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Synthesis of *N*-pentafluorophenyl aromatic aldimines $C_6F_5N{=}CHAr$ and an X-ray structure analysis of *N*-pentafluorophenyl-4-methylphenyl aldimine, $C_6F_5N{=}CHC_6H_4CH_3$-4

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Abstract

N-Pentafluorophenyl aromatic aldimines have been prepared in good yield by the condensation of *N*-sulfinylpentafluoroaniline (obtained from refluxing pentafluoroaniline with excess thionyl chloride) with aromatic aldehydes. The X-ray structural analysis of *N*-pentafluorophenyl-4-methylphenyl aldimine $C_6F_5N{=}CHC_6H_4CH_3$-4 is presented.

Introduction

Imines which have a polar carbon–nitrogen double bond have much potential in organic synthesis. They can serve as useful intermediates and undergo many organic transformations [1, 2]. We have recently reported the synthesis of *N*-perfluoroalkanesulfonyl aromatic imines $R_fSO_2N{=}CHAr$ [3]. During the study of *N*-sulfinylpentafluoroaniline, we prepared some *N*-pentafluorophenyl aromatic aldimines and studied their structure by X-ray methods.

The condensation of benzaldehydes with various amines RNH_2 (R = alkyl or aryl) affords aldimine derivatives [4–8]. Under similar reaction conditions, however, pentafluoroaniline fails to give the corresponding $C_6F_5N{=}CHAr$ due to its low nucleophilicity.

$$C_6F_5NH_2 + ArCHO \longrightarrow \text{no reaction}$$

Although *N*-sulfinylpentafluoroaniline was first prepared in 1968 [9], it has only been extensively studied as far as its physical properties and spectroscopy are concerned, e.g. the effect of the replacement of hydrogen atoms by fluorine on the energy of the NSO group vibrations, the Raman intensities of the aromatic ring vibrations and ^{15}N, ^{17}O, ^{19}F and ^{13}C NMR spectra [10–12], and electron impact mass spectrometries [13], but its chemistry has been little reported [14, 15]. The substitution of hydrogen atoms for fluorine atoms makes the sulfur atom very electrophilic, and it can react easily with aromatic aldehydes affording the title compounds.

Results and discussion

N-Sulfinylpentafluoroaniline (2) is obtained by refluxing pentafluoroaniline (1) with excess thionyl chloride [9]. The condensation reaction of 2 with aromatic aldehydes occurs in benzene under reflux.

$$\underset{(1)}{C_6F_5NH_2} \xrightarrow[\text{reflux/8–10 h}]{SOCl_2\ (\text{excess})}$$

$$\underset{(2)}{C_6F_5NSO} \xrightarrow[\substack{\text{reflux/6 h} \\ 74\text{–}85\%}]{ArCHO/C_6H_6} \underset{(3)}{C_6F_5N{=}CHAr}$$

(**a**) Ar = C_6H_5; (**b**) C_6H_4Me-4; (**c**) C_6H_4OMe-4; (**d**) C_6H_4Br-3; (**e**) $C_6H_4NO_2$-4; (**f**) C_6H_4Cl-4

All the products are colourless solids and their recrystallization from benzene produces fine crystals. In comparison with the moisture-sensitive *N*-perfluoroalkane sulfonyl aromatic imines [3], compounds **3** (Table 1) are very stable since the $C_6F_5N{=}$ group is less electron-withdrawing than the $R_fSO_2N{=}$ group. Attempts to break the nitrogen–carbon double bond failed. For example, heating **3a** with water or alcohol at 60 °C for 4 h led to complete recovery of compound **3a**.

The molecular structure of **3b** and the cell packing map are shown in Figs. 1 and 2, respectively. Selected

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TABLE 1. Preparation of compounds **3**

Product	Temp. (°C)	Time (h)	Yield (%)	M.p. (°C)
3a	80	6	82	109–110
3b	80	6	83	118
3c	80	6	85	124–126
3d	80	6	80	88–90
3e	80	6	74	135–136
3f	80	6	77	122–123

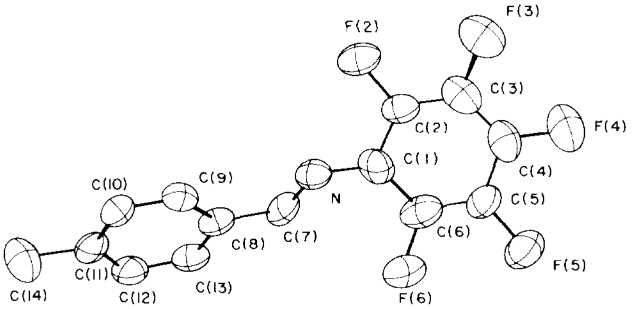

Fig. 1. A view of compound **3b** with the atom-numbering scheme.

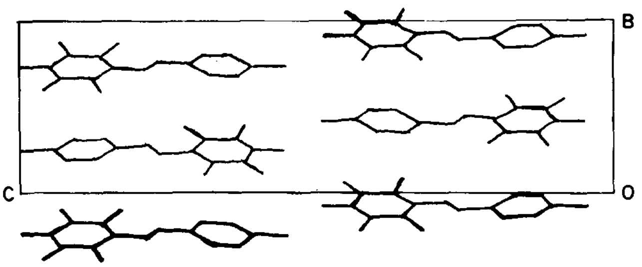

Fig. 2. Molecular packing map of compound **3b**.

bond lengths and angles are listed in Table 2 while the positional and thermal parameters are listed in Table 3.

The C(7)−N bond length of 1.27 Å and the N−C(1) bond length of 1.40 Å are 0.10 Å shorter and 0.03 Å longer than the normal nitrogen–carbon double bond respectively, the latter being indicative of the predominantly double bond character. However, the C(7)–C(8) bond length (1.47 Å) is very close to that of the normal carbon–carbon single bond (1.50 Å). From these bond lengths we can conclude that there is no extended conjugated system in the molecule, and this is compatible with the fact that the phenyl and the pentafluorophenyl planes are not coplanar (the angle between the two planes is 49.2°), also their UV absorption spectrum does not show an obvious red shift ($\lambda_{max} = 272$ nm) (compound **3b**).

The packing map shows that the pentafluorophenyl plane in one molecule is parallel and just overlaps with the phenyl planes in the other two molecules, the phenyl plane also lying between the two pentafluorophenyl

TABLE 2. Bond lengths (Å) and bond angles (°) for compound **3b**

C(2)–C(1)	1.385(9)	C(6)–C(1)	1.384(9)
N–C(1)	1.399(7)	C(3)–C(2)	1.347(9)
F(2)–C(2)	1.358(7)	C(4)–C(3)	1.38(1)
F(3)–C(3)	1.353(8)	C(5)–C(4)	1.36(1)
F(4)–C(4)	1.342(7)	C(6)–C(5)	1.359(8)
F(5)–C(5)	1.343(7)	F(6)–C(6)	1.357(7)
C(8)–C(7)	1.468(8)	N–C(7)	1.271(7)
C(9)–C(8)	1.388(9)	C(13)–C(8)	1.382(9)
C(10)–C(9)	1.38(1)	C(11)–C(10)	1.37(1)
C(12)–C(11)	1.389(9)	C(14)–C(11)	1.52(1)
C(13)–C(12)	1.378(9)	H(7)–C(9)	0.85(7)
H(2)–C(7)	0.91(6)	H(8)–C(12)	0.85(7)
H(1)–C(10)	1.01(6)	H(4)–C(14)	1.0(1)
H(3)–C(13)	0.93(7)	H(6)–C(14)	0.96(9)
H(5)–C(14)	0.9(2)		
C(6)–C(1)–C(2)	115.0(6)	N–C(1)–C(2)	119.2(7)
N–C(1)–C(6)	125.6(7)	C(3)–C(2)–C(1)	123.0(7)
F(2)–C(2)–C(1)	118.7(6)	F(2)–C(2)–C(3)	118.3(7)
C(4)–C(3)–C(2)	120.1(8)	F(3)–C(3)–C(2)	120.8(8)
F(3)–C(3)–C(4)	119.1(7)	C(5)–C(4)–C(3)	119.0(6)
F(4)–C(4)–C(3)	120.9(7)	F(4)–C(4)–C(5)	120.1(7)
C(6)–C(5)–C(4)	120.0(7)	F(5)–C(5)–C(4)	120.3(6)
F(5)–C(5)–C(6)	119.6(7)	C(5)–C(6)–C(1)	122.9(7)
F(6)–C(6)–C(1)	118.6(6)	F(6)–C(6)–C(5)	118.3(6)
N–C(7)–C(8)	123.0(6)	C(9)–C(8)–C(7)	119.2(7)
C(13)–C(8)–C(7)	122.0(6)	C(13)–C(8)–C(9)	118.8(7)
C(10)–C(9)–C(8)	120.7(8)	C(11)–C(10)–C(9)	120.9(8)
C(12)–C(11)–C(10)	118.1(7)	C(14)–C(11)–C(10)	120.2(8)
C(14)–C(11)–C(12)	121.6(8)	C(13)–C(12)–C(11)	121.6(7)

TABLE 3. Positional and thermal parameters with estimated standard deviations for compound **3b**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C(1)	−0.381(1)[a]	0.4069(9)	0.1842(2)	0.048(3)
C(2)	−0.190(1)	0.4795(8)	0.1644(2)	0.053(4)
C(3)	−0.147(1)	0.4841(9)	0.1147(3)	0.060(5)
C(4)	−0.296(1)	0.415(1)	0.0812(2)	0.059(4)
C(5)	−0.488(1)	0.3439(9)	0.0988(2)	0.054(4)
C(6)	−0.529(1)	0.3422(8)	0.1490(2)	0.048(3)
C(7)	−0.581(1)	0.4427(9)	0.2568(2)	0.050(4)
C(8)	−0.623(1)	0.4269(9)	0.3108(2)	0.047(3)
C(9)	−0.825(1)	0.4838(9)	0.3300(3)	0.054(5)
C(10)	−0.866(1)	0.479(1)	0.3809(2)	0.056(4)
C(11)	−0.711(1)	0.4140(9)	0.4138(2)	0.054(4)
C(12)	−0.511(1)	0.356(1)	0.3944(2)	0.055(4)
C(13)	−0.466(1)	0.3626(8)	0.3437(2)	0.050(4)
C(14)	−0.756(2)	0.416(2)	0.4698(3)	0.084(6)
N	−0.4022(9)	0.3917(6)	0.2363(2)	0.051(3)
F(2)	−0.0402(6)	0.5533(5)	0.1962(1)	0.071(2)
F(3)	0.0415(7)	0.5584(5)	0.0971(1)	0.080(2)
F(4)	−0.2549(8)	0.4160(6)	0.0316(1)	0.087(3)
F(5)	−0.6340(6)	0.2710(6)	0.0671(1)	0.079(2)
F(6)	−0.7175(6)	0.2644(5)	0.1654(1)	0.063(2)

[a] Numbers in parentheses are estimated standard deviations for the last digits.

planes. The distance between the two parallel planes is 3.37 Å. These alternate overlapped molecules suggest some interaction between the π-electron systems. The average volume per non-H atom is 15.2 Å^3. On the basis of the above fact, it may be concluded that the molecular packing in the cell is very dense.

Experimental

Melting points were measured on a Thiele apparatus and are reported uncorrected. Benzene was purified before use. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Varian 360L instrument using Me_4Si and CF_3COOH as internal and external standards, respectively. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan GC–MS 4021 instrument. Elemental analyses were performed by the Analysis Department of this Institute.

The following general procedure was used for the synthesis of compounds **3**. A solution of phenyl aldehyde (1.15 ml, 9.0 mmol) in 5 ml of dry benzene was added dropwise to a solution consisting of 2.10 g of C_6F_5NSO (9.2 mmol) [9] in 10 ml of dry benzene in a 25 ml flask equipped with a reflux condenser, drying tube and magnetic stirring bar. The reaction mixture was stirred for 6 h at 80 °C. Pure **3a** (2.23 g) was obtained by recrystallization from benzene. Other *N*-pentafluorophenyl aromatic aldimines were prepared similarly.

$C_6F_5N{=}CHC_6H_5$ (**3a**): IR(ν_{max} cm^{-1}): 3030 (w); 1630 (m); 1500 (s); 1000 (m); 970 (s); 750 (m); 690 (m). ^{1}H NMR δ: 9.03 (s, =CH); 7.78–8.33 (m, 5H arom) ppm. ^{19}F NMR δ: 84.4 (d, 2F); 93.8 (t, 1F); 95.8 (t, 2F) ppm. MS (*m/z*, %): 272 (M + 1, 10.57); 271 (M, 100.00); 270 (M − 1, 83.61); 194 (M − C_6H_5, 10.72); 167 (C_6F_5, 8.07); 77 (C_6H_5, 54.31). Analysis: $C_{13}H_6F_5N$ requires: C, 57.56; H, 2.39; N, 5.17%. Found: C, 57.58; H, 2.20; N, 4.85%.

$C_6F_5N{=}CHC_6H_4Me$-4 (**3b**): IR (ν_{max} cm^{-1}): 3030 (w); 2940 (w); 1630 (m); 1600 (m); 1500 (s); 1000 (m); 975 (s); 760 (m); 700 (m). ^{1}H NMR δ: 8.50 (s, =CH); 7.17–7.85 (AA'BB', 4H arom); 2.37 (s, CH_3) ppm. ^{19}F NMR δ: 84.2 (d, 2F); 93.5 (t, 1F); 95.7 (t, 2F) ppm. MS (*m/z*, %): 286 (M + 1, 15.73); 285 (M, 100.00); 284 (M − 1, 81.72); 194 (M − C_6H_4Me, 12.71); 167 (C_6F_5, 7.09); 77 (C_6H_5, 27.76). Analysis: $C_{14}H_8F_5N$ requires: C, 58.94; H, 2.81; N, 4.91%. Found: C, 58.92; H, 2.89; N, 5.12%.

$C_6F_5N{=}CHC_6H_4OMe$-4 (**3c**): IR (ν_{max} cm^{-1}): 3030 (w); 1630 (m); 1605 (m); 1500 (s); 1260 (m); 1100 (w); 1020 (w); 1000 (m); 970 (s); 840 (m); 820 (m). ^{1}H NMR δ: 8.68 (s, =CH); 7.03–8.05 (AA'BB', 4H arom); 3.91 (s, OMe) ppm. ^{19}F NMR δ: 82.2 (d, 2F); 91.0 (t, 1F); 92.5 (t, 2F) ppm. MS (*m/z*, %): 303 (M + 2, 2.84); 302 (M + 1, 25.70); 301 (M, 100); 300 (M − 1, 46.26); 167 (C_6F_5, 3.60); 77 (C_6H_5, 2.27). Analysis: $C_{14}H_8NF_5O$ requires: C, 55.81; H, 2.66; N, 4.65%. Found: C, 55.90; H, 2.68; N, 4.28%.

$C_6F_5N{=}CHC_6H_4Br$-3 (**3d**): IR (ν_{max} cm^{-1}): 3030 (w); 1630 (m); 1570 (w); 1510 (m); 1500 (s); 1370 (m); 1210 (m); 1000 (m); 970 (s); 900 (w); 790 (m); 780 (w). ^{1}H NMR δ: 8.80 (s, =CH); 7.49–8.20 (m, 4H arom) ppm. ^{19}F NMR δ: 81.8 (d, 2F); 90.0 (t, 1F); 92.5 (t, 2F) ppm. MS (*m/z*, %): 350/352 (M, 69.65/17.97); 349/351 (M − 1, 93.41/100.00); 270 (M − Br, 7.15); 194 (M − C_6H_4Br, 27.71); 155/157 (C_6H_4Br, 17.65/15.63). Analysis: $C_{13}H_5BrF_5N$ requires: C, 44.57; H, 1.43; N, 4.00; F, 27.13%. Found: C, 44.56; H, 1.44; N, 3.60; F, 26.42%.

$C_6F_5N{=}CHC_6H_4NO_2$-4 (**3e**): IR (ν_{max} cm^{-1}): 3030 (w); 2880 (w); 1600 (s); 1510 (s); 1345 (m), 1315 (m); 850 (s); 765 (s); 690 (s). ^{1}H NMR δ: 9.05 (s, =CH); 8.15–8.58 (AA'BB', 4H arom) ppm. ^{19}F NMR δ: 82.0 (d, 2F); 90.1 (t, 1F); 92.5 (t, 2F) ppm. MS (*m/z*, %): 317 (M + 1, 18.71); 316 (M, 100.00); 315 (M − 1, 35.66); 270 (M − NO_2, 3.92); 251 (M − NO_2 − F, 27.93); 167 (C_6F_5, 7.77). Analysis: $C_{13}H_5F_5N_2O_2$ requires: C, 49.37; H, 1.58; N, 8.86; F, 30.06%. Found: C, 49.39; H, 1.63; N, 8.75; F, 30.51%.

$C_6F_5N{=}CHC_6H_4Cl$-4 (**3f**): IR (ν_{max} cm^{-1}): 3030 (w); 1635 (s); 1600 (m); 1570 (m); 1500 (s); 1410 (m); 1380 (w); 1095 (m); 1010 (s); 975 (s); 835 (m); 510 (m). ^{1}H NMR δ: 8.53 (s, =CH); 7.30–7.99 (AA'BB', 4H arom) ppm. ^{19}F NMR δ: 82.2 (d, 2F); 91.0 (t, 1F); 92.5 (t, 2F) ppm. MS (*m/z*, %): 303 (M + 2, 2.84); 302 (M + 1, 25.70); 301 (M, 100.00); 300 (M − 1, 46.26). Analysis requires: C, 51.09; H, 1.64; N, 4.53; F, 30.66%. Found: C, 51.09; H, 1.65; N, 4.58; F, 31.08%.

Crystal data

$C_6F_5N{=}CHC_6H_4Me$-4 (**3b**): $C_{14}H_8NF_5$, M = 285.2, orthorhombic; space group $P2_1\ 2_1\ 2_1$; $a = 6.053(1)$ Å, $b = 7.533(1)$ Å, $c = 26.630(5)$ Å, $V = 1214.2(4)$ Å^3, $Z = 4$; $D_c = 1.56$ g cm^{-3}, $\lambda = 1.5418$ Å (Cu Kα), $\mu = 11.75$ mm^{-1}, $F(000) = 576.0$; crystal dimensions 0.15 × 0.1 × 0.5 mm, Rigaku AFC-5R diffractometer, Cu Kα radiation, $\omega/2\theta$ scanning technique, room temperature. Cell parameters defined by 23 reflections with $19° < 2\theta < 34°$; 742 unique reflections measured with $2\theta_{max} = 120°$, $0 < h < 6$, $0 < k < 8$, $0 < l < 29$. Two standard reflections monitored every 120 reflections were measured but no significant variation was found. The structure was solved by direct methods. Full matrix least-squares refinement was used. Anisotropic temperature factors for non-H atoms (213 variables), 736 observed reflections ($F > 1.92\sigma(F)$) with unit weights were used in refinement to a final R value of 0.040. All computations were performed on a MICROVAX II computer with SHELXS 86 programs.

Atomic scattering factors were taken from *International Tables for X-Ray Crystallography* (1974, Vol. IV).

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