]^+$), 125 (15), 95 (22), 81 (14), 75 (18), 69 (9), 53 (29), 52 (13), 51 (24). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 6.17 (1H, dd, *J* = 3.4, *J* = 1.2, H-4); 6.89 (1H, d, *J* = 3.4, H-3); 6.97 (1H, d, *J* = 8.0, H-3'); 7.22 (1H, t, *J* = 8.0, H-5'); 7.50 (1H, t, *J* = 8.0, H-4'); 7.64 (1H, d, *J* = 8.0, H-6'); 8.02 (1H, s, CH=N).

N-(2-Thienylmethylidene)-2-trifluoromethylaniline (4c). Mass spectrum, *m/z* (I_{rel}, %): 256 (16, $[M+H]^+$), 255 (89, M^+), 254 (100, $[M-H]^+$), 236 (6, $[M-F]^+$), 186 (6, $[M-CF_3]^+$), 172 (5), 145 (48, $[C_6H_4CF_3]^+$), 125 (12), 95 (17), 84 (7, $[ThH]^+$), 75 (12), 69 (10), 58 (7), 51 (6). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.04 (1H, d, *J* = 8.0, H-3'); 7.13 (1H, dd, *J* = 5.2, *J* = 3.8, H-4); 7.2-7.3 (2H, m, H-4', H-5'); 7.4-7.6 (2H, m, H-3, H-5); 7.66 (1H, d, *J* = 8.0, H-6'); 8.45 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-2-trifluoromethylaniline (4d). Mass spectrum, *m/z* (I_{rel} %): 270 (15, $[M+H]^+$); 269 (85, M^+), 268 (100, $[M-H]^+$), 250 (5, $[M-F]^+$), 248 (5), 200 (6, $[M-CF_3]^+$), 172 (6), 145 (40, $[C_6H_4CF_3]^+$), 125 (9), 97 (26, $[MeTh]^+$), 95 (17), 77 (11), 69 (12), 53 (11), 51 (8). ^{1}H NMR spectrum, δ, ppm (*J*, MHz): 2.54 (3H, d, *J* = 1.0, CH_3); 6.80 (1H, dd, *J* = 3.8, *J* = 1.0, H-4); 7.03 (1H, d, *J* = 7.8, H-3'); 7.24 (1H, t, *J* = 7.8, H-5'); 7.31 (1H, d, *J* = 3.8, H-3); 7.51 (1H, t, *J* = 7.8, H-4'); 7.51 (1H, d, *J* = 7.8, H-6'); 8.34 (1H, s, CH=N).

N-(2-Pyridylmethylidene)-2-trifluoromethylaniline (5a). Mass spectrum, *m/z* (I_{rel}, %): 250 (2, M^+), 249 (3, $[M-H]^+$), 231 (2, $[M-F]^+$), 223 (1, $[M-CN]^+$), 222 (1, $[M-HCN]^+$), 203 (7, $[M-CN-F-H]^+$), 181 (100, $[M-CF_3]^+$), 172 (5, $[M-Py]^+$), 154 (6), 145 (25, $[C_6H_4CF_3]^+$), 125 (6), 105 (12, $[M-C_6H_4CF_3]^+$), 95 (10), 79 (19, $[PyH]^+$), 78 (14, Py^+), 76 (9), 69 (5, $[CF_3]^+$), 52 (14), 51 (13). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.12 (1H, d, *J* = 8.0, H-3'); 7.32 (1H, t, *J* = 8.0, H-5'); 7.39 (1H, ddd, *J* = 8.0, *J* = 4.8, *J* = 1.1, H-5); 7.57 (1H, t, *J* = 8.0, H-4'); 7.69 (1H, d, *J* = 8.0, H-6'); 7.83 (1H, dt, *J* = 8.0, *J* = 1.4, H-4); 8.27 (1H, dt, *J* = 8.0, *J* = 1.1, H-3); 8.51 (1H, s, CH=N); 8.70 (1H, m, *J* = 4.8, *J* = 1.4, *J* = 1.1, H-6).

N-(3-Pyridylmethylidene)-2-trifluoromethylaniline (5b). Mass spectrum, *m/z* (I_{rel}, %): 251 (14, $[M+H]^+$), 250 (100, M^+), 249 (96, $[M-H]^+$), 231 (7, $[M-F]^+$), 181 (5, $[M-CF_3]^+$), 172 (18, $[M-Py]^+$), 152 (5), 145 (68, $[C_6H_4CF_3]^+$), 125 (13), 115 (5), 105 (9, $[M-C_6H_4CF_3]^+$), 95 (20), 79 (22, $[PyH]^+$), 78 (10, Py^+), 75 (17), 69 (6, $[CF_3]^+$), 63 (14), 51 (22). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.06 (1H, d, *J* = 7.6, H-3'); 7.31 (1H, t, *J* = 7.6, H-5'); 7.43 (1H, dd, *J* = 8.0, *J* = 5.0, H-5); 7.56 (1H, t, *J* = 7.6, H-4'); 7.70 (1H, d, *J* = 7.6, H-6'); 8.33 (1H, dt, *J* = 8.0, *J* = 2.0, H-4); 8.42 (1H, s, CH=N); 8.72 (1H, dd, *J* = 5.0, *J* = 2.0, H-6); 9.00 (1H, dd, *J* = 2.0, *J* = 0.8, H-2).

N-(4-Pyridylmethylidene)-2-trifluoromethylaniline (5c). Mass spectrum, *m/z* (I_{rel}, %): 251 (13, $[M+H]^+$), 250 (100, M^+), 249 (68, $[M-H]^+$), 231 (7, $[M-F]^+$), 172 (47, $[M-Py]^+$), 152 (5), 145 (86, $[C_6H_4CF_3]^+$), 125 (13), 105 (10, $[M-C_6H_4CF_3]^+$), 95 (21), 79 (43, $[PyH]^+$), 78 (10, Py^+), 75 (18), 69 (6, $[CF_3]^+$), 63 (10), 52 (16), 51 (29). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.06 (1H, d, *J* = 7.8, H-3'); 7.33 (1H, t, *J* = 7.8, H-5'); 7.57 (1H, t, *J* = 7.8, H-4'); 7.70 (1H, d, *J* = 7.8, H-6'); 7.77 (2H, dd, *J* = 4.2, *J* = 1.4, H-3, H-5); 8.38 (1H, s, CH=N); 8.78 (2H, dd, *J* = 4.2, *J* = 1.4, H-2, H-6).

N-[3-(2-Furyl)-2-propenylidene]-2-trifluoromethylaniline (6a). Mass spectrum, *m/z* (I_{rel}, %): 266 (10, $[M+H]^+$), 265 (66, M^+), 264 (35, $[M-H]^+$), 246 (4, $[M-F]^+$), 244 (5), 237 (30, $[M-CO]^+$), 236 (100, $[M-HCO]^+$), 224 (43), 216 (19), 211 (33), 196 (18), 172 (16, $M-FurCHCH]^+$), 168 (59), 167 (44), 145 (70, $[C_6H_4CF_3]^+$), 125 (18), 95 (16), 75 (28), 69 (11, $[CF_3]^+$), 66 (29), 65 (41), 51 (32). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.48 (1H, dd, *J* = 5.0, *J* = 2.0, H-4); 6.59 (1H, d, *J* = 5.0, H-3); 6.9-7.1 (3H, m, H-3', CH=CH); 7.28 (1H, t, *J* = 7.8, H-5'); 7.45-7.55 (2H, m, H-5, H-4'); 7.64 (1H, d, *J* = 7.8, H-6'); 8.04 (1H, dd, *J* = 6.8, *J* = 0.6, CH=N).

N-[3-(5-Methyl-2-furyl)-2-propenylidene]-2-trifluoromethylaniline (6b). Mass spectrum, *m/z* (I_{rel}, %): 280 (9, $[M+H]^+$), 279 (51, M^+), 264 (35, $[M-Me]^+$), 244 (12), 236 (42, $[M-MeCO]^+$), 216 (33), 196 (13), 172 (10, $[M-FurCHCH]^+$), 168 (17), 167 (55), 145 (45, $[C_6H_4CF_3]^+$), 125 (14), 107 (10), 95 (19), 77 (22), 69 (7, $[CF_3]^+$), 66 (11), 63 (13), 51 (21). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.35 (3H, s, CH_3); 6.08 (1H, d, *J* = 3.4, H-4); 6.48 (1H, d, *J* = 3.4, H-3); 6.8-7.0 (3H, m, H-3', CH=CH); 7.24 (1H, t, *J* = 8.8, H-5'); 7.50 (1H, t, *J* = 8.8, H-4'); 7.63 (1H, d, *J* = 8.8, H-6'); 8.02 (1H, d, *J* = 8.0, CH=N).

N-[3-(5-Nitro-2-furyl)-2-propenylidene]-2-trifluoromethylaniline (6c). Mass spectrum, *m/z* (I_{rel}, %): 310 (24, M^+), 291 (5, $[M-F]^+$), 265 (17), 264 (100, $[M-NO_2]^+$), 244 (10), 235 (11), 216 (28), 196 (22), 172 (15), 167 (69), 145 (62, $[C_6H_4CF_3]^+$), 125 (12), 107 (5), 95 (17), 75 (15), 69 (2, $[CF_3]^+$), 65 (14), 63 (21), 51 (20). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.76 (1H, d, *J* = 3.8, H-3); 6.96 (1H, d, *J* = 16.0, α-CH); 6.97 (1H, d, *J* = 8.0, H-3'); 7.28 (1H, dd, *J* = 16.0, *J* = 8.6, β-CH); 7.29 (1H, t, *J* = 8.0, H-5'); 7.36 (1H, d, *J* = 3.8, H-4); 7.54 (1H, t, *J* = 8.0, H-4'); 7.66 (1H, d, *J* = 8.0, H-6'); 8.07 (1H, d, *J* = 8.6, CH=N).

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