Synthesis and Structure of *N*-Silylated Anilines

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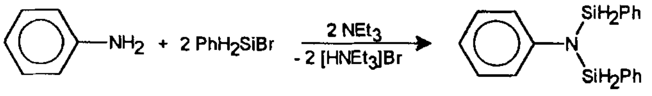
Received December 8, 1993

Key Words: *N*-Silylanilines / Anilines, *N*-silylated

The new *N*-(arylsilyl)anilines **1**–**5** have been obtained by the reaction of aryl(halo)silanes with the corresponding anilines in the presence of the auxiliary base triethylamine. The benzene parts of the anilines have been chosen such that their fluoro, methyl, and methoxy substituents exert different electronic effects. The molecular structures of the monosilylated anilines **3** and **4** have been determined by single-crystal X-ray diffraction analysis. The coordination geometry of the nitrogen atoms have been found to be planar. Heteronuclear NMR spectra (^{1}H, ^{13}C, ^{15}N, ^{29}Si) have been recorded and the structural results correlated with the one-bond coupling constant $^1J(^{29}Si^{15}N)$.

The unusual characteristics of silylamines, like their short Si–N bonds, the planar coordination geometry[1], and the low basicity of the nitrogen atoms led to an intense study of this class of compounds. After a series of classical investigations which led to consistent results for the silylamines[2], the structures of some compounds with a non-standard coordination of silicon and nitrogen[3] and the recent findings of *pyramidal* nitrogen coordination in aminosilanes[4] and silylhydroxylamines[5] have again stimulated activities in this field. In recent papers we have reported on new structural and spectroscopic data of silylamines[6], -hydrazines[7], and hydroxylamines[8], which are assumed to be potential volatile precursors for the chemical vapor deposition (CVD[9]) of silicon nitride and oxynitride. We now attend to *N*-silylated anilines in an effort to delineate the effect of π systems directly attached to the N atom on its coordination geometry in silylamines. By a variation of the substitution pattern of the benzene part of the aniline specific effects were expected to become noticeable at the nitrogen atom.



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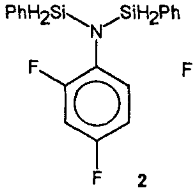

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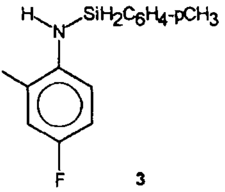

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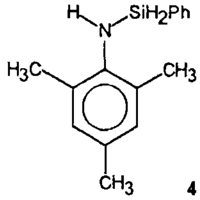

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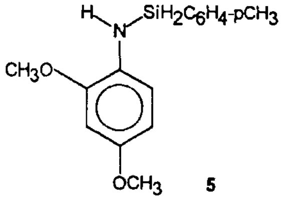

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Preparation of the Silylanilines

Aniline is only partially silylated by reaction with chloro(phenyl)silane in hexane and in the presence of the auxiliary base triethylamine. However, the use of the more reactive bromo(phenyl)silane in an analogous procedure leads to the doubly silylated aniline **1** and considerably improved yield (77%).

2,4-Difluoroaniline, which is less basic at nitrogen than aniline, is silylated even more sluggishly. The reaction with bromo(phenyl)silane proceeds incompletely even if the reaction is carried out in a sealed tube at elevated temperatures. The yield of **2** is only 41% after 2 days at 130°C.

With the less reactive chloro(*p*-tolyl)silane, 2,4-difluoroaniline is found to accept only a single silyl group to give **3**, albeit in high yield (88%). The NH and SiH functions present in the product do not result in any evolution of hydrogen even if the compound is heated to the boiling point.

Likewise, the sterically more shielded 2,4,6-trimethylaniline is monosilylated selectively by chloro(phenyl)silane under mild reaction conditions to give **4**. In an analogous reaction 2,4-dimethoxyaniline is monosilylated to yield the product **5**.

The *N*,*N*-disilylanilines **1** and **2** can be purified by distillation without decomposition.The *mono-N*-silylated compounds **3**, **4**, and **5** are best purified by crystallization, though they do not undergo disproportionation on heating. Compounds **1**–**5** are moisture-sensitive, their hydrolysis leading to the corresponding disiloxanes and the free anilines.

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Crystal Structure of 3 and 4

Crystals of **3** and **4** belong to the monoclinic system, space group $P2_1/n$ and $P2_1/c$, respectively. Both species are present as monomeric molecules in the crystals. The molecular geometries are shown in Figures 1 and 2, respectively, selected bond lengths and angles are listed in Table 1. The nitrogen atoms exhibit a planar coordination geometry. This is in contrast to the pyramidal geometry suggested for *N*-(trimethylsilyl)aniline as deduced from the $^1J(^{15}N^1H)$ coupling constant[10]. Since the $^1J(^{15}N^1H)$ value of **3** is similar to that of *N*-(trimethylsilyl)aniline, this assumption is now lacking direct support and should be revised.

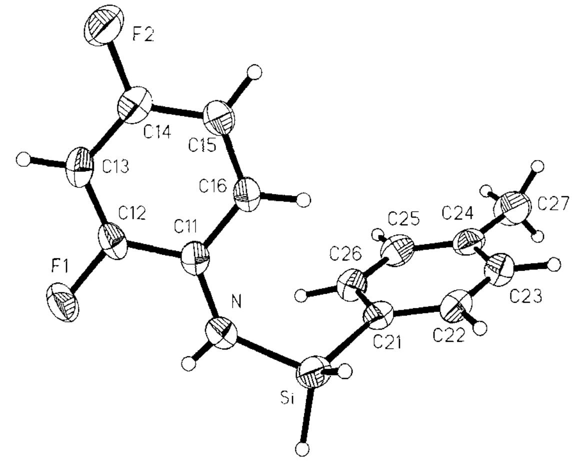

Figure 1. Molecular structure of **3**

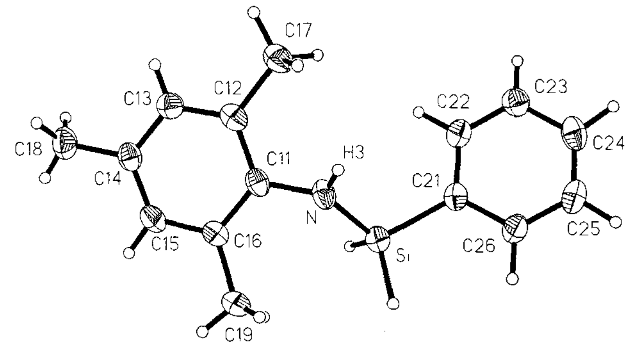

Figure 2. Molecular structure of **4**

The bond angles C11−N−Si in **3** and **4** are expanded at the expense of the angles H3−N−Si and H3−N−C11. Although the electronic nature of the aniline part of the molecules is rather different, the sums of the angles at nitrogen as well as the bond distances N−Si are very similar. By contrast, the bond lengths N−C11 are found to be clearly different. This variation can be ascribed to the relative orientations of the planes of the nitrogen substituents and the plane of the *N*-phenyl ring associated with appreciably different π conjugation. In **3** the dihedral angle Si−N−C11−C6 is only 16.8°, while in **4** it is as high as 48.3°, clearly originating from steric effects. In *N*-(*tert*-butyl phenylfluorosilyl)-*N*-[difluoro(phenyl)silyl]-2,4,6-trimethylaniline[11] an even more severe congestion leads to a nearly orthogonal dihedral angle and an even more stretched N−C bond [147.0(6)] than in the molecules **3** [139.3(2)] and **4** [141.5(3) pm]. In this context it should be noted that the π-bond order N−Ph in *N*-(trimethylsilyl)aniline has been calculated to be 0.4[12].

Table 1. Selected structural data of **3** and **4**

		3	**4**
Bond lengths [pm]:	N-Si	171.9(2)	171.3(2)
	N-C11	139.3(2)	141.5(3)
	Si-C21	185.2(2)	186.0(2)
	N-H3	80(3)	74(3)
Bond angles [°]:	C11-N-Si	127.3(1)	129.5(2)
	H3-N-Si	116(2)	117(2)
	H3-N-C11	116(2)	112(2)
	N-Si-C21	111.2(1)	108.3(1)
Sums of angles at N [°]:		359.3	358.1

Bond lenghts and angles concerning the aniline ring of **4**: C11-C12 139.3(2), C12-C13 137.3(3), C13-C14 137.6(3), C14-C15 137.0(3), C15-C16 138.7(3), C16-C11 1.400 (3) / C16-C11-C12 116.0(2), C11-C12-C13 124.4(2), C12-C13-C14 116.7(2), C13-C14-C15 122.6(2), C14-C15-C16 119.0(2), C15-C16-C11 121.3(2).

The aniline ring of **4** shows a distorted geometry clearly originating from the electron-withdrawing effect of the fluorine substituents. According to the VSEPR model[13], an electronegative substituent causes a widening of the ring angle at the *ipso*-C atom (C12: 124.4°, C14: 122.6°) and a contraction of the C−C bonds including the same atom [C12−C13: 137.3(3), C13−C14: 137.6(3), C14−C15: 137.0(3) pm] as compared with the bond length of 138.1 pm in benzene. The rest of the ring geometry follows the constraints discussed above (see Table 1).

Table 2. Heteronuclear NMR data of the silylanilines
(δ values *J* in Hz)

Compound	$\delta(^{13}C)$,C11	$\delta(^{15}N)$	$\delta(^{29}Si)$	$^1J(^{15}N^{29}Si)$
1	147.7	-345.9	-24.1	13.3
2	111.2	-361.2	-21.6	12.6
3	111.1	-352.9	-34.2	17.6
4	134.6	-351.4	-39.3	18.0
5	129.8	-353.1	-35.8	19.0

NMR Studies

NMR data for four nuclei (^1H, ^{13}C, ^{15}N, ^{29}Si) have been measured. The complete data sets with assignments are given in the experimental section. Selected parameters are listed in Table 2 for comparison.

The $\delta(^{15}N)$-values of the *doubly N*-silylated molecules **1** and **2** differ by about 14 ppm. The higher shielding of the ^{15}N nucleus in **2** is attributed to the effect of the F substituent placed in syn-periplanar orientation. The chemical shift values of the *singly N*-silylated anilines **3**, **4**, and **5** are very similar in $\delta(^{15}N)$ and $\delta(^{29}Si)$ and seem to be independent of the substitution pattern of the aniline rings. These values are explained by a nullification of countercurrent electronic and conformational effects.

The one-bond coupling constants $^1J(^{29}Si^{15}N)$ are found in the expected range indicating the number of silicon atoms attached to nitrogen. We have recently established this correlation and also the influence of bond lengths on $^1J(^{29}Si^{15}N)$[14]. The chemical shifts δ(^{29}Si) show a similar dependence on the degree of silylation of the N atom while δ(^{15}N) seems to be unaffected by this variation.

The fluoroanilines **2** and **3** exhibit characteristic $^nJ(^{19}F^{15}N)$ couplings. In the case of **2** a $^3J(^{15}NCC^{19}F)$ interaction can be resolved, and in the ^{15}N-NMR spectrum of **3** an additional $^5J(^{15}NCCCC^{19}F)$ splitting is detected.

This work has been supported by *Deutsche Forschungsgemeinschaft, Bundesministerium für Forschung und Technologie*, and *Fonds der Chemischen Industrie*. The authors are indebted to Mr. *J. Riede* for carefully establishing the crystallographic data sets.

Experimental

All the reactions were carried out under dry nitrogen. The solvents and triethylamine were dried with CaH_2 and distilled prior to use. All glassware was heated to 160°C, evacuated several times, and filled with dry nitrogen. – NMR: Jeol JNM GX-400, solutions in C_6D_6 at 25°C with internal TMS (^{1}H, ^{13}C, ^{29}Si) and external CH_3NO_2 (^{15}N) as standards. – IR: Perkin Elmer 1650 FT-IR. – Preparation of starting materials: chloro(aryl)silanes[15], bromo(phenyl)silane[16].

N,N-Bis(phenylsilyl)aniline (**1**): A solution of 30.2 ml of bromo(phenyl)silane (0.219 mol) in the same volume of hexane is added dropwise to a solution of 10.0 ml of aniline (0.109 mol, dried with BaO and distilled) and 30.4 ml of triethylamine (0.219 mol) in 400 ml of hexane. The mixture is heated to reflux for 30 min, then cooled and filtered. The solvent is removed from the filtrate under reduced pressure and the liquid residue distilled to yield 25.5 g (77%) of **1**, b.p. 147–149°C/0.01 mbar. – ^{1}H NMR (399.78 MHz): δ = 5.38 (s, 4H, H_2Si), 6.71–6.75 (m, 1H, *p*-C_6H_5N), 6.89–6.93 (m, 2H, *m*-C_6H_5N), 7.02–7.13 [m, 9H, (*m,p*)-C_6H_5Si and *o*-C_6H_5N], 7.52–7.55 (m, 4H, *o*-C_6H_5Si). – $^{13}C\{^1H\}$ NMR (100.54 MHz): δ = 123.5 (s, *p*-C_6H_5N), 125.4 (s, *o*-C_6H_5N), 128.4 (s, *o*-C_6H_5Si), 129.5 (s, *p*-C_6H_5Si), 130.5 (s, *m*-C_6H_5N), 133.7 (s, *i*-C_6H_5Si), 135.0 (s, *m*-C_6H_5Si), 147.7 (s, *i*-C_6H_5N). – $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz): δ = –345.9 [s, ^1J(SiN) = 13.3 Hz]. – ^{29}Si NMR (DEPT, 79.43 MHz): δ = –24.1 [tm, ^1J(SiH) = 212.6 Hz].

2,4-Difluoro-N,N-bis(phenylsilyl)aniline (**2**): 3.9 g of 2,4-difluoroaniline (30.2 mmol), 8.4 ml of triethylamine (60.2 mmol), 7.9 ml of chloro(phenyl)silane (60.4 mmol), and 30 ml of pentane are mixed and the mixture sealed in a thick-walled glass ampoule and heated to 130°C for 2 d in an autoclave filled with pentane. After slowly cooling to ambient temp. the suspension is filtered and the solvent removed from the filtrate under reduced pressure. The residue is distilled to yield 4.2 g (41%) of **2**, b.p. 147°C/0.01 mbar. – ^{1}H NMR (399.78 MHz): δ = 5.23 [d, ^5J(HSiNCCF) = 2.8 Hz, 4H, H_2Si], 6.26 [tm, ^4J(HCCCF) = 7.6 Hz, 1H, 6-H], 6.40 (m, 1H, 5-H), 6.77 [ddd, ^3J(HCCF) = 9.2, ^4J(HCCCH) = 6.1 Hz, 1H, 3-H], 7.09–7.14 [m, 3H, (*m,p*)-C_6H_5Si], 7.50–7.52 (m, 2H, *o*-C_6H_5Si). – $^{13}C\{^1H\}$ NMR (100.54 MHz): δ = 104.7 [dd, ^2J(CCF) = 26.0, ^2J(CCF) = 25.0 Hz, C-3], 111.2 [dd, ^2J(CCF) = 21.8, ^4J(CCCCF) = 3.9 Hz, C-1], 128.3 (s, *o*-C_6H_4Si), 130.0 [dd, ^3J(CCCF) = 9.4, ^3J(CCCF) = 2.5 Hz, C-6], 130.6 [s, *p*-C(SiPh)], 130.8 [dd, ^2J(CCF) = 9.1, ^4J(CCCCF) = 2.9 Hz, C-5], 133.0 [s, *i*-C(SiPh)], 135.2 [s, *m*-C(SiPh)], 158.7 [dd, ^1J(CF) = 247.4, ^3J(CCCF) = 11.0 Hz, C-2], 159.6 [dd, ^1J(CF) = 247.3, ^3J(CCCF) = 12.4 Hz, C-4]. – $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz): δ = –361.2 [d, ^3J(NCCF) = 1.4, ^1J(SiN) = 12.6 Hz]. – ^{29}Si NMR (DEPT, 79.43 MHz): δ = –21.6 [tm, ^1J(SiH) = 214.1 Hz]. – IR (film): ṽ = 2155 cm^{-1} s (vSiH). – MS (GC-coupled), *m/z*: 341 [M$^+$], 262 [M$^+$ – 2H – Ph], 214, 184, 166, 125, 107.

2,4-Difluoro-N-(p-tolylsilyl)aniline (**3**): 5.0 ml of 2,4-difluoroaniline (49 mmol) and 6.8 ml of triethylamine (49 mmol) are dissolved in 100 ml of hexane. Then a solution of 7.45 ml of chloro(*p*-tolyl)silane (49 mmol) in 10 ml of hexane is added dropwise. The mixture is stirred for 4 h, then filtered and distilled to remove the solvent. The residue is crystallized by cooling it rapidly to –196°C (liquid nitrogen) to generate crystal nuclei, then allowed to melt partially and recrystallized at –20°C. Liquid impurities are withdrawn by a pipette, and the crystalline material is washed at –78°C with small amounts of cold pentane. Yield: 10.73 g of **3** (88%), m.p. 13°C. – ^{1}H NMR (399.78 MHz): δ = 2.10 (s, 3H, H_3C), 3.56 (s, 1H, HN), 5.00 (m, 2H, H_2Si), 6.34–6.40 (m, 1H, 6-H), 6.51–6.57 (m, 2H, 3- + 5-H), 6.98 [d, ^3J(HCCH) = 7.5 Hz, 2H, *o*-C_6H_5], 7.40 (d, 2H, *m*-C_6H_5). – $^{13}C\{^1H\}$ NMR (100.54 MHz): δ = 21.4 (s, CH_3), 103.9 [dd, ^2J(CCF) = 26.2, ^2J(CCF) = 23.4 Hz, C-3], 111.1 [dd, ^2J(CCF) = 22.1, ^4J(CCCCF) = 3.7 Hz, C-1], 116.6 [dd, ^2J(CCF) = 8.7, ^4J(CCCCF) = 4.1 Hz, C-5], 128.1 (s, *o*-C_6H_4Si), 129.4 (s, *p*-C_6H_4Si), 131.5 [dd, ^3J(CCCF) = 12.9, ^3J(CCCF) = 3.2 Hz, C-6], 135.0 (s, *m*-C_6H_4Si), 140.9 (s, *i*-C_6H_4Si), 152.3 [dd, ^1J(CF) = 241.3, ^3J(CCCF) = 11.5 Hz, C-2], 160.3 [dd, ^1J(CF) = 239.5, ^3J(CCCF) = 11.0 Hz, C-4]. – ^{15}N NMR (DEPT, 40.51 MHz): δ = –352.9 [dddm, ^1J(NH) = 80.3, ^3J(NCCF) = 1.0, ^5J(NCCCCF) = 0.6, ^1J(SiN) = 17.6 Hz]. – ^{29}Si NMR (DEPT, 79.43 MHz): δ = –34.2 [ttm, ^1J(SiH) = 214.0, ^3J(SiCCH) = 5.9 Hz]. – IR (film): ṽ = 3416 cm^{-1} m (vNH), 2151 s (vSiH).

2,4,6-Trimethyl-N-(phenylsilyl)aniline (**4**): 10.0 ml of 2,4,6-trimethylaniline (71 mmol) and 19.7 ml of triethylamine (142 mmol, 100% excess) are dissolved in 400 ml of hexane. Then 18.6 ml of chloro(phenyl)silane (141 mmol, 100% excess) is added to the solution. The mixture is heated to reflux for 3 h, cooled to 0°C and filtered, and the solvent is removed from the filtrate under reduced pressure. The oily residue is cooled to –21°C to crystallize, liquid material is pipetted off, and the solid is recrystallized at 4°C. By repeating this procedure three times, pure **4** is obtained (16.2 g, 94%), m.p. 16–18°C. – ^{1}H NMR (399.78 MHz): δ = 1.84 (s, 3H, 4-CH_3), 1.87 (s, 6H, 2,6-CH_3), 4.90 [d, ^3J(HSiNH) = 3.1 Hz, 2H, H_2Si], 6.42 (s, 2H, 3,5-H), 6.80–6.85 [m, 3H, (*m,p*)-C_6H_5], 7.24–7.27 (m, 2H, *o*-C_6H_5). – $^{13}C\{^1H\}$ NMR (100.54 MHz): δ = 19.5 (s, 2,6-CH_3), 20.7 (s, 4-CH_3), 128.4 (s, *o*-C_6H_5), 129.7 (s, C-3/5), 130.3 (s, *p*-C_6H_5), 130.5 (s, C-2/6), 134.2 (s, C-4), 134.6 (s, *i*-C_6H_5), 134.9 (s, *m*-C_6H_5), 139.9 (s, C-1). – $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz): δ = –351.4 [s, ^1J(SiN) = 18.0 Hz]. – ^{29}Si NMR (DEPT, 79.43 MHz): δ = –39.3 [ttm, ^1J(SiH) = 210.7, ^3J(SiCCH) = 6.1 Hz]. – IR (film): ṽ = 3468 cm^{-1} w und 3389 w (vNH), 2153 s (vSiH).

2,4-Dimethoxy-N-(p-tolylsilyl)aniline (**5**): 4.9 ml (32 mmol) of chloro(*p*-tolyl)silane is added dropwise to a solution of 5.0 g of 2,4-dimethoxyaniline (32 mmol) and 4.52 ml of triethylamine (32 mmol) in 70 ml hexane/diethyl ether (2:1). The mixture is heated to reflux for 1 h and filtered. The solvent is removed from the filtrate under reduced pressure, and the residue is purified by crystallization as described for **4**. 5.97 g (68%) of **5** is obtained, m.p. 27–29°C. – ^{1}H NMR (399.78 MHz): δ = 2.07 (s, 3H, H_3CC), 3.28 (s, 3H, 4-CH_3O), 3.38 (s, 3H, 2-CH_3O), 5.26 [d, ^3J(HSiNH) = 2.4 Hz, 2H, H_2Si], 6.21 [d, ^3J(HCCH) = 8.6 Hz, 1H, 5-H], 6.43 (m, 1H, 3-H), 6.75 [d, ^3J(HCCH) = 8.6 Hz, 1H, 6-H], 6.98 [d, ^3J(HCCH) = 7.8 Hz, 2H, *o*-C_6H_4Si], 7.55 [d, ^3J(HCCH) = 7.8 Hz, 2H, *m*-C_6H_4Si]. – $^{13}C\{^1H\}$ NMR (100.54 MHz): δ = 21.2 (s, CH_3C), 54.9 (s, 4-CH_3O), 55.2 (s, 2-CH_3O), 99.9 (s, C-3), 104.3 (s, C-6), 114.6 (s, C-5), 129.3 (s, *m*-C_6H_4Si), 129.8 (s, *i*-C_6H_4Si), 130.5 (s, *p*-C_6H_4Si), 135.0 (s, *o*-C_6H_4Si), 140.3 (s, C-1), 149.2 (s, C-4), 153.5 (s, C-2). – ^{15}N NMR (DEPT, 40.51 MHz): δ = −353.1 [dtd, ^1J(NH) = 79.4, ^2J(NSiH) = 5.1, ^3J(NCCH) = 2.0, ^1J(SiN) = 19.0 Hz]. – ^{29}Si NMR (DEPT, 79.43 MHz): δ = −35.8 [tdm, ^1J(SiH) = 210.6, ^2J(SiNH) = 2.8 Hz].

Crystal Structure Analyses: Single crystals of the compounds **3** and **4** were obtained from the melt diluted with a minimum amount of pentane. They were sealed in glass capillaries under argon and mounted on a CAD4 diffractometer. Crystal and structure solution data are compiled in Table 3. Reduced cell calculations did not indicate a higher cell symmetry. The measured reflections were not corrected for absorption or extinction effects. The structures were solved by Direct Methods and completed by difference Fourier syntheses. After refinement of all non-hydrogen atoms with anisotropic displacement parameters all hydrogen atoms could be located in the difference Fourier maps and were included in the final refinement with isotropic displacement parameters. All computations were carried out with the SHELXTL suite of programs.

Table 3. Crystal data, structure solution and refinement for compounds **3** and **4**

Compound	**3**	**4**
Formula	$C_{13}H_{13}NF_2Si$	$C_{15}H_{19}NSi$
M_r	249.34	241.41
Crystal system	monoclinic	monoclinic
Space group [#]	$P2_1/n$ [14]	$P2_1/c$ [14]
a [Å]	6.808(1)	11.251(2)
b [Å]	18.424(2)	17.559(1)
c [Å]	10.069(2)	16.366(2)
β [°]	94.72(1)	92.44(1)
Z	4	4
V [$Å^3$]	1258.6(4)	1390.6(3)
$\rho_{calc.}$ [g/cm^3]	1.316	1.153
F(000) [e]	520	520
μ(Mo-K_α) [cm^{-1}]	1.9	1.5
Radiation	Mo-K_α	Mo-K_α
T	-80°C	-80°C
Scan	ω	ω
Scan width (ω) deg	0.8 + 0.35tanΘ	0.7 + 0.35tanΘ
hkl range	9, -24, ±13	14, 9, ±20
Measured reflections	3384	3416
Unique reflections	2717	2685
$R_{int.}$	0.0098	0.0195
H atoms found	all	all
Observed reflections $F_o \geq 3\sigma(F_o)$	2277	2229
Refined parameters	206	230
R/R_w	0.0404/0.0426	0.0439/0.0546
$\Delta\rho_{max./min.}$ [e/$Å^3$]	0.26 /-0.24	+0.27 /-0.27

Further information on the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58044, the names of the authors, and the journal citation.

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