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Difluorenylsilane derivatives, a class of compounds exhibiting strong intra- and intermolecular C–H··· π interactions. Crystal and molecular structures of bis(9-methylfluoren-9-yl)dimethylsilane and (9-methylfluoren-9-yl)(fluoren-9-yl) dimethylsilane

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Abstract

The crystal and molecular structures of substituted difluorenyl-(dimethyl)silanes $\text{Me}_2\text{Si}(\text{CR}'\text{R}_2)(\text{CR}''\text{R}_2)$ ($\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$ **1** and $\text{R}' = \text{R}'' = \text{Me}$ **2**, $\text{CR}_2 = \text{fluorenyl}$) have been determined by X-ray diffraction and compared with the conformations available in the gas phase. **1** and **2** crystallize in the $P2(1)/m$ and $P2(1)/c$ space groups with the cell parameters: $a = 7.191 \text{ \AA}$, $b = 17.658 \text{ \AA}$, $c = 8.982 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 101.880^\circ$ (**1**) and $a = 13.132 \text{ \AA}$, $b = 7.463 \text{ \AA}$, $c = 24.438 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 99.73^\circ$ (**2**), respectively. Both compounds as well as the unsubstituted parent silane $\text{Me}_2\text{Si}(\text{CHR}_2)_2$ (**3**) exhibit extensive intramolecular and intermolecular C–H··· π interactions leading to supramolecular associations. Gas phase conformations predicted on the basis of AM1 semiempirical molecular orbital calculations support the existence of these intramolecular interactions and correlate well with the temperature dependent proton NMR spectra. © 2002 Elsevier Science B.V. All rights reserved.

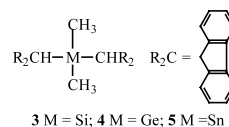
Keywords: Difluorenylsilanes; Crystal structures of; Molecular structures of; Conformational analysis; AM1 semiempirical calculations; Inter- and intramolecular C–H··· π interactions

1. Introduction

The special steric and electronic properties of the fluorenyl group (large size but flat arrangement of atoms and the possibility of strong π -conjugation) make this system a versatile ligand in organometallic chemistry [1–11]. Thus, stabilization of boraalkenes [2,3], phosphaaalkenes [4,5], germenenes [6–9], stannenes [10] or silenes [11] has been enhanced by using this protective group. Significant industrial applications are foreseen also for the C9-bridged fluorenylidene derivatives of zirconium which are considered as precursors of

catalysts for the polymerization of ethylene or propylene [1,12–19].

Most of the derivatives investigated in the cited papers contain only one fluorenyl bound to a main group element. In view of the above mentioned properties of this group, we have been interested in the influence a second fluorenyl group brings to a site already containing one fluorenyl. In this view, we have synthesized the derivatives with general formula $\text{Me}_2\text{M}(\text{CHR}_2)_2$ (where $\text{M} = \text{Si}$, **3**; Ge , **4**; Sn **5** and $\text{CHR}_2 = 9\text{-fluorenyl}$ group) containing two fluorenyl groups bound to the same Group 14 element [20].



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Previously, it was found by molecular orbital calculation (AM1 level) that the parent difluorenylsilane $\text{Me}_2\text{Si}(\text{CR}'\text{R}_2)(\text{CR}''\text{R}_2)$ ($\text{R}' = \text{R}'' = \text{H}$) [21] can adopt four types of conformations which differ by the relative orientations of the R' and R'' groups towards the opposite fluorenyl groups (Scheme 1)

For $\text{Me}_2\text{Si}(\text{CHR}_2)_2$ an H-in-H-out conformation is preferred in solid state [21] and this was also the lowest energy conformer (gas phase) found by AM1 molecular orbital calculations. However, ^1H -NMR spectra could not indicate the presence of only this conformer in solution, which is normal given the small barriers of rotation around the Si–C(fluorenyl) bonds [21]. One of the factors which influences the flexibility of difluorenyl derivatives is the presence of a substituent different than hydrogen at C9 on the fluorenyl groups (see Scheme 3 for atom numbering). Systems of the type $\text{Me}_2\text{Si}(\text{CR}'\text{R}_2)(\text{CR}''\text{R}_2)$ with the fluorenyl groups of **3** partially ($\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$, **1**) or fully ($\text{R}' = \text{R}'' = \text{Me}$, **2**) substituted on C9, were synthesized and reported previously by our group [20]. Herein we report the crystal and molecular structure of **1** and **2** in relation with the 2D-NMR data and semiempirical AM1 calculations on the various conformations of these systems.

2. Results and discussion

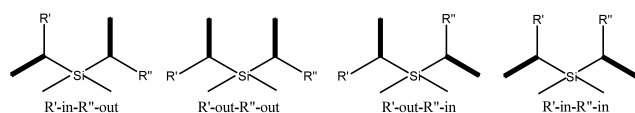
The reaction of $\text{Me}_2\text{Si}(\text{CHR}_2)_2$ (Scheme 2) with one or two equivalents of butyllithium followed by addition of MeI (one or two equivalents) to the reaction mixture affords the monosubstituted $\text{Me}_2\text{Si}(\text{CHR}_2)(\text{CMeR}_2)$ (**1**) and disubstituted $\text{Me}_2\text{Si}(\text{CMeR}_2)_2$ (**2**) derivatives, respectively, [20].

2.1. NMR data and conformational analysis of **1** and **2**

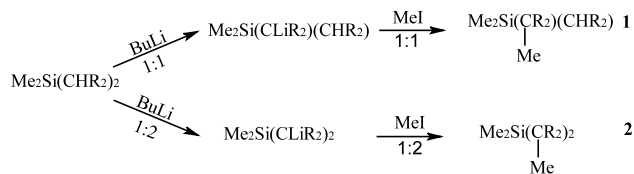
The ^1H - and ^{13}C -NMR spectra of **1** and **2** (Tables 1 and 2) were previously reported [20] but some peculiar features could not be discussed that time due to the lack of more complete experimental data.

As data of Table 1 show, there are remarkable changes in the chemical shift of the proton bound to C9 in the CHR_2 group of $\text{Me}_2\text{Si}(\text{CHR}_2)(\text{CMeR}_2)$ (2.95 ppm) compared with $\text{Me}_2\text{Si}(\text{CHR}_2)_2$ (4.24 ppm). A doublet of doublet at high field is present for some aromatic protons of **1** (Table 3).

The analysis of 2D-NMR spectra recorded for **1** indicates an interaction of the proton H9 with the carbon atoms of the five-membered ring of the opposite



Scheme 1.



Scheme 2.

Table 1
 ^1H chemical shifts (ppm) of $\text{Me}_2\text{Si}(\text{CR}'\text{R}_2)(\text{CR}''\text{R}_2) \cdot (\text{CDCl}_3)$

Compound	δ (CH_3) ₂ Si	δ CHR ₂	δ C(CH_3)R ₂
$\text{Me}_2\text{Si}(\text{CHR}_2)_2$	−0.49 (s, 6H)	4.24 (s, 1H)	
$\text{Me}_2\text{Si}(\text{CHR}_2)\text{C}(\text{CH}_3)\text{R}_2$	0.04 (s, 6H)	2.95 (s, 1H)	1.63 (s, 3H)
$\text{Me}_2\text{Si}[\text{C}(\text{CH}_3)\text{R}_2]_2$	0.27 (s, 6H)		1.17 (s, 6H)

Table 2
 ^{13}C chemical shifts (ppm) of $\text{Me}_2\text{Si}(\text{CR}'\text{R}_2)(\text{CR}''\text{R}_2) \cdot (\text{CDCl}_3)$

Compound	δ (CH_3) ₂ Si	δ CHR ₂	δ C(CH_3)R ₂	δ C(CH_3)R ₂
$\text{Me}_2\text{Si}(\text{CHR}_2)_2$	−6.63	40.47		
$\text{Me}_2\text{Si}(\text{CHR}_2)\text{C}(\text{CH}_3)\text{R}_2$	−3.41	38.66	18.57	44.64
$\text{Me}_2\text{Si}[\text{C}(\text{CH}_3)\text{R}_2]_2$	−10.72		18.39	49.64

Table 3
 ^1H and ^{13}C chemical shifts for aromatic carbons and protons in $\text{Me}_2\text{Si}(\text{CHR}_2)\text{C}(\text{CH}_3)\text{R}_2$ (**2**)

X (X: H, C)	δ ^{13}C	δ ^1H
X4X5	119.53	7.63 (d, 2H; $^3J = 7.4$ Hz)
X4'X5'	120.27	7.83 (d, 2H; $^3J = 7.6$ Hz)
X1'X8'	123.63	7.45 (d, 2H; $^3J = 7.6$ Hz)
X1X8	124.79	6.46 (dd, 2H; $^3J = 7.6$ Hz; $^4J = 1.5$ Hz)
X3X6	125.03	7.19 (t, 2H; $^3J = 7.6$ Hz)
X2X7	125.60	7.03 (td, 2H; $^3J = 7.6$ Hz; $^4J = 1.5$ Hz)
X3'X6'	126.03	7.33–7.43 (m, 4H)
X2'X7'	126.46	
X12'X13'	139.90	
X12X13	140.23	
X10X11	145.61	
X10'X11'	150.26	

fluorenyl group explaining the shielding observed in the 1D-NMR spectrum. This is a clear evidence for a strong C–H $\cdots\pi$ interaction (related with an upfield shift of ca. 1.2 ppm). The doublet of doublet at a surprising high field (6.46 ppm) for an aromatic proton was assigned (also on the basis of 2D-NMR spectra) to the protons bound to carbons 1 and 8. They proved to interact with the protons 2' and 7' of the opposite fluorenyl (Table 3).

^1H -NMR spectra for $\text{Me}_2\text{Si}(\text{CHR}_2)(\text{CMeR}_2)$ show a slight dependence on temperature. The signals that are mostly affected by the increase of the temperature are

Table 4
The variation of H1, H8 and H9 chemical shifts (ppm) with temperature for **1**

Temperature (K)	276	296	316	336	346
H1, H8	6.39, $^3J_{\text{HH}} = 8$ Hz	6.46, $^3J_{\text{HH}} = 8$ Hz	6.51, $^3J_{\text{HH}} = 8$ Hz	6.56, $^3J_{\text{HH}} = 8$ Hz	6.59, $^3J_{\text{HH}} = 8$ Hz
H9	2.92	3.01	3.08	3.15	3.18

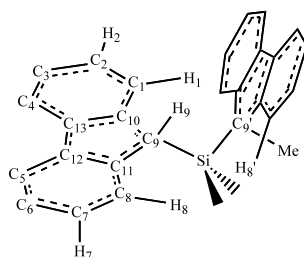
those assigned to protons H9 and H1, H8 (Table 4, see Scheme 3 for atom numbering).

The modifications in the chemical shift of H9 are not impressive (2.92–3.18 ppm), but still indicative of a deshielding of these protons which can be correlated with rotations around the Si–C(flourenyl) bonds. Thus, at 276 K the conformation with dihedral H9C9SiC9' at zero and H9 pointing towards the centre of the opposite fluorenyl (Scheme 4b) is preferred. As the temperature rises, small rotations around the Si–fluorenyl bond bring H9 in positions where it interacts with one of the lateral rings of the opposite fluorene and then, by larger rotations, the in–in conformation is attained.

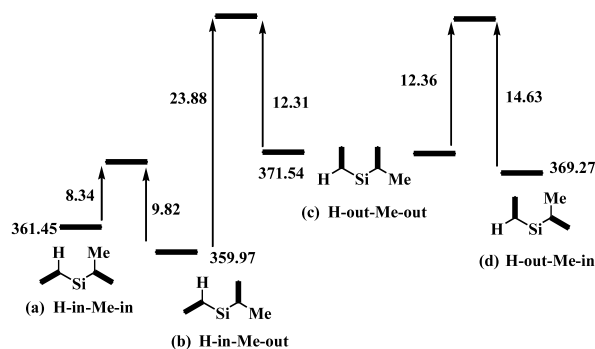
In order to get an insight into these transformations, a conformational analysis of Me₂Si(CHR₂)C(CH₃)R₂ was performed at the semiempirical AM1 level of theory [22] by using SPARTAN 5.1 package of programs [23]. The global minimum obtained by varying the two torsional angles around the Si–C(flourenyl) bonds has been found to correspond to the H-in-Me-out conformation (Scheme 4 for **1**; the fluorenyl rings are schematized by a thick line, all energy values are in kJ mol⁻¹).

This conformer is separated from the H-out-Me-out one by a barrier of 23.88 kJ mol⁻¹ but only by 9.82 kJ mol⁻¹ from the in–in conformer (Scheme 4). This is in agreement with a relatively free rotation around the Si–C(flourenyl–Me) bond which causes the observed deshielding of H9. This means also that the in–out conformation observed in the solid state is determined by the crystal packing forces.

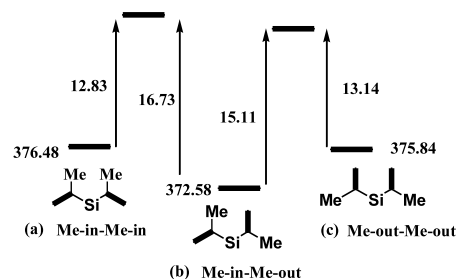
In the ¹H-NMR spectrum of Me₂Si(CMeR₂)₂ there is only one signal for the two methyl groups at C9 and C9' (Table 1); so, at least at room temperature, these groups are equivalent. The AM1 treatment of **2** (Scheme 5) gives a barrier of rotation of 15.11 kJ mol⁻¹ to the out–out conformer and 16.73 kJ mol⁻¹ to the in–in conformer, which are comparable with those found for the rotation of 9-Me-fluorenyl groups in **1** (14.63 kJ



Scheme 3.



Scheme 4.



Scheme 5.

mol⁻¹, Scheme 4) These findings suggest a greater flexibility around the Si–fluorenyl(Me) bond than around the Si–fluorenyl(H) bond in **1** and supports the equivalence of the C9 and C9' methyl groups observed in the ¹H- and ¹³C-NMR spectra of **2**.

2.2. Molecular structures of **1** and **2**

Data collection, crystal data and refinement data for **1** and **2** are summarized in Table 5. Both **1** and **2** crystallize in the monoclinic system (space groups *P2*₁/*m* and *P2*₁/*c*) with 2 and 4 molecules per unit cell, respectively.

Fig. 1 shows the molecular structures of **1** and **2**. The values of bond lengths and bond angles are listed in Tables 6 and 7. For selected geometrical parameters of **3**, see reference [21].

Due to the symmetry, the two Si–Me bonds in **1** are equivalent and the Si–C distances are very close to the values found in **3** (1.855–1.862 Å [21]). These bonds are, however, slightly longer and inequivalent in **2**. Si–C(flourenyl) distances are also somewhat longer in **1**

Table 5

Crystal data and structure refinement data for (9-methylfluoren-9-yl)(fluoren-9-yl) dimethylsilane (**1**) and bis(9-methylfluoren-9-yl) dimethylsilane (**2**)

Data	Me ₂ Si(CHR ₂)C(CH ₃)R ₂ (1)	Me ₂ Si[C(CH ₃)R ₂] ₂ (2)
Empirical formula	C ₂₉ H ₂₆ Si	C ₃₀ H ₂₈ Si
Formula weight	402.58	416.61
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	7.191(1)	13.132(1)
<i>b</i> (Å)	17.658(3)	7.463(1)
<i>c</i> (Å)	8.982(1)	24.438(1)
<i>α</i> (°)	90	90
<i>β</i> (°)	101.88(1)	99.73(2)
<i>γ</i> (°)	90	90
Volume (Å ³)	1116.1(1)	2360.6(10)
<i>Z</i>	2	4
Density (calculated) (mg m ⁻³)	1.198	1.172
Absorption coefficient (mm ⁻¹)	0.118	0.114
<i>F</i> (000)	428	888
Crystal size (mm)	0.24 × 0.20 × 0.16 colorless prism	0.44 × 0.32 × 0.14 colorless-block
<i>θ</i> range for data collection (°)	1.50–30.00	1.50–25.00
Index ranges	0 < <i>h</i> < 10, 0 < <i>k</i> < 24, -12 < <i>l</i> < 12	0 < <i>h</i> < 15, 0 < <i>k</i> < 8, -29 < <i>l</i> < 28
Reflections collected	3586	4341
Independent reflections	3351 (<i>R</i> _{int} = 0.0296)	4148 (<i>R</i> _{int} = 0.0734)
Absorption correct	None	None
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3351/0/143	4148/0/281
Goodness-of-fit on <i>F</i> ²	0.795	0.008
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0512, <i>wR</i> ₂ = 0.1113	<i>R</i> ₁ = 0.0976, <i>wR</i> ₂ = 0.2269
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1313, <i>wR</i> ₂ = 0.1361	<i>R</i> ₁ = 0.2361, <i>wR</i> ₂ = 0.3208
Extinction coefficient	0.005(2)	0.0001(16)
Largest difference peak and hole (e Å ⁻³)	0.186 and -0.236	0.295 and -0.314

System refinement: SHELXL-97 (Sheldrick, 1997); System data collection XSCANS version 2.1 (Siemens, 1994); Diffractometer used: Siemens P4/PC.

and **2** than in the parent molecule **3** (1.907–1.923 Å [21]) in agreement with the increase of the sterical demands brought by the substitution in position 9. The C(fluorenyl)SiC(fluorenyl) angle (105.8° in **3**) increases on substitution at C9 (to 108.8° in **1**) and even more after substitution at C9' of the second fluorenyl (116.2° in **2**).

A notable feature of **1** and **2** is the presence of intramolecular C–H···π interactions [23] facilitated by the relative orientations of the two fluorenyl rings. As a consequence, the H9 proton of **1** and one of the protons of C17 from **2** come very close to the centroid of the opposite fluorenyl ring (2.65 and 2.88 Å, respectively). These interactions stabilize the in–out conformations of **1** and **2** (substituent of C9 oriented in, substituent at C9' oriented out).

2.3. Crystal structures of **1** and **2**

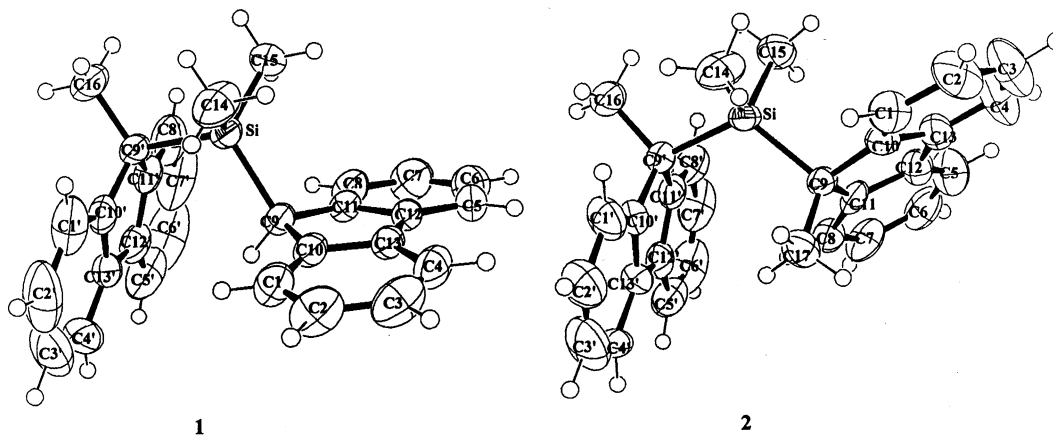
The crystal structure of **1** consists of parallel arrangements of columns formed by stacking of the fluorenyl groups (Fig. 2).

One row of columns extended on the *c*-direction has all the methyl substituents (from position 9) oriented

upward while the next, parallel row, has these groups oriented on the opposite side (downwards). Neighbouring columns are not in contact since the inter-columnar H···H distances are relatively large (3.357, 3.598 Å), beyond the sum of the van der Waals radii (2.40 Å, [24]).

The arrangement of the molecules in a column reveals C–H···π interactions between the methyl groups of the SiMe₂ fragments and the two phenyl rings of a fluorenyl group belonging to a neighbour molecule (Fig. 3a). The short distance (2.752 Å) between the SiMe₂–hydrogen atoms and the centroids of the lateral rings of the fluorene suggests that these interactions are quite strong [25,26].

Some weaker, but still significant interactions occur between the H3 (H6) and H4 (H5) protons of a fluorene and the π-electrons from a neighbour molecule (Fig. 3b). The shortest such contacts are between H4 (H5) and C10' (C11') (2.889 Å), while the distance from these hydrogens to the centroid of the five-membered ring is 3.247 Å. Of the same order (3.219 Å) are also the intermolecular distances between H3 (H6) and C2' (C7').

Fig. 1. The molecular structures of **1** and **2**.Table 6
Selected bond lengths (Å) in **1** and **2**

	1	2
<i>Bond lengths</i>		
Si–C9	1.929(3)	1.941(8)
Si–C9'	1.935(3)	1.940(8)
Si–C14	1.857(3)	1.871(8)
Si–C15	1.857(3)	1.864(8)
C9–C17		1.540(11)
C9'–C16	1.532(4)	1.550(12)
C9–C10	1.509(3)	1.531(10)
C10–C13	1.409(3)	1.395(12)
C12–C13	1.459(4)	1.448(13)
C11–C12	1.409(3)	1.392(11)
C9–C11	1.509(3)	1.513(11)
C8–C11	1.389(3)	1.385(12)
C1–C10	1.389(3)	1.383(12)
C5–C12	1.394(3)	1.348(13)
C4–C13	1.394(3)	1.386(11)
C3–C4	1.377(3)	1.339(17)
C2–C3	1.385(4)	1.393(16)
C1–C2	1.380(3)	1.391(12)
C9'–C10'	1.510(3)	1.517(12)
C9'–C11'	1.510(3)	1.520(12)
C11'–C12'	1.393(3)	1.403(12)
C12'–C13'	1.455(3)	1.461(13)
C10'–C13'	1.393(3)	1.389(13)
C1'–C10'	1.384(3)	1.395(12)
C1'–C2'	1.400(5)	1.374(19)
C2'–C3'	1.353(6)	1.317(19)
C4'–C13'	1.358(4)	1.448(14)

The crystal structure of **2** has a few common features with that of **1**. Thus, in **2**, columnar arrangements are also distinguishable with inter-columnar H···H distances (3.369 Å), similar to those found in **1**; but, shorter (2.660 Å) intra-columnar SiCH₃···H(fluorenyl) distances are noted. Due to these differences the intermolecular C–H···π interactions involve mainly the protons (positions 4 and 5) of one fluorene and

Table 7
Selected bond angles (°) in **1** and **2**

	1	2
<i>Bond angles</i>		
C9–Si–C9'	108.18(13)	116.2(3)
C9–Si–C14	110.95(10)	109.0(4)
C9–Si–C15	110.95(10)	106.6(4)
C9'–Si–C14	109.26(10)	105.6(4)
C9'–Si–C15	109.26(10)	111.1(4)
C14–Si–C15	108.20(2)	108.0(5)
C11–C9–Si	112.16(14)	111.1(5)
C10–C9–Si	112.16(14)	110.9(7)
C10–C9–C11	102.20(2)	100.9(6)
C11'–C9'–Si	107.58(14)	113.0(5)
C10'–C9'–Si	107.58(14)	111.6(6)
C10'–C9'–C11'	100.8(2)	101.8(7)
C16–C9'–C10'	115.0(2)	112.5(7)
C16–C9'–C11'	115.0(2)	111.0(8)
C16–C9'–Si	110.2(2)	106.9(6)

two of the rings of a neighbored fluorene. The relevant distances (2.978 and 3.107 Å) are shown in Fig. 4.

Besides this, π···π intermolecular contacts (3.463 Å) arise from the almost parallel disposition of the other fluorene rings.

An analogous crystal structure is observed for the unsubstituted bis(fluorenyl)dimethylsilane [21] **3** in which the columnar arrangement is also supported by multiple C–H···π interactions with typical C–H···fluorene distances of 2.7–3.2 Å

3. Conclusions

The experimental and theoretical data show that Me₂Si(CHR₂)(CMeR₂) exists in the same conformation both in the solid state, in solution and presumably, in gas phase. The proton in position 9 is orientated toward the opposite fluorenyl group and this arrangement

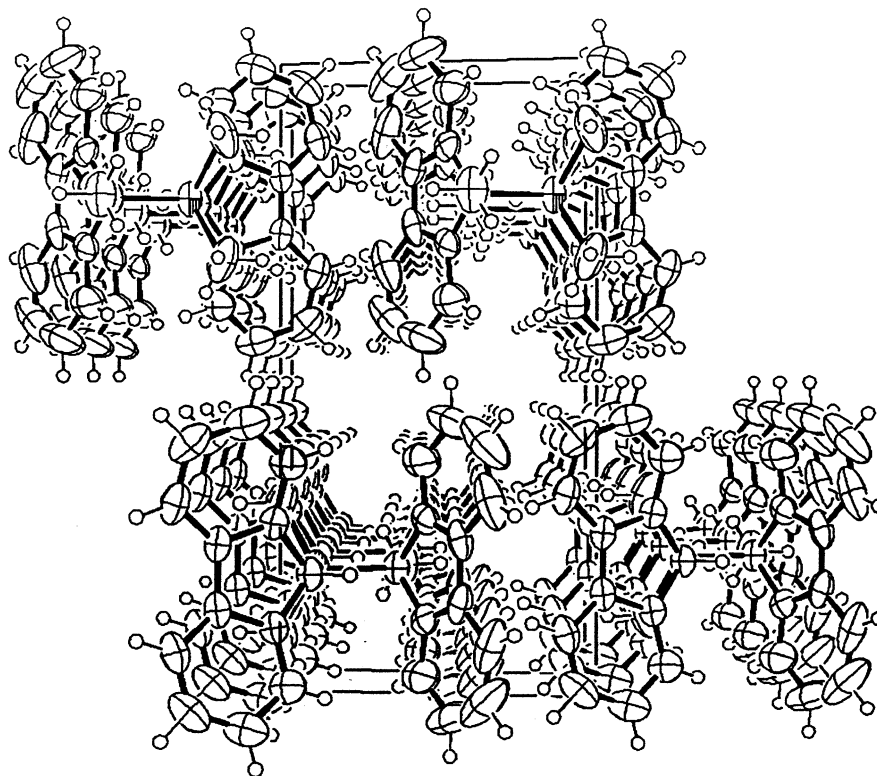


Fig. 2. The packing of **1** viewed perpendicular to the (*bc*) plane (along the *a* axis).

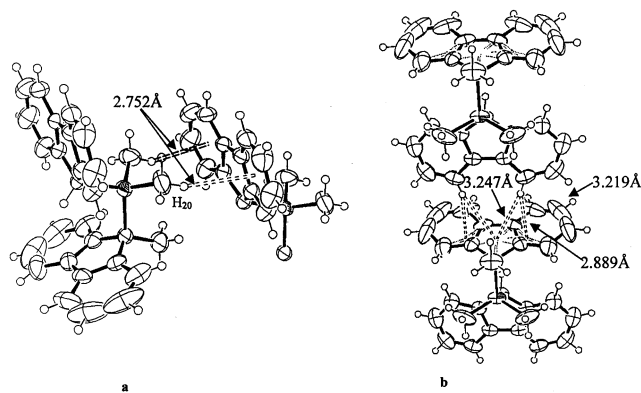


Fig. 3. Intermolecular Me···fluorenyl (a) and fluorenyl···fluorenyl CH··· π interactions (b) in **1**.

favorizes relatively important CH··· π intramolecular interactions. Substitution of H9 in **1** by a second methyl

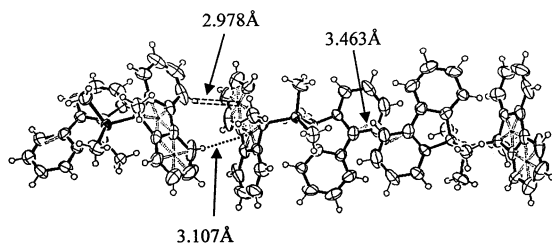


Fig. 4. Significant intermolecular distances in **2** as a result of CH··· π interactions.

group eliminates the possibility of these strong intramolecular interactions, reduces the barriers of rotation around the Si–C(fluorenyl) bonds and make these two methyl groups equivalents at the time scale of NMR.

4. Experimental

bis(9-Methylfluoren-9-yl) dimethylsilane (**1**), (9-methylfluoren-9-yl)(fluoren-9-yl) dimethylsilane (**2**) and bis(fluoren-9-yl)dimethylsilane (**3**) have been obtained according to the literature [20].

Proton and carbon NMR spectra were recorded on a Bruker AC 200 spectrometer at 200 MHz and the 2D spectra were recorded on an Avance DRX400 machine, at 400 MHz.

5. Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 175771 for compound **1** and 175770 for compound **2**, respectively, and can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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