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X-ray analysis and NMR-studies of *E*- and *Z*-1,2-bis(fluorodimethylsilyl)-1,2-diphenylethenes

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Abstract

The *E*- and *Z*-isomers (**1a,1b**) of 1,2-bis(fluorodimethylsilyl)-1,2-diphenylethene have been investigated by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, mass spectrometry and single crystal X-ray structure analysis. The NMR spectra of both compounds were markedly different, caused by the non-equivalence of all methyl groups and through non-bonding F–F interactions (through-space coupling) in isomer **1b**. X-ray investigations reveal a widening of the C=C-Si angles at the expense of Si–C–Ph; the C=C bond of the *Z*-isomer is lengthened to 135.4(2) pm. © 1998 Elsevier Science S.A.

Keywords: Fluorine; Silicon; NMR; X-Ray analysis of *E*- and *Z*-(ethylene)isomers; Through-space coupling

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1. Introduction

The synthesis of the *Z*-isomer **1b** of the title compound has already been published in the course of studies of the twofold silylation of acetylenes by disilanes [1]. The bidentate Lewis acid **1b** would be expected to be a strong organic host for fluoride ion in organic solvents, an important feature which has been observed for similar *ortho*-disilylbenzenes [2,3]. This note describes a comparison of the *E*- and *Z*-isomers by NMR studies and X-ray crystallographic analysis.

2. Results and discussion

Chemical shifts of fluorine atoms bonded to silicon are related to the coordination geometry of the silicon atom. Typical $\delta(^{19}\text{F})$ values for fluorine species involving tetracoordinate silicon lie between -120 and -160 ppm whereas Si–F compounds with pentacoordinate silicon exhibit $\delta(^{19}\text{F})$ values between -80 and -140 ppm [4]. The ^{19}F NMR data of **1a** and **1b** indicated a tetrahedral character and thus excluded interaction of silicon with two fluorine atoms, a phenomenon which was reported recently by Ebata et al. for hexakis(fluorodimethylsilyl)benzene [5]. All the NMR data (^{1}H, ^{13}C and ^{19}F) of the *E*-isomer **1a** were in agreement with expectation, whereas the *Z*-isomer **1b** exhibited coupling between the fluorine atoms, as observed by proton-decoupled ^{19}F NMR studies. The ^{19}F-NMR spectrum displayed (a) a strong singlet at -153.8 ppm from the two fluorine atoms bonded to two ^{28}Si atoms and (b) the AB part of an ABX spin-system, from the fluorine atom bonded to ^{29}Si interacting with fluorine bonded to ^{28}Si in the same molecule ($J(\text{FF}) = 21.59$ Hz). This kind of long-range coupling may be interpreted as through-space interaction.

Pairs of fluorine atoms that are forced into intramolecular proximity are well-known to exhibit unusually large F–F spin–spin coupling constants in their ^{19}F-NMR spectra [6,7].

Such F–F coupling shows a strong inverse dependence on the F–F distance, because such interactions involve overlapping of lone pair orbitals from the two atoms [8], a possibility which exists only for isomer **1b**. Cases of five-bond F–F coupling were also observed for

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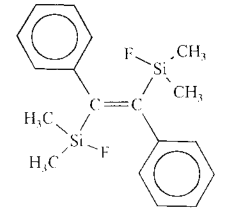
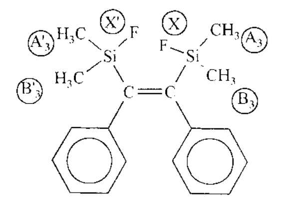
other molecules containing the F-Si-C=C-Si-F moiety and similar values were obtained [9], whereas 1-methyl-4,5-difluorophenanthrene shows an unusually large five-bond F–F coupling of 174 Hz [10].

The non-equivalence of all methyl groups in **1b** was concluded from ^{1}H- and ^{13}C-NMR spectra which were of higher order and may be rationalized by assuming hindered rotation about the C–Si bonds, caused by steric effects.

The proton-coupled ^{19}F NMR spectrum of **1b** displayed an $A_3A'_3B_3B'_3XX'$ spin-system and the coupling constants were determined by the computer simulation program *g-NMR* (Cherwell Scientific Publ., Oxford, UK) (Table 1). The simulated ^{1}H- and ^{19}F-NMR spectra were in a good agreement with the experimental spectra (Fig. 1). The mass spectra of both isomers exhibited the same pattern, $[M]^+$ was the parent ion.

Table 1
NMR spectroscopic data for **1a** and **1b**

			
m.p.: 77 °C **1a**		m.p.: 76 °C **1b**	
δ(^{1}H) (ppm)	J(Hz)	δ(^{1}H) (ppm)	J(Hz)
CH_3 = -0.14(d)	$^3J(HF)$ = 7.71	(A_3) = 0.33	$^4J(HH)$ A_3-B_3 = 1.47
		(A_3') = 0.33	$^7J(HH)$ A_3-A'_3 = 0.01
		(B_3) = 0.28	$^7J(HH)$ A_3-B'_3 = 0.10
		(B_3') = 0.28	$^7J(HH)$ A'_3-B_3 = 0.11
			$^4J(HH)$ A'_3-B'_3 = 1.47
			$^7J(HH)$ B'_3-B_3 = 0.30
H(aryl) 7.13-7.40 (m, 10H)		H(aryl) 6.72-7.00 (m, 4H)	
		7.02-7.09 (m, 6H)	
δ (^{13}C) (ppm)	J(Hz)	δ (^{13}C) (ppm)	J(Hz)
C(methyl) = 0.20(d)	$^2J(CF)$ = 15.8	C(methyl) = -0.01(d)	$^2J(CF)$ = 9.8
C(alkene) = 159.14(d)	$^2J(CF)$ = 14.6	C(alkene) = 157.31(t)	$^2J(CF)$ = 7.3
C(aryl) = 127.12, 128.36,		C(aryl) = 125.83, 128.00,	
128.50, 143.17		128.09, 142.74	
δ (^{19}F) (ppm)	J(Hz)	δ (^{19}F) (ppm)	J(Hz)
-156.6	$^1J(SiF)$ = 281.7	(X) = -153.8	$^3J(HF)$ A_3-X = 7.49
	$^3J(HF)$ = 7.71	(X') = -153.8	$^6J(HF)$ X-A'_3 = 1.89
			$^3J(HF)$ X-B_3 = 7.62
			$^6J(HF)$ X-B'_3 = 0.84
			$^6J(HF)$ A_3-X' = 1.89
^{1}H NMR (200.1 MHz, $CDCl_3$)			$^3J(HF)$ A'_3-X' = 7.49
^{13}C NMR (50.3 MHz, $CDCl_3$)			$^6J(HF)$ X'-B_3 = 0.84
^{19}F NMR (188.3 MHz, $CDCl_3$)			$^3J(HF)$ X'-B'_3 = 7.62
			$^5J(FF)$ X-X' = 21.59

The values for the methyl groups of **1b** $\delta(^1H)$, $J(HH)$, $J(HF)$ and $J(FF)$ were determined by applying a least square matrix calculation (computer simulation).

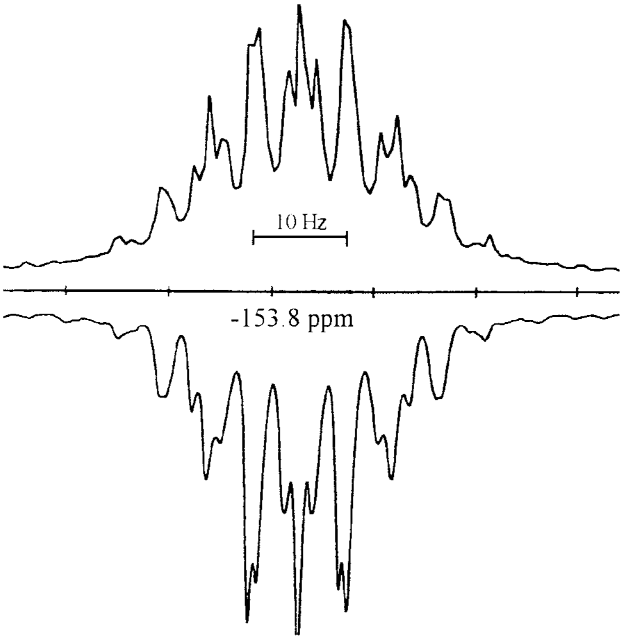


Fig. 1. Experimental (above) and simulated (below) proton-coupled ^{19}F-NMR spectrum of **1b**.

2.1. Molecular structures of **1a** and **1b**

The molecules of **1a** and **1b** are shown in Figs. 2 and 3, respectively; selected bond lengths and angles are listed in Tables 2 and 3. The *E*-isomer **1a** displays crystallographic inversion symmetry with a symmetry-imposed antiperiplanar configuration, whereas in the *Z*-isomer **1b** Si1 and Si2 are almost syn-periplanar (torsion angle Si2–C2–C1–Si1 3.9°).

The bulky $SiMe_2F$ substituents might be expected to lead to distortions of the standard molecular geometry. The C=C double bond in **1b** [C1–C2 135.4(2) pm] is indeed appreciably longer than in **1a** [C1–C1# 132.8(6)

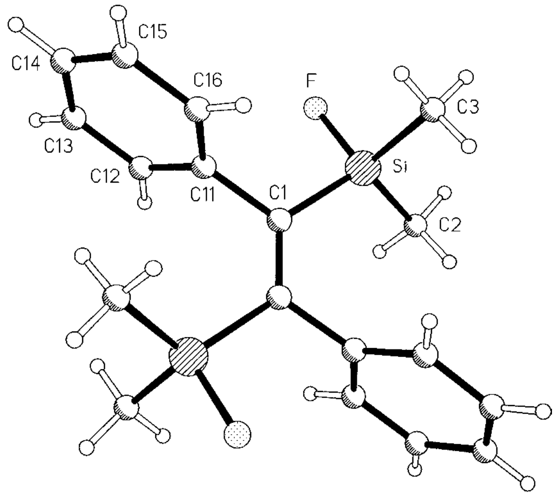


Fig. 2. The structure of molecule **1a** in the crystal. Radii are arbitrary.

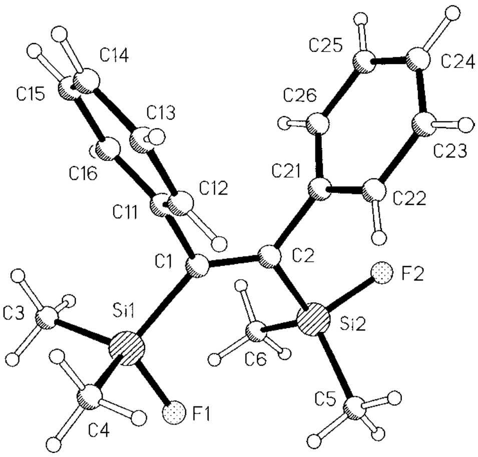


Fig. 3. The structure of molecule **1b** in the crystal. Radii are arbitrary.

pm]. Major effects are also observed on the bond angles at the sp^2 carbons; whereas the C=C-Ph angles are essentially normal (119–121°), the C=C-Si angles are greatly widened (126.8(3)° in **1a**, 128.0(1), 126.7(1)° in **1b**) at the expense of Si–C–Ph (113.5(2), 111.1(1), 113.8(1)° respectively). There is no out-of-plane distortion, the angle sum at all sp^2 carbons being 360°.

The silicon atoms in both molecules show the expected slightly distorted tetrahedral coordination geometry with a maximum deviation of about 8° [**1a**: C2–Si–C1 117.4(2)°]. The Si–F bond lengths in **1a** [Si–F 159.7(2) pm] and **1b** [Si1–F1 159.66(12) pm, Si2–F2 160.11(12) pm] do not differ significantly. The Si–C bond distances in **1a** [188.4(3)] and in **1b** [Si1–C1 187.5(2) pm, Si2–C2 189.1(2) pm] are also comparable and in good agreement with the typical value of 187 pm [11].

2.2. X-ray structure determinations

See Table 4 for crystal data and refinement details.

2.2.1. Data collection and reduction

Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 with LT-2 low temperature attachment). Monochromated Mo K$_\alpha$ radiation was employed. The orientation matrices were refined from setting angles of 54 (**1a**) and 62 (**1b**) reflections in the 2θ range 6–25°. No absorption corrections were applied.

Table 2
Selected bond lengths (pm) and angles (°) for **1a**

Si–F	159.7(2)	Si–C(3)	183.2(4)
Si–C(2)	183.6(3)	Si–C(1)	188.4(3)
C(1)–C(1)#1	132.8(6)	C(1)–C(11)	151.4(4)
F–Si–C(3)	106.8(2)	F–Si–C(2)	105.2(2)
C(3)–Si–C(2)	111.7(2)	F–Si–C(1)	102.91(13)
C(3)–Si–C(1)	111.73(14)	C(2)–Si–C(1)	117.4(2)
C(1)#1–C(1)–C(11)	119.7(3)	C(1)#1–C(1)–Si	126.8(3)
C(11)–C(1)–Si	113.5(2)		

Symmetry operator: #1 $1-x, -y, 1-z$.

Table 3
Selected bond lengths (pm) and angles (°) for **1b**

Si(1)–F(1)	159.56(12)	Si(1)–C(3)	183.2(2)
Si(1)–C(4)	184.2(2)	Si(1)–C(1)	187.5(2)
Si(2)–F(2)	160.11(12)	Si(2)–C(5)	183.8(2)
Si(2)–C(6)	184.2(2)	Si(2)–C(2)	189.1(2)
C(1)–C(2)	135.4(2)	C(1)–C(11)	150.9(2)
C(2)–C(21)	150.5(2)		
F(1)–Si(1)–C(3)	108.09(11)	F(1)–Si(1)–C(4)	106.33(11)
C(3)–Si(1)–C(4)	112.21(13)	F(1)–Si(1)–C(1)	107.82(7)
C(3)–Si(1)–C(1)	111.30(8)	C(4)–Si(1)–C(1)	110.83(9)
F(2)–Si(2)–C(5)	105.68(11)	F(2)–Si(2)–C(6)	104.89(9)
C(5)–Si(2)–C(6)	113.90(10)	F(2)–Si(2)–C(2)	103.16(7)
C(5)–Si(2)–C(2)	113.22(9)	C(6)–Si(2)–C(2)	114.55(8)
C(2)–C(1)–C(11)	120.91(13)	C(2)–C(1)–Si(1)	128.02(12)
C(11)–C(1)–Si(1)	111.06(10)	C(1)–C(2)–C(21)	119.53(14)
C(1)–C(2)–Si(2)	126.67(12)	C(21)–C(2)–Si(2)	113.79(11)

2.2.2. Structure solution and refinement

The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G.M. Sheldrick, Universität Göttingen). H atoms were included using a riding model or rigid methyl groups. The weighting schemes were of the

Table 4
Crystal data and refinement details for compounds **1a** and **1b**

Complex	**1a**	**1b**
Formula	$C_{18}H_{22}F_2Si_2$	$C_{18}H_{22}F_2Si_2$
M_r	332.54	332.54
Crystal habit	colorless plate	colorless tablet
Crystal size (mm^3)	$0.7\times0.45\times0.1$	$0.9\times0.8\times0.3$
Temperature (°C)	-100	-100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell constants		
a (pm)	623.0(2)	897.08(8)
b (pm)	1757.1(4)	1725.93(8)
c (pm)	889.1(2)	1221.76(14)
β (°)	109.27(2)	106.184(6)
U (nm^{-3})	0.9187(4)	1.8167(14)
Z	2	4
D_x (mg m^{-3})	1.202	1.216
μ (mm^{-1})	0.205	0.208
$F(000)$	352	704
$2\theta_{max(°)}$	50	55
Reflections measured	1743	4694
Independent reflections	1593	4167
R_{int}	0.023	0.012
$wR(F^2$, all reflections)	0.135	0.114
$R(F>4\sigma(F))$	0.051	0.040
No. of parameters	102	203
S	0.906	1.021
max. Δ/σ	<0.001	<0.001
max. $\Delta\rho$ (e nm^{-3})	547	471

form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein–Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD 406748 (**1a**), 406749 (**1b**).

3. Experimental

The *E*-isomer **1a** was obtained from the *Z*-isomer **1b** [1] by thermal isomerization around 200°C, followed by purification by preparative GLC, silicone DC 550, column temperature 230°C.

The NMR spectra were recorded in $CDCl_3$ at 298 K using a Bruker AC-200 instrument at 200.1 MHz (^1H), 188.3 MHz (^{19}F) and 50.3 MHz (^{13}C) and referenced internally to residual solvent resonances. Electron impact mass spectra were taken from solid samples using a Finnigan MAT 8430 (70 eV) instrument. Melting points were taken in sealed capillaries and are uncorrected (Instrument: Büchi 510).

Acknowledgements

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