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SYNTHESIS AND STRUCTURE OF SOME N-[3-(HET)ARYL-2-PROPENYLIDENE]-TRIFLUOROMETHYLANILINES*

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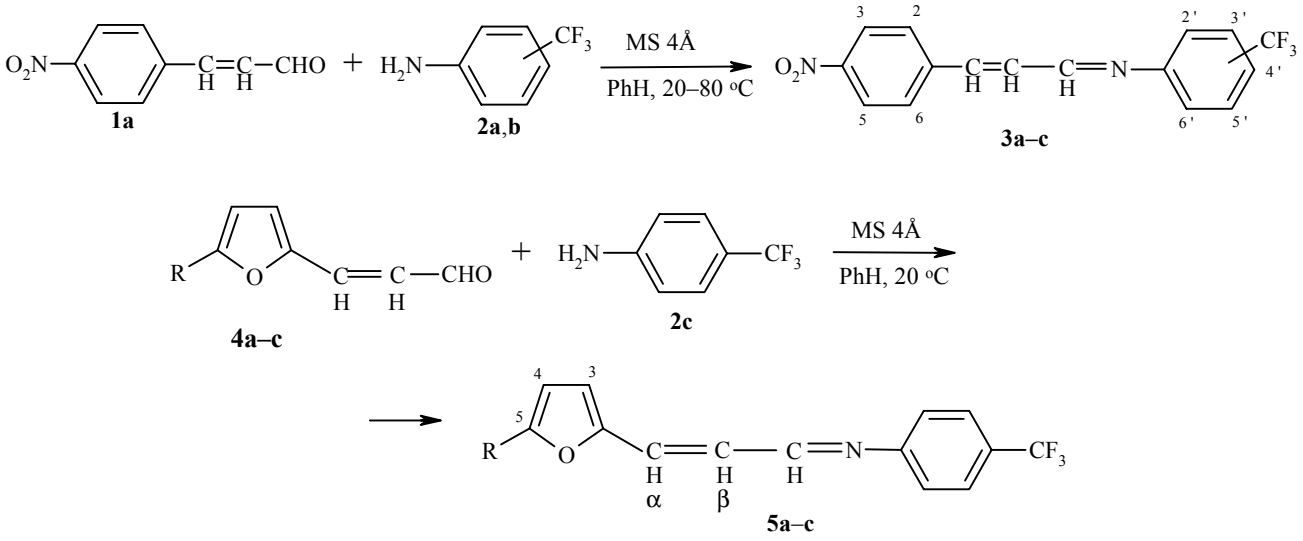
The reactions of 4-nitrocinnamaldehyde with trifluoromethylanilines in the presence of molecular sieves were studied, and a series of new aromatic and heterocyclic aldimines were synthesized. The molecular and crystal structure of some of them were determined by X-ray crystallographic analysis.

Keywords: nitrocinnamaldehyde, Schiff bases, trifluoromethylaniline, furylacrolein, molecular sieves.

We developed a convenient method for the synthesis of a wide series of imines by the condensation of aromatic and heterocyclic aldehydes with anilines in the presence of molecular sieves [1-5]. In these processes the molecular sieves play not only the role of dehydrating agent but also of acid catalyst, which in many cases is active even at room temperature and does not lead (unlike most homogeneous systems) to resinification of the acidophobic substrates. In the present work a series of syntheses were realized by this method, and (hetero)aromatic aldimines with a trifluoromethyl substituent, which are potential biologically active compounds [6] and are also attractive as potential synthons, were obtained.



2, **3** position of CF_3: **a** 2' , **b** 3', **c** 4'; **4, 5 a** R = H, **b** R = Me, **c** R = NO_2

* Dedicated to Prof. A. F. Pozharskii on his 65th birthday.

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The reactions of 4-nitrocinnamaldehyde (**1a**) with 2-, 3-, and 4-trifluoromethylanilines **2a-c** and also of furylacrolein and its 5-methyl and 5-nitro derivatives **4a-c** with 4-trifluoromethylaniline in the presence of 4Å molecular sieves were studied. Earlier we investigated the condensation of furylacroleins with 2- and 3-trifluoromethylanilines [1, 5]. Benzene was used as solvent. The reactions took place at room temperature, and only 2-trifluoromethylaniline (**2a**) required heat (80°C). Apparently the CF_3 group at the closest position to the nitrogen atom of the aromatic amine creates hindrances for condensation. 4-Trifluoromethylaniline is characterized by the highest reactivity. These data agree with the results [1-5] obtained during investigation of the reactions of other aldehydes with 2-, 3-, and 4-trifluoromethylanilines. In the condensation of furylacroleins the most active was the nitro derivative, and the least active was 5-methylfurylacrolein, i.e., the acceptor group in the furan ring promotes reaction through the system of conjugated bonds while the donating group retards it. The occurrence of such processes indicates as in the case of the synthesis of azomethines that the acrylic aldehydes react through nucleophilic attack by the base (the amine) at the carbonyl carbon atom. Here, the acid centers of the molecular sieves clearly activate the aldehydes but do not protonate the bases irreversibly. The latter would hinder condensation. As a result of the work the respective imines N-[(het)arylpropenylidene]-trifluoromethylanilines **3a-c** and **5a-c** were synthesized with yields of 54-82% (Table 1). All the obtained compounds were yellow crystalline substances, and their spectral data (Tables 2 and 3) and elemental analysis (Table 1) corresponded to the structure of the targeted imines.

To determine the molecular and crystal structure of the heterocyclic aldimines **5a-c** single crystals of the compounds were obtained and investigated by X-ray diffraction (Fig. 1-3. Tables 4-11).

The molecules of compounds **5a**,**b** have the *syn-trans-E*-configuration, while the molecule of compound **5c** has the *anti-trans-E*-configuration. In the molecules it is possible to distinguish three planar fragments: the benzene ring, the diene system, and the furan ring. The molecule of **5c** is almost planar; the dihedral angles between the furan and diene fragments and also between the benzene ring and the diene are 2.3 and 11.2° respectively. The corresponding angles in the structures **5a** and **5b** are larger and amount to 9.9 and 22.7° for **5a** and 6.4 and 47.6° for **5b**. The fluorine atoms in the crystal structures of **5b** and **5c** are disordered (Figs. 2 and 3). In both structures the *g* factor for all six atoms F(1), F(2), F(3), F(1'), F(2'), and F(3') is 0.5.

TABLE 1. The Characteristics of the Reactions and of the Synthesized Compounds

Imine	Reaction conditions		Empirical formula (M_{calc})	Found, % / Calculated, %			mp, °C*	Yield, %
	T, °C	Time, h		C	H	N		
3a	80	6	$C_{16}H_{11}F_3N_2O_2$ (320.27)	59.85 / 60.00	3.35 / 3.46	8.65 / 8.75	93-95	60
3b	20	36	$C_{16}H_{11}F_3N_2O_2$ (320.27)	59.90 / 60.00	3.40 / 3.46	8.57 / 8.75	127-129	55
3c	20	24	$C_{16}H_{11}F_3N_2O_2$ (320.27)	59.88 / 60.00	3.32 / 3.46	8.64 / 8.75	136-138	54
5a	20	24	$C_{14}H_{10}F_3NO$ (265.24)	63.17 / 63.40	3.72 / 3.80	5.14 / 5.28	93-94	65
5b	20	25	$C_{15}H_{12}F_3NO$ (279.26)	64.49 / 64.52	4.32 / 4.33	4.89 / 5.02	116-118	56
5c	20	24	$C_{14}H_9F_3N_2O_3$ (310.23)	54.17 / 54.20	2.79 / 2.92	8.92 / 9.03	102-103	82

* Solvents for recrystallization: ethyl acetate–hexane (compounds **3a-c** and **5c**) and hexane (compounds **5a**,**b**).

TABLE 2. The ^{1}H NMR Spectra of the Synthesized Compounds

Com-pound	Chemical shifts, δ, ppm (SSCC, *J*, Hz)		
	CH=N	CH=CH	Ring protons
3a	8.17 (dd, *J* = 1.2, *J* = 5.0)	7.24 (m, *J* = 1.2, *J* = 5.0)	6.98 (1H, d, *J* = 7.8, H-3'); 7.30 (1H, t, *J* = 7.8, H-5'); 7.55 (1H, t, *J* = 7.8, H-4'); 7.67 (1H, d, *J* = 7.8, H-6'); 7.69 (2H, m, *J* = 1.8, *J* = 8.6, H-2, H-6); 8.26 (2H, m, *J* = 1.8, *J* = 8.6, H-3, H-5)
3b	8.30 (dd, *J* = 2.2, *J* = 6.0)	7.24 (m, *J* = 2.2, *J* = 6.0)	7.3-7.4 (2H, m, H-4', H-5'); 7.5-7.6 (2H, m, H-2', H-6'); 7.69 (2H, m, *J* = 8.8, H-2, H-6); 8.27 (2H, m, *J* = 8.8, H-3, H-5)
3c	8.27 (dd, *J* = 2.0, *J* = 6.6)	7.2-7.3 (m, *J* = 2.0, *J* = 6.6)	7.2-7.3 (2H, m, *J* = 8.0, H-3', H-5'); 7.6-7.75 (4H, m, *J* = 8.0, *J* = 8.6, H-2', H-6', H-2, H-6); 8.2-8.35 (2H, m, *J* = 8.6, H-3, H-5)
5a	8.14 (dd, *J* = 4.4)	6.96 (m, *J* = 4.4)	6.49 (1H, dd, *J* = 2.0, 3.6, H-4); 6.60 (1H, d, *J* = 3.6, H-3); 7.19 (2H, m, *J* = 8.4, H-3', H-5'); 7.51 (1H, m, *J* = 2.0, H-5); 7.61 (2H, d, *J* = 8.4, H-2', H-6')
5b*	8.12 (dd, *J* = 4.0)	6.88 (m, *J* = 4.0)	6.09 (1H, d, *J* = 3.8, H-4); 6.49 (1H, d, *J* = 3.8, H-3); 7.18 (2H, m, *J* = 8.2, H-3', H-5'); 7.60 (2H, m, *J* = 8.2, H-2', H-6')
5c	8.22 (d, *J* = 8.0)	6.95 (1H, d, *J* = 16.0, H_α); 7.38 (1H, dd, *J* = 8.0, *J* = 16.0, H_β)	6.80 (1H, d, *J* = 4.2, H-3); 7.24 (2H, m, *J* = 7.8, H-3', H-5'); 7.40 (1H, d, *J* = 4.2, H-4); 7.69 (2H, m, *J* = 7.8, H-2', H-6')

* ^{1}H NMR spectrum: δ 2.36 ppm (CH_3, s).

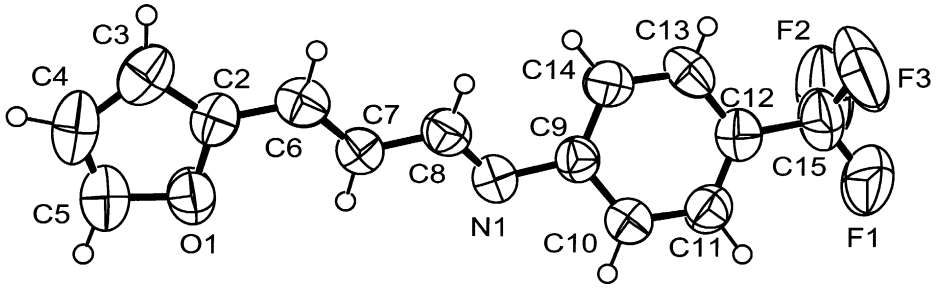

Fig. 1. Three-dimensional model of the N-[3-(2-furyl)-2-propenylidene]-4-trifluoromethylaniline (**5a**) molecule.

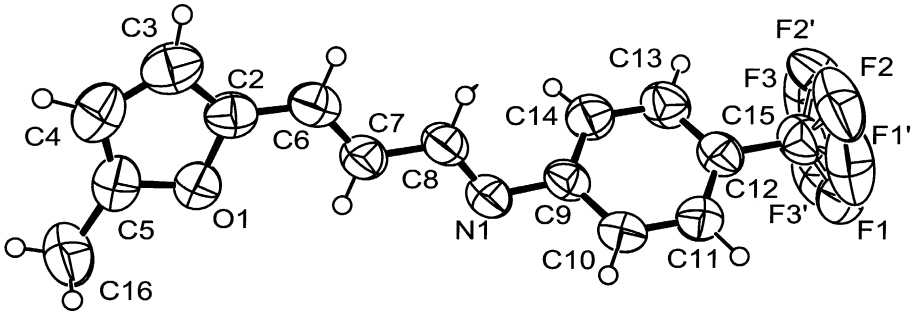

Fig. 2. Three-dimensional model of the N-[3-(5-methyl-2-furyl)-2-propenylidene]-4-trifluoromethylaniline (**5b**) molecule.

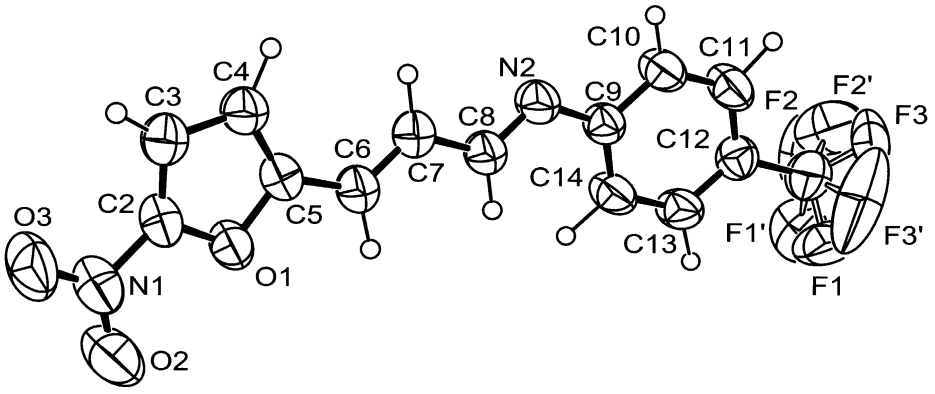

Fig. 3. Three-dimensional model of the N-[3-(5-nitro-2-furyl)-2-propenylidene]-4-trifluoromethylaniline (**5c**) molecule.

During examination of the bond lengths in the central chain of atoms C(Fur)–CH=CH–CH=N–C(Ar) appreciable differences between the single and double bonds are seen in all the molecules (Tables 5, 7, 9, and 11). Thus, the interatomic distances amount to 1.267-1.275 for C=N and 1.324-1.336 Å for C=C, while the length of the C–C single bond between the central atoms of the chain appreciably exceeds these values and amounts to 1.426-1.446 Å.

TABLE 3. The Mass Spectra of the Synthesized Aldimines

Compound	*m/z* (I_{rel}, %)*
3a	320 (38) $[M^+]$, 319 (52) $[M - H]^+$, 303 (14), 289 (25), 274 (28), 273 (100) $[M–H–NO_2]^+$, 261 (5), 253 (7) $[M–H–NO_2– HF]^+$, 234 (5), 222 (5), 205 (10), 204 (30) $[M–H–NO_2–CF_3]^+$, 178 (5), 172 (6), 152 (7), 145 (42) $[C_6H_4CF_3]^+$, 125 (7), 119 (8), 102 (22), 95 (19), 91 (9), 75 (27), 63 (17), 51 (19)
3b	320 (40) $[M^+]$, 319 (59) $[M–H]^+$, 303 (11), 301 (10) $[M–F]^+$, 290 (9), 289 (32) $[M–H–HF]^+$, 274 (25), 273 (100) $[M–H–NO_2]^+$, 272 (39), 261 (8), 252 (3), 251 (3), 204 (20) $[M–H–NO_2–CF_3]^+$, 172 (8), 145 (54) $[C_6H_4CF_3]^+$, 125 (11), 114 (5), 102 (20), 95 (14), 91 (7), 77 (16), 75 (20), 63 (15), 51 (13)
3c	320 (42) $[M^+]$, 319 (58) $[M–H]^+$, 303 (10), 301 (12) $[M–F]^+$, 290 (15), 289 (35) $[M–H–HF]^+$, 274 (22), 273 (100) $[M–H–NO_2]^+$, 272 (47), 204 (20) $[M–H–NO_2–CF_3]^+$, 172 (10), 145 (60) $[C_6H_4CF_3]^+$, 125 (13), 114 (6), 102 (26), 95 (18), 91 (9), 77 (14), 75 (15), 63 (19), 51 (13)
5a	265 (45) $[M^+]$, 264 (24) $[M–H]^+$, 246 (12) $[M–F]^+$, 237 (23), 236 (100) $[M–HCO]^+$, 224 (30), 211 (32), 196 (5) $[M–CF_3]^+$, 185 (3), 172 (6), 168 (17), 167 (39) $[M–HCO–CF_3]^+$, 145 (49) $[C_6H_4CF_3]^+$, 125 (13), 115 (10), 105 (5), 95 (18), 75 (15), 65 (22), 51 (19)
5b	279 (33) $[M^+]$, 278 (30) $[M–H]^+$, 264 (58) $[M–Me]^+$, 260 (11) $[M–F]^+$, 237 (19), 236 (100) $[M–MeCO]^+$, 216 (10) $[M–MeCO–HF]^+$, 196 (3), 168 (11), 167 (57), 145 (40) $[C_6H_4CF_3]^+$, 125 (11), 107 (6), 95 (17), 77 (18), 69 (7) $[CF_3]^+$, 65 (10), 63 (10), 51 (18)
5c	310 (37) $[M^+]$, 291 (15), $[M–F]^+$, 280 (16), 279 (23), 278 (17), 277 (7), 265 (13), 264 (100) $[M– NO_2]^+$, 250 (13), 249 (20), 236 (25), 235 (38), 198 (46) $[M–O_2NC_4H_2O]^+$, 170 (10), 167 (8), 145 (60) $[C_6H_4CF_3]^+$, 125 (13), 121 (6), 95 (18), 83 (9), 81 (15), 79 (14), 75 (15), 69 (10) $[CF_3]^+$, 63 (19), 55 (13)

* The signals of the characteristic ions are given.

TABLE 4. The Crystallographic Data for Compounds **5a-c**

Characteristic	**5a**	**5b**	**5c**
Color	Yellowish	Yellow	Yellow
Size of crystal, mm	0.07×0.28×0.59	0.08×0.12×0.45	0.11×0.18×0.37
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal lattice parameters:			
a, Å	29.925(2)	15.6524(8)	12.4594(6)
b, Å	5.3392(5)	8.7722(5)	14.5882(7)
c, Å	16.092(2)	9.9986(5)	7.5985(3)
β, deg.	101.733(4)	92.518(3)	95.171(2)
Volume of unit cell, *V*, Å^3	2517.4(4)	1371.5(1)	1375.5(1)
Space group	*C* 2/*c*	*P* 2$_1$/*c*	*P* 2$_1$/*c*
Number of molecules in unit cell, *Z*	8	4	4
Density, *d*, g/cm^3	1.400	1.352	1.498
Absorption coefficient, μ, mm^1	0.12	0.11	0.13
Maximum diffraction angle, 2θ$_{max}$, deg	50	55	45
Number of unique reflections	2565	3559	1845
Number of reflections with $I > 3\sigma(I)$	956	1575	1300
Number of refined parameters	212	256	226
Final divergence factor, *R*	0.054	0.050	0.048
Employed programs	[10, 11]	[10, 11]	[9, 11]

TABLE 5. The Main Bond Lengths (*d*) in the Molecules of Compounds **5a-c** (d_{min} = 0.70, d_{max} = 1.60 Å)

Compound **5a**		Compound **5b**		Compound **5c**	
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
1	2	3	4	5	6
N(1)–C(8)	1.273(3)	N(1)–C(8)	1.275(4)	O(1)–C(5)	1.367(3)
N(1)–C(9)	1.418(3)	N(1)–C(9)	1.416(4)	O(1)–C(2)	1.345(3)
C(13)–C(14)	1.383(4)	O(1)–C(5)	1.377(4)	N(2)–(9)	1.417(3)
C(13)–C(12)	1.385(4)	O(1)–C(2)	1.377(4)	N(2)–C(8)	1.267(4)
O(1)–C(2)	1.365(3)	C(8)–C(7)	1.426(4)	C(7)–C(6)	1.325(4)
O(1)–C(5)	1.375(4)	C(10)–C(11)	1.377(4)	C(7)–C(8)	1.442(4)
C(7)–C(8)	1.446(4)	C(10)–C(9)	1.381(4)	C(5)–C(6)	1.436(4)
C(7)–C(6)	1.324(4)	C(14)–C(9)	1.381(4)	C(5)–C(4)	1.365(4)
C(10)–C(9)	1.381(3)	C(14)–C(13)	1.379(5)	O(3)–N(1)	1.221(4)
C(10)–C(11)	1.372(4)	C(11)–C(12)	1.384(4)	C(12)–C(11)	1.384(4)
C(14)–C(9)	1.387(4)	C(7)–C(6)	1.336(5)	C(12)–C(13)	1.365(4)
C(6)–C(2)	1.428(4)	C(6)–C(2)	1.422(4)	C(12)–C(15)	1.497(5)
C(2)–C(3)	1.344(4)	C(12)–C(13)	1.378(5)	C(9)–C(10)	1.373(4)
C(15)–C(12)	1.469(4)	C(12)–C(15)	1.488(4)	C(9)–C(14)	1.394(4)
C(15)–F(3)	1.306(4)	C(5)–C(4)	1.343(6)	N(1)–C(2)	1.421(4)
C(15)–F(1)	1.310(4)	C(5)–C(16)	1.478(6)	N(1)–O(2)	1.224(4)
C(15)–F(2)	1.299(3)	C(15)–F(1)	1.287(10)	C(2)–C(3)	1.339(4)
C(12)–C(11)	1.377(4)	C(15)–F(2)	1.303(8)	C(10)–C(11)	1.387(4)
C(3)–C(4)	1.414(5)	C(15)–F(3)	1.303(11)	C(14)–C(13)	1.382(4)
C(5)–C(4)	1.302(5)	C(15)–F(3')	1.298(10)	C(3)–C(4)	1.410(4)
C(13)–H(13)	0.84(2)	C(15)–F(1')	1.298(8)	F(2)–C(15)	1.318(15)
C(7)–H(7)	0.95(2)	C(15)–F(2')	1.271(8)	F(2)–F(1')	1.51(2)
C(8)–H(8)	0.96(3)	C(2)–C(3)	1.357(5)	F(3)–C(15)	1.301(9)
C(10)–H(10)	0.96(2)	C(4)–C(3)	1.402(6)	F(3)–F(3')	1.17(3)

TABLE 5 (continued)

1	2	3	4	5	6
C(14)–H(14)	0.97(3)	F(1)–F(3')	0.94(2)	F(3)–F(2')	1.39(2)
C(6)–H(6)	0.96(3)	F(1)–F(1')	1.34(2)	F(1)–C(15)	1.273(15)
C(11)–H(11)	0.99(3)	F(2)–F(1')	1.051(13)	F(1)–F(3')	1.34(3)
C(3)–H(3)	0.99(3)	F(2)–F(2')	1.44(2)	C(15)–F(3')	1.30(2)
C(5)–H(5)	1.02(4)	F(3)–F(3')	1.48(2)	C(15)–F(1')	1.286(12)
C(4)–H(4)	0.94(3)	F(3)–F(2')	0.81(2)	C(15)–F(2')	1.237(13)
		C(8)–H(8)	0.94(3)	C(7)–H(7)	1.03(3)
		C(10)–H(10)	0.88(3)	C(6)–H(6)	1.07(3)
		C(14)–H(14)	0.89(4)	C(10)–H(10)	1.03(3)
		C(11)–H(11)	1.00(4)	C(8)–H(8)	1.03(3)
		C(7)–H(7)	0.94(3)	C(14)–H(14)	1.11(4)
		C(6)–H(6)	0.91(3)	C(11)–H(11)	1.12(4)
		C(13)–H(13)	0.96(4)	C(3)–H(3)	0.96(3)
		C(4)–H(4)	0.94(4)	C(13)–H(13)	1.09(4)
		C(3)–H(3)	0.94(5)	C(4)–H(4)	1.08(3)
		C(16)–H(16A)	0.98(8)		
		C(16)–H(16B)	0.89(7)		
		C(16)–H(16C)	0.87(8)		

However, since the last values are rather lower than the classical lengths of single C–C bonds, e.g., in alkanes (1.513-1.542 Å [7]), this indicates that conjugation exists in the indicated chains of atoms.

TABLE 6. The Coordinates of the Non-hydrogen Atoms and their Equivalent Isotropic Temperature Parameters in the Structure of **5a**

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
N(1)	0.47135(12)	0.2371(8)	0.5786(3)	0.073(2)
C(13)	0.34594(16)	0.3078(12)	0.4996(4)	0.081(4)
O(1)	0.62476(11)	0.5355(6)	0.7372(2)	0.086(2)
C(7)	0.53224(15)	0.4795(10)	0.6559(3)	0.067(3)
C(8)	0.48589(17)	0.4486(12)	0.6093(3)	0.070(3)
C(10)	0.41730(17)	0.0110(10)	0.4777(3)	0.071(3)
C(14)	0.38944(17)	0.3593(10)	0.5448(3)	0.075(3)
C(6)	0.54901(16)	0.6903(11)	0.6929(3)	0.073(3)
C(9)	0.42567(14)	0.2100(8)	0.5336(3)	0.061(3
C(2)	0.59460(16)	0.7261(9)	0.7392(3)	0.068(3)
C(15)	0.29077(17)	0.0490(13)	0.4020(4)	0.094(4)
C(12)	0.33792(15)	0.1061(10)	0.4445(3)	0.069(3)
F(3)	0.26734(12)	0.2421(9)	0.3674(3)	0.161(3)
C(11)	0.37405(17)	-0.0411(10)	0.4336(3)	0.073(3)
F(1)	0.28729(12)	-0.1098(9)	0.3390(3)	0.158(3)
F(2)	0.26624(11)	-0.0471(9)	0.4519(2)	0.172(4)
C(3)	0.6160(2)	0.9118(11)	0.7881(4)	0.090(4)
C(5)	0.6657(2)	0.6109(17)	0.7861(4)	0.100(5)
C(4)	0.6616(2)	0.8332(16)	0.8170(4)	0.100(5)

TABLE 7. The Bond Angles (θ) in the Molecules of Compound **5a**

Angle	θ, deg	Angle	θ, deg
C(8)–N(1)–C(9)	120.4(2)	C(2)–C(3)–C(4)	106.7(3)
C(14)–C(13)–C(12)	120.9(3)	O(1)–C(5)–C(4)	110.2(4)
C(2)–O(1)–C(5)	106.5(3)	C(3)–C(4)–C(5)	107.7(3)
C(8)–C(7)–C(6)	124.5(3)	C(14)–C(13)–H(13)	120.(2)
N(1)–C(8)–C(7)	121.2(3)	C(12)–C(13)–H(13)	119.(2)
C(9)–C(10)–C(11)	121.3(3)	C(8)–C(7)–H(7)	114.3(14)
C(13)–C(14)–C(9)	119.6(3)	C(6)–C(7)–H(7)	121.2(14)
C(7)–C(6)–C(2)	125.7(3)	N(1)–C(8)–H(8)	122.(2)
N(1)–C(9)–C(10)	116.1(2)	C(7)–C(8)–H(8)	116.(2)
N(1)–C(9)–C(14)	124.9(3)	C(9)–C(10)–H(10)	119.0(14)
C(10)–C(9)–C(14)	118.9(3)	C(11)–C(10)–H(10)	119.6(14)
O(1)–C(2)–C(6)	117.0(3)	C(13)–C(14)–H(14)	122.(2)
O(1)–C(2)–C(3)	109.0(3)	C(9)–C(14)–H(14)	118.(2)
C(6)–C(2)–C(3)	134.0(3)	C(7)–C(6)–H(6)	121.(2)
C(12)–C(15)–F(3)	114.6(3)	C(2)–C(6)–H(6)	113.(2)
C(12)–C(15)–F(1)	114.4(3)	C(10)–C(11)–H(11)	119.0(15)
C(12)–C(15)–F(2)	113.8(3)	C(12)–C(11)–H(11)	120.9(15)
F(3)–C(15)–F(1)	103.2(3)	C(2)–C(3)–H(3)	124.(2)
F(3)–C(15)–F(2)	104.7(3)	C(4)–C(3)–H(3)	129.(2)
F(1)–C(15)–F(2)	104.9(3)	O(1)–C(5)–H(5)	111.(2)
C(13)–C(12)–C(15)	119.0(3)	C(4)–C(5)–H(5)	139.(2)
C(13)–C(12)–C(11)	119.2(3)	C(3)–C(4)–H(4)	130.(2)
C(15)–C(12)–C(11)	121.8(3)	C(5)–C(4)–H(4)	122.(2)
C(10)–C(11)–C(12)	120.1(3)		

TABLE 8. The Coordinates of the Non-hydrogen Atoms and their Equivalent Isotropic Temperature Parameters in the Structure of **5b**

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
N(1)	0.02553(12)	0.1436(2)	0.6629(2)	0.0695(10)
O(1)	-0.26097(10)	0.12921(19)	0.88222(16)	0.0712(9)
C(8)	0.00292(14)	0.1474(3)	0.7838(3)	0.0669(13)
C(10)	0.14192(15)	0.0437(3)	0.5426(2)	0.0666(13)
C(14)	0.17166(17)	0.2435(3)	0.6992(3)	0.0760(14)
C(11)	0.22723(15)	0.0349(3)	0.5153(3)	0.0681(13)
C(7)	-0.08477(16)	0.1426(3)	0.8169(3)	0.0689(13)
C(9)	0.11368(13)	0.1454(3)	0.6364(2)	0.0608(11)
C(6)	-0.11114(16)	0.1339(3)	0.9419(3)	0.0695(13)
C(12)	0.28512(14)	0.1326(3)	0.5795(2)	0.0656(12)
C(13)	0.25688(17)	0.2377(3)	0.6699(3)	0.0769(15)
C(5)	-0.33765(17)	0.1140(3)	0.9433(3)	0.0781(14)
C(15)	0.37751(17)	0.1224(4)	0.5514(3)	0.0817(17)
C(2)	-0.19714(16)	0.1228(3)	0.9813(2)	0.0691(13)
C(4)	-0.3225(2)	0.0982(4)	1.0758(3)	0.0906(18)
C(3)	-0.2338(2)	0.1036(3)	1.1007(3)	0.0872(17)
F(1)	0.3934(6)	0.089(3)	0.4296(9)	0.164(9)
C(16)	-0.4154(2)	0.1179(6)	0.8539(5)	0.102(2)
F(2)	0.4184(4)	0.0215(15)	0.6253(12)	0.131(5)
F(3)	0.4221(7)	0.2447(12)	0.579(2)	0.182(7)
F(3')	0.3942(6)	0.1951(18)	0.4425(12)	0.138(7)
F(1')	0.4031(4)	-0.0152(7)	0.527(2)	0.151(6)
F(2')	0.4263(4)	0.184(2)	0.6407(11)	0.154(6)

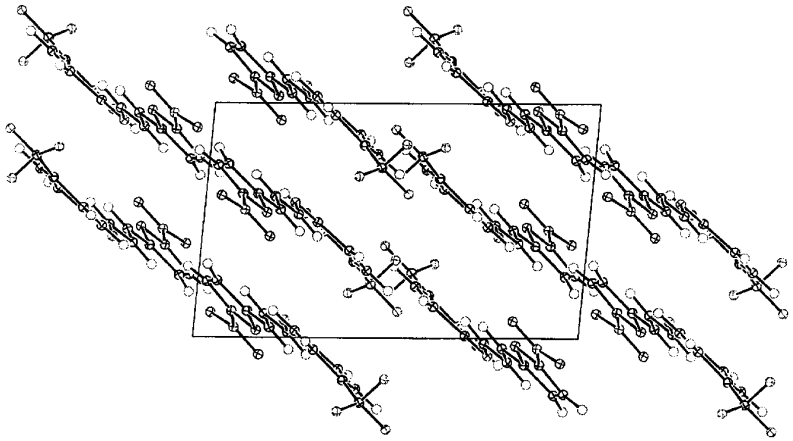

Fig. 4. Projection of the crystal structure of compound **5c** onto the *xz* plane.

In the crystals of all three compounds the molecules are packed at distances not less than the sums of the van der Waals radii of the contacting atoms [8]. Figure 4 shows a fragment of the crystal structure of compound **5c** in a projection onto the *xz* plane.

TABLE 9. The Bond Angles (θ) in the Molecules of Compound **5b**

Angle	θ, deg	Angle	θ, deg
1	2	3	4
C(8)–N(1)–C(9)	119.4(2)	O(1)–C(2)–C(3)	108.5(3)
C(5)–O(1)–C(2)	107.2(3)	C(6)–C(2)–C(3)	133.9(3)
C(9)–C(14)–C(13)	120.2(3)	C(15)–F(1)–F(3')	69.4(10)
C(10)–(11)–C(12)	119.6(3)	C(15)–F(1)–F(1')	59.1(6)
C(8)–C(7)–C(6)	124.0(3)	F(3')–F(1)–F(1')	125.(2)
N(1)–C(9)–C(10)	117.6(2)	C(15)–F(2)–F(1')	65.9(6)
N(1)–C(9)–C(14)	123.2(3)	C(5)–C(4)–C(3)	107.6(4)
C(10)–C(9)–C(14)	119.2(3)	C(2)–C(3)–C(4)	107.6(3)
C(7)–C(6)–C(2)	126.8(3)	C(15)–F(2)–F(2')	54.9(5)
C(11)–C(12)–C(13)	119.7(3)	F(1')–F(2)–F(2')	114.7(10)
C(11)–C(12)–C(15)	119.8(3)	C(15)–F(3)–F(3')	55.1(7)
C(13)–C(12)–C(15)	120.4(3)	C(15)–F(3)–F(2')	69.5(11)
C(14)–C(13)–C(12)	120.3(3)	F(3')–F(3)–F(2')	121.(2)
O(1)–C(5)–C(4)	109.2(3)	C(15)–F(3')–F(1)	68.1(10)
C(14)–C(13)–C(12)	120.3(3)	C(15)–F(3')–F(3)	55.4(6)
O(1)–C(5)–C(4)	109.2(3)	F(1)–F(3')–F(3)	115.(2)
O(1)–C(5)–C(16)	116.1(4)	C(15)–F(1')–F(1)	58.3(6)
C(4)–C(5)–C(16)	134.7(4)	C(15)–F(1')–F(2)	66.5(8)
C(12)–C(15)–F(1)	114.9(6)	F(1)–F(1')–F(2)	118.9(12)
C(12)–C(15)–F(2)	113.0(4)	C(15)–F(2')–F(2)	57.0(6)
C(12)–C(15)–F(3)	115.2(7)	C(15)–F(2')–F(3)	73.8(12)
C(12)–C(15)–F(3')	111.2(6)	F(2)–F(2')–F(3)	124.(2)
C(12)–C(15)–F(3)	115.2(7)	N(1)–C(8)–H(8)	120.(2)
C(12)–C(15)–F(3')	111.2(6)	C(7)–C(8)–H(8)	118.(2)

TABLE 9 (continued)

1	2	3	4
C(12)–C(15)–F(1')	113.6(4)	C(11)–C(10)–H(10)	119.(2)
C(12)–C(15)–F(2')	113.6(6)	C(9)–C(10)–H(10)	120.(2)
F(1)–C(15)–F(2)	105.9(8)	C(9)–C(14)–H(14)	115.(2)
F(1)–C(15)–F(3)	105.3(10)	C(13)–C(14)–H(14)	124.(2)
F(1)–C(15)F(3')	42.4(7)	C(10)–C(11)–H(11)	119.(2)
F(1)–C(15)–F(1')	62.6(8)	C(12)–C(11)–H(11)	121.(2)
F(1)–C(15)–F(2')	128.8(8)	C(8)–C(7)–H(7)	119.(2)
F(2)–C(15)–F(3)	101.1(9)	C(6)–C(7)–H(7)	117.(2)
F(2)–C(15)–F(3')	134.2(7)	C(7)–C(6)–H(6)	117.(2)
F(2)–C(15)–F(1')	47.7(6)	C(2)–C(6)–H(6)	117.(2)
F(2)–C(15)–F(2')	68.1(8)	C(14)–C(13)–H(13)	121.(2)
F(3)–C(15)–F(3')	69.5(9)	C(12)–C(13)–H(13)	119.(2)
F(3)–C(15)–F(1')	129.7(7)	C(5)–C(4)–H(4)	122.(2)
F(3)–C(15)–F(2')	36.7(8)	C(3)–C(4)–H(4)	131.(2)
F(3')–C(15)–F(1')	103.0(9)	C(2)–C(3)–H(3)	122.(3)
F(3')–C(15)–F(2')	104.0(8)	C(4)–C(3)–H(3)	130.(3)
F(1')–C(15)–F(2')	110.4(9)	C(5)–C(16)–H(16A)	116.(4)
O(1)–C(2)–C(6)	117.6(3)	C(5)–C(16)–H(16B)	110.(4)
C(5)–C(16)–H(16C)	115.(4)	H(16A)–C(16)–H(16C)	120.(7)
H(16A)–C(16)–H(16B)	93.(5)	H(16B)–C(16)–H(16C)	97.(5)

TABLE 10. The Coordinates of the Non-hydrogen Atoms and their Equivalent Isotropic Temperature Parameters in the Structure of **5c**

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
O(1)	0.83896(13)	0.95128(12)	0.0315(2)	0.0625(9)
N(2)	0.76870(17)	1.35350(16)	0.0730(3)	0.0637(12)
C(7)	0.8201(2)	1.19683(19)	0.0994(3)	0.0593(14)
C(5)	0.8663(2)	1.03301(17)	0.1115(3)	0.0565(13)
O(3)	0.96041(19)	0.74099(15)	0.1067(3)	0.0979(14)
C(6)	0.8058(2)	1.11116(19)	0.0442(4)	0.0621(15)
C(12)	0.6009(2)	1.57257(19)	-0.1783(3)	0.0614(15)
C(9)	0.7057(2)	1.42464(17)	-0.0108(3)	0.0553(13)
N(1)	0.8969(2)	0.79839(17)	0.0431(4)	0.0753(15)
C(2)	0.9067(2)	0.88911(18)	0.1109(3)	0.0599(14)
C(10)	0.7367(2)	1.5128(2)	0.0317(4)	0.0686(16)
C(8)	0.7561(2)	1.27125(19)	0.0218(3)	0.0582(14)
C(14)	0.6166(2)	1.4115(2)	-0.1328(4)	0.0690(17)
C(11)	0.6864(2)	1.5878(2)	-0.0522(4)	0.0740(17)
C(3)	0.9762(2)	0.9261(2)	0.2358(4)	0.0679(16)
C(13)	0.5654(2)	1.4857(2)	-0.2166(3)	0.0680(16)
C(4)	0.9503(2)	1.0202(2)	0.2373(4)	0.0640(16)
O(2)	0.8268(2)	0.78315(17)	-0.0766(4)	0.1073(17)
F(2)	0.4731(11)	1.6902(10)	-0.188(2)	0.146(9)
F(3)	0.6113(7)	1.7237(6)	-0.2912(19)	0.113(4)
F(1)	0.505(2)	1.6364(8)	-0.4284(15)	0.166(11)
C(15)	0.5493(3)	1.6531(3)	-0.2744(4)	0.082(2)
F(3')	0.6041(12)	1.6715(16)	-0.408(3)	0.209(11)
F(1')	0.4566(8)	1.6327(7)	-0.353(2)	0.131(6)
F(2')	0.529(2)	1.7187(8)	-0.1797(15)	0.189(11)

TABLE 11. The Bond Angles (θ) in the Molecules of Compound **5c**

Angle	θ, deg	Angle	θ, deg
C(5)–O(1)–C(2)	105.5(2)	F(2)–C(15)–F(3')	139.0(12)
C(9)–N(2)–C(8)	120.5(2)	F(2)–C(15)–F(1')	70.6(9)
C(6)–C(7)–C(8)	121.8(2)	F(2)–C(15)–F(2')	36.9(13)
O(1)–C(5)–C(6)	115.6(2)	F(3)–C(15)–F(1)	106.0(10)
O(1)–C(5)–C(4)	109.7(2)	F(3)–C(15)–F(3')	53.2(12)
C(6)–C(5)–C(4)	134.7(3)	F(3)–C(15)–F(1')	130.9(8)
C(7)–C(6)–C(5)	125.8(3)	F(3)–C(15)–F(2')	66.2(11)
C(11)–C(12)–C(13)	120.7(3)	F(1)–C(15)–F(3')	62.6(14)
C(11)–C(12)–C(15)	118.8(3)	F(1)–C(15)–F(1')	39.6(13)
C(13)–C(12)–C(15)	120.5(3)	F(1)–C(15)–F(2')	126.1(12)
N(2)–C(9)–C(10)	116.6(2)	F(3')–C(15)–F(1')	101.5(11)
N(2)–C(9)–C(14)	125.0(2)	F(3')–C(15)–F(2')	116.2(13)
C(10)–C(9)–C(14)	118.4(2)	F(1')–C(15)–F(2')	103.2(12)
O(3)–N(1)–C(2)	117.6(2)	F(1)–F(3')–C(15)	57.7(9)
O(3)–N(1)–O(2)	124.3(3)	F(2)–F(1')–C(15)	55.7(8)
C(2)–N(1)–O(2)	118.1(2)	F(3)–F(3')–F(1)	110.(2)
O(1)–C(2)–N(1)	115.8(2)	F(3)–F(3')–C(15)	63.4(12)
O(1)–C(2)–C(3)	112.7(2)	F(3)–F(2')–C(15)	59.1(9)
N(1)–C(2)–C(3)	131.4(3)	C(6)–C(7)–H(7)	122.(2)
C(9)–C(10)–C(11)	121.6(3)	C(8)–C(7)–H(7)	116.(2)
N(2)–C(8)–C(7)	122.6(2)	C(7)–C(6)–H(6)	118.(2)
C(9)–C(14)–C(13)	120.4(3)	C(5)–C(6)–H(6)	116.(2)
C(12)–C(11)–C(10)	118.6(3)	C(9)–C(10)–H(10)	119.(2)
C(2)–C(3)–C(4)	105.3(3)	C(11)–C(10)–H(10)	119.(2)
C(12)–C(13)–C(14)	120.1(3)	N(2)–C(8)–H(8)	121.(2)
C(5)–C(4)–C(3)	106.8(2)	C(7)–C(8)–H(8)	117.(2)
C(15)–F(2)–F(1')	53.7(7)	C(9)–C(14)–H(14)	121.(2)
C(15)–F(3)–F(3')	63.4(11)	C(13)–C(14)–H(14)	118.(2)
C(15)–F(3)–F(2')	54.7(7)	C(12)–C(11)–H(11)	120.(2)
F(3')–F(3)–F(2')	114.8(12)	C(10)–C(11)–H(11)	120.(2)
C(15)–F(1)–F(3')	59.7(14)	C(2)–C(3)–H(3)	120.(2)
C(12)–C(15)–F(2)	112.2(7)	C(4)–C(3)–H(3)	135.(2)
C(12)–C(15)–F(3)	115.9(5)	C(12)–C(13)–H(13)	116.(2)
C(12)–C(15)–F(1)	115.5(6)	C(14)–C(13)–H(13)	124.(2)
C(12)–C(15)–F(3')	108.0(10)	C(5)–C(4)–H(4)	124.(2)
C(12)–C(15)–F(1')	111.9(6)	C(3)–C(4)–H(4)	129.(2)
C(12)–C(15)–F(2')	115.1(7)		
F(2)–C(15)–F(3)	100.6(8)		
F(2)–C(15)–F(1)	105.1(13)		

EXPERIMENTAL

The ^{1}H NMR spectra were investigated on a Varian Mercury spectrometer (200 MHz) in deuterochloroform with TMS as internal standard. The mass spectra were obtained on an HP 6890 GC/MS chromato-mass spectrometer with an HP 5 MS capillary column (30.0 m × 250 μ × 0.25 μ) at programed temperature from 70 to 260°C (10 deg/min).

Before use the benzene was distilled over CaH_2. The amines supplied by Acros were used without further purification. The aldehydes were recrystallized from benzene or purified by vacuum distillation, after which their properties agreed with published data. The molecular sieves were 4Å (VEB Laborchemie Apolda).

General Method for the Synthesis of the Aldimines 3a-c and 5a-c. In a round-bottom flask with a reflux condenser we placed dry benzene (10 ml) and each of the initial aldehyde and the amine (5 mmol) and then freshly baked molecular sieves (5 g). The reaction was conducted in an atmosphere of argon at room temperature with heating on a water bath at 80°C (Table 1). Samples were taken periodically and analyzed by TLC and GLC MS. At the end of the reaction the sieves were filtered off and rinsed with benzene. The filtrate was evaporated at reduced pressure (40°C/15 mm Hg), and the slight residues of the initial substances were removed under vacuum (45-50°C/0.1 mm Hg). The products were crystalline substances. They were purified by recrystallization from hexane or its mixture with ethyl acetate, and their ^{1}H NMR spectra were recorded.

X-ray Crystallographic Investigations. Single crystals of compounds **5a-c** were obtained by slow crystallization from a 1:1 mixture of benzene and hexane. The diffraction patterns were recorded at 20°C on a Nonius KappaCCD automatic diffractometer (Mo*K*α radiation). The structures of compounds **5a-c** were interpreted by the direct method and refined by full-matrix least-squares treatment in anisotropic approximation. The calculations were performed with SHELXS 07 [9], SIR 97 [10], and maXus [11] software.

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