

On the structure of bis(9-fluorenyl) dimethylsilane: a sterically crowded molecule with relatively low barriers of rotations around the Si–C(fluorenyl) bonds

X-ray diffraction analysis and AM1 molecular orbital calculations

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Abstract

The X-ray structure of bis(9-fluorenyl)dimethylsilane, the first silane compound containing two voluminous fluorenyl groups, has been determined. The crystal system is orthorhombic with *Aba2* space group. The unit cell ($a = 18.672$, $b = 36.089$, $c = 12.802$ Å) contains two sets of four molecules, each one of one set being symmetrically related with the others of the same set. The conformations around the HC(fluorenyl)SiC(fluorenyl) bonds may be grossly described as in–in, in–out and out–out. The AM1 calculations have shown that the barrier between the in–out and in–in conformations is relatively low while that between the in–out and out–out is higher; thus, probably, the first two are the most populated in solution. These results provide a better understanding of some unusual chemical shifts previously observed in ¹H-NMR for Me₂Si(CHR₂)₂ and Me₂Si(CHR₂)(CR'R₂). © 1997 Elsevier Science B.V.

Keywords: Bis(9-fluorenyl)dimethylsilane; X-Ray structure; AM1 molecular orbital calculations; Conformations of bis(9-fluorenyl)dimethylsilane

1. Introduction

The fluorenyl group has steric and electronic properties which make it a versatile ligand in organometallic chemistry. The special stereoelectronic properties (large size but flat group and the possibility of strong π -conjugation) make this system particularly suitable for stabilization of double bonded main group elements, e.g. bora-alkenes $\text{—B=C} < [1,2]$, phospho-alkenes $\text{P=C} < [3,4]$, germanes $\text{>Ge=C} < [5–8]$ and stannenes [9].

Recently the reactions of Me₂EX₂ (E = Si [10,11], Ge [10] and Sn [10]) with fluorenyl lithium have been investigated leading to both mono- and more sterically crowded difluorenyl derivatives (Me₂Si(CHR₂)₂, CHR₂ = fluorenyl).

By our best knowledge bis(9-fluorenyl)dimethylsilane, Me₂Si(CHR₂)₂, is the first example of a silicon

compound containing two bulky fluorenyl groups bound to the same silicon atom. In order to characterize it in more detail and for a better understanding of its reactivity and spectral behavior (especially the ¹H-NMR data), the X-ray structure has been determined and molecular mechanics followed by RHF/AM1 semiempirical molecular orbital calculations have been performed on several conformations of this compound.

2. Results and discussion

2.1. Crystal and molecular structure of Me₂Si(CHR₂)₂

The solid state structure has been determined by X-ray diffraction, using a crystal grown from diethyl ether. Space group *Aba2* was found with unit cell dimensions $a = 18.6720(10)$; $b = 36.089(3)$ and $c = 12.802(2)$ Å, $V = 8626.7(16)$ Å³ and $Z = 8$. The unit

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cell is presented in Fig. 1. Data collection, Crystal data and Refinement data are summarized in Table 1.

Two nonidentical molecules (not related by symmetry operations) having slightly different molecular parameters were found in the unit cell (they are shown in Fig. 2 and we will further refer at them as Si(I) and Si(II)). The main difference between these two molecules resides in the relative orientation of the two fluorenyl groups: the angle between their planes is 80.1° in Si(I) and 96.8° in Si(II).

The molecular structure of $\text{Me}_2\text{Si}(\text{CHR}_2)_2$ with the numbering scheme (for Si(I)) is shown in Fig. 3 and selected parameters (bond distances and bond angles) are presented in Table 2. The set of refined atomic coordinates and equivalent isotropic displacements are listed in Table 3.

The bond angles around the silicon atoms are within the ranges for a tetrahedral geometry. However, the two C(fluorenyl)–Si–C(fluorenyl) angles in Si(I) and Si(II) are both deviated to the lower values as: C(1)–Si(1)–

Table 1
Structure determination summary

<i>Crystal data</i>	
Empirical formula	$\text{C}_{56}\text{H}_{48}\text{Si}_2$
Color; Habit	colorless, irregular
Crystal size (mm)	$0.62 \times 0.25 \times 0.17$
Crystal system	Orthorhombic
Space group	Aba2
Unit cell dimensions	$a = 18.6720(10) \text{ \AA}$ $b = 36.089(3) \text{ \AA}$ $c = 12.802(2) \text{ \AA}$
Volume	$8626.7(16) \text{ \AA}^3$
Z	8
Formula weight	777.1
Density (calc.)	1.197 kg/m^3
Absorption coefficient	0.120 mm^{-1}
$F(000)$	3296
<i>Data collection</i>	
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ Range	6.0 to 60.0°
Scan type	2θ – θ
Scan speed	Variable; 4.00 to $60.00^\circ/\text{min}$ in ω
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50% of total scan time
Standard reflections	3 measured every 97 reflections
Index ranges	$-1 \leq h \leq 26$, $-49 \leq k \leq 1$, $-1 \leq l \leq 18$
Reflections collected	7651
Independent reflections	7048 ($R_{\text{int}} = 1.84\%$)
Observed reflections	3836 ($F > 3.0 \sigma(F)$)
Absorption correction	N/A
<i>Solution and refinement</i>	
Quantity optimized	$\sum w(F_o - F_c)^2$
Absolute structure	N/A
Extinction correction	$\chi = 0.00014(2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Rigid model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008 F^2$
Number of parameters refined	523
Final R indices (obsd. data)	$R = 8.17\%$, $wR = 7.80\%$
R indices (all data)	$R = 13.12\%$, $wR = 8.68\%$
Goodness-of-fit	1.48
Largest and Mean Δ/σ	0.423, 0.039
Data-to-parameter ratio	7.3:1
Largest difference peak	0.94 e\AA^{-3}
Largest difference hole	-0.51 e\AA^{-3}

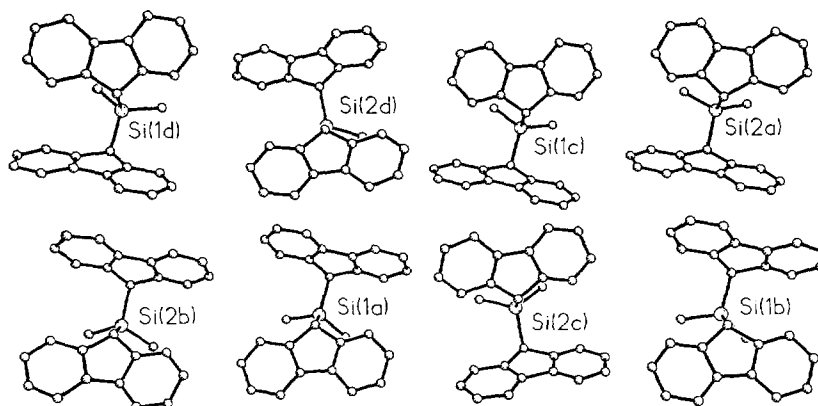


Fig. 1. The arrangement of the eight bis(9-fluorenyl)dimethylsilane molecules in the unit cell. Each of the four molecules of one set (1 or 2) are symmetry related with the others of the same set.

$C(14) = 105.8(3)$ in Si(I) and $C(51)-Si(2)-C(64) = 105.5(3)$ in Si(II). This is due to the relative positions of H(14A) and H(51A) toward the opposite fluorenyl groups which seems to influence these angles as well as some other geometrical parameters of the two molecules. Thus, the four $C(\text{fluorenyl})-Si-C(\text{Me})$ angles are also

slightly different in the two Si(I) and Si(II) molecules (see Table 2).

The $Si-C(\text{fluorenyl})$ bonds (1.91–1.92 Å) are somewhat longer than in the less crowded η^1 -trimethylsilyl-cyclopentadiene [12] (1.90 Å) and approximately of the same length as some of the $Si-C$ bonds in bis(penta-

Table 2
Selected geometrical parameters in $Me_2Si(CHR_2)_2$ (bond lengths in Å, bond angles in degrees) from the solid state structures and calculated (AM1 for the lowest energy conformers c108 and a180)

Si(I)	Si(II)	AM1 results			
		c108	a180		
Bond lengths					
Si1–C1	Si2–C51	1.907(6)	1.917(6)	1.878	1.879
Si1–C14	Si2–C64	1.923(9)	1.910(8)	1.878	1.876
Si1–C100	Si2–C200	1.858(9)	1.857(8)	1.825	1.827
Si1–C101	Si2–C201	1.855(8)	1.862(8)	1.825	1.828
Bond angles					
C1–Si1–C14	C51–Si2–C64	105.8(3)	105.5(3)	108.9	108.5
C1–Si1–C100	C51–Si2–C200	112.6(3)	111.4(3)	108.6	107.3
C1–Si1–C101	C51–Si2–C201	109.4(4)	112.0(4)	110.5	108.0
C14–Si1–C100	C64–Si2–C200	109.5(3)	110.6(3)	110.5	113.0
C14–Si1–C101	C64–Si2–C201	111.7(3)	110.6(3)	108.6	113.1
C100–Si1–C101	C200–Si2–C201	107.7(4)	106.8(4)	109.6	106.6
Si1–C1–C2	Si2–C51–C52	112.9(4)	114.3(5)	111.0	112.0
Si1–C1–C13	Si2–C51–C63	110.4(4)	113.5(5)	112.5	112.4
Si1–C14–C26	Si2–C64–C76	113.6(4)	109.9(4)	111.0	112.8
Si1–C14–C15	Si2–C64–C65	111.3(4)	110.9(4)	112.5	112.1
Dihedral angles					
C14–Si1–C1–H1A	C64–Si2–C51–H51A	174.6(0.2)	4.0(0.2)	59.0	–175.8
C1–Si1–C14–H14A	C(51)–Si(2)–C(64)–H(64A)	–17.8(0.2)	–174.7(0.2)	59.0	–6.1

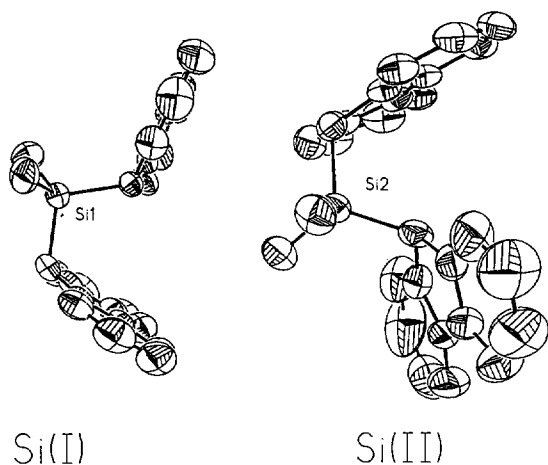
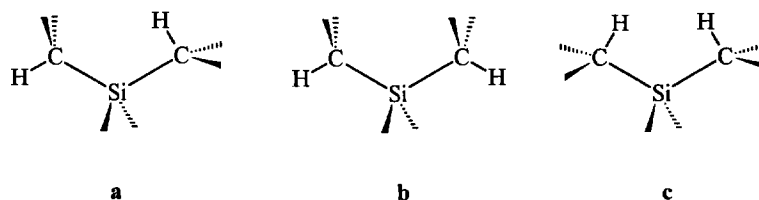


Fig. 2. A view of the two nonequivalent molecules from the unit cell. They differ mainly in the following dihedral angles: $C1-Si1-C14-H14A = -17.8^\circ$ and $C64-Si2-C51-H51A = 4.0^\circ$ (see Fig. 3 for atom numbering). These are very similar with conformations **a116** and **a180** calculated by AM1 (see Fig. 6).

methylcyclopentadienyl)silanediol tetramer [13]. On the other hand, the Si–C(Me) bonds (1.85–1.86 Å) are noticeably shorter than in $CpSiMe_3$ [12] (1.90 Å) and also shorter than in tetramethylsilane (1.93 Å) [14,15] or in $(t-Bu)_2SiCl_2$ [16] (1.891 Å). The distance from Si(1) to the carbon bearing the inside oriented proton (Si(1)–C(14)) is larger than Si(1)–C(1) by 0.016 Å (see Table



The conformations we searched for are those related to the rotation of the HC(flourenyl)SiC(flourenyl) dihedral angles, when **a** is transformed into **b** or **c**. The profiles of the variation of the formation enthalpy during these torsional deformations are shown in Fig. 4 and Fig. 5.

Thus, the rotation from **a** to **b** involves a relatively high barrier (cca 4 kcal/mol) and the **b0** conformer with the two fluorenyl groups placed in almost parallel planes is the highest energy conformer found. This seems normal since in this conformation there is the closest overall contact between the two bulky substituents and thus the repulsion between them is maximum (n.b. the molecular mechanics MM2 calculations gives the global minimum strain energy for this conformation!).

The rotation from **a** to **c** can proceed more smoothly since now the barrier separating the two minima is

2), while the same difference between the analogous bonds in Si(II) is smaller. This finding can be related again to the two different dihedral angles involving H(14A) and H(51A) and the C(flourenyl)–Si–C(flourenyl) atoms: $H(14A)-C(14)-Si(1)-C(1) = -17.8^\circ$ in Si(I) and $H(51A)-C(51)-Si(2)-C(64) = 4^\circ$ in Si(II).

The presence of the two molecules with different conformations in the unit cell shows that despite the volume of the fluorenyl substituents, these systems might be quite flexible toward the rotations around the Si–fluorenyl groups. The relatively high value of *R* might be interpreted also as a result of this flexibility. To see how easily these bonds can be rotated we carried out semiempirical molecular orbital calculations (AM1) on the conformations generated by a systematic search (MM2 molecular mechanics) along the two H–C(flourenyl)–Si–C(flourenyl) dihedral angles.

2.2. Some of the favored conformations of $Me_2Si(CHR_2)_2$

Consider the following three limiting structures showing (the topological) relative disposal of one of H–C(flourenyl) hydrogens toward the opposite fluorenyl rings: **a**(in, out), **b**(out, out) and **c**(in, in).

smaller (1.50 kcal/mol) than for the previous rotation. The minimum corresponding to **c** has a heat of formation by only 0.7 kcal/mol higher than **a** and is separated from it by 0.8 kcal/mol. When the constraint used for obtaining the data of Fig. 4 and Fig. 5 were completely relaxed and a full optimization performed on each of the individual points, the six conformations shown in Fig. 6 were obtained.

We included also the enthalpies of formation, the relative values of the enthalpies of formation, and a code for identifying some conformers. Thus, for example, **a116** points out that this is an **a** type conformer (in–out, respectively) and the actual H–C(flourenyl1)–C(flourenyl2)–H angle has reached 108° after the complete optimization.

Note that (up to the present search) the global minimum is **c108** where the repulsion between the in–in protons is greatly alleviated since one of the Me is in

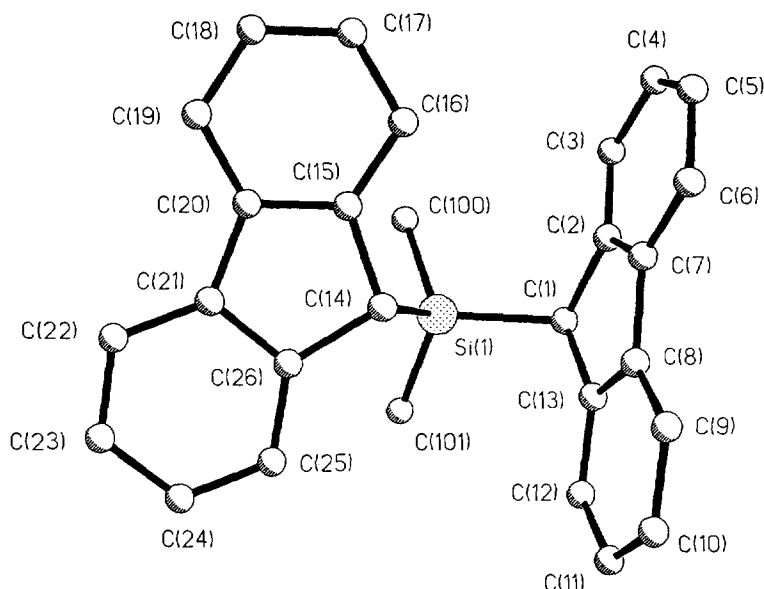


Fig. 3. The detailed molecular structure of bis(9-fluorenyl)dimethylsilane (the Si(I) form) showing the atom numbering scheme. Note that this differs from the 'gas phase' structure calculated by AM1 (see Fig. 6, c108).

gauche to the HC(fluorenyl), the other one is in *trans*, and the H–C(fluorenyl1)–C(fluorenyl2)–H dihedral angle is 108° (some bond parameters for this conformation are included in Table 2). The minimum corresponding to the full optimized structure starting from **c** (with both of the dihedral angles of 0°) retains the in–in orientation of the two hydrogen atoms but also, in order to reduce the repulsion between them the system rearranges so that the HC(fluorenyl1)C(fluorenyl2)H dihedral angle increases to cca 47° (c47). The full optimizations started from points closed to **a** lead to two conformers **a180**

and **a116** differing by cca 22° in the $H_{int}C(fluorenyl1)SiC(fluorenyl2)$ dihedrals, and having slightly different enthalpies of formation. Actually these two are the conformers which much more closely resemble the solid state structures. This means that c108, which is minimum in the gas phase, is converted in the solid state to **a180** and **a116** by the influence of the packing forces.

Thus the AM1 data confirm that in spite of the large volume of the two fluorenyl groups, some rotations around the Si–C(fluorenyl) bonds are still allowed and the system can relatively easily transit from the in–out to the in–in conformation.

Finally, a remark on the influence of the geometry of c108 (global minimum) on the 1H -NMR spectra. In this conformer, both of the Me substituents on silicon are exactly in equivalent positions toward the fluorenyl groups. In solution, there are no packing forces; thus, we can suppose that $Me_2Si(CHR_2)_2$ exists mainly in the conformation **c** like in the gas phase. This assumption is corroborated by the experiment: the 1H -NMR displays an extremely high field shift for the methyl groups on silicon (-0.49 ppm [10]). A similar high field shift is observed in isologue compounds $Me_2Ge(CHR_2)_2$ (-0.28 ppm [10]) and $Me_2Sn(CHR_2)_2$ (-0.25 ppm [10]). This abnormal shift is of course in relation with the position of the two methyl groups in the anisotropy cone of the two fluorenyl groups (distance of the Me proton to the mean plane of the opposite fluorenyl group: 2.99 \AA). By contrast, every CHR_2 proton, which is only close to the H of the other CHR_2 group, resonates in the expected range (4.25 ppm).

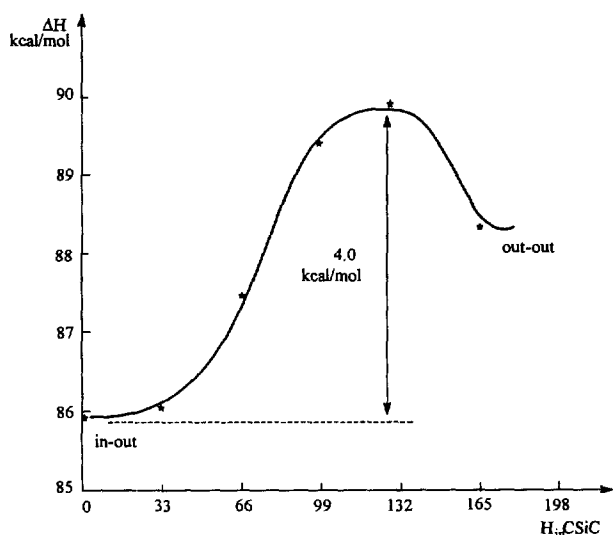


Fig. 4. The variation of the enthalpy of formation as function of the $H_{in}CSiC$ dihedral angle during the transformation of the in–out (**a**) conformer into the out–out conformer (**b**). The relatively large barrier makes the population of **b** less important (for comparison, see Fig. 5).

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic U_{eq} displacement coefficients ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Si(1)	2452(1)	1336(1)	311(1)	48(1)
Si(2)	2290(1)	3794(1)	7753(2)	48(1)
C(1)	1463(3)	1202(2)	282(6)	50(2)
C(2)	1318(3)	830(2)	784(6)	52(2)
C(3)	1514(4)	478(2)	429(8)	67(3)
C(4)	1326(5)	182(2)	1068(10)	87(4)
C(5)	1001(5)	226(3)	2019(10)	89(4)
C(6)	808(4)	575(2)	2357(8)	80(3)
C(7)	980(4)	876(2)	1726(7)	60(3)
C(8)	790(3)	1272(2)	1862(6)	56(2)
C(9)	428(4)	1457(3)	2629(8)	76(3)
C(10)	298(5)	1832(3)	2517(9)	91(4)
C(11)	540(5)	2019(3)	1644(10)	87(4)
C(12)	904(4)	1841(2)	865(7)	66(3)
C(13)	1038(3)	1456(2)	983(6)	54(2)
C(14)	2709(3)	1363(2)	1764(5)	44(2)
C(15)	3142(3)	1027(2)	2098(5)	42(2)
C(16)	2941(4)	658(2)	2135(6)	58(2)
C(17)	3454(4)	397(2)	2419(7)	71(3)
C(18)	4140(4)	502(2)	2662(8)	72(3)
C(19)	4343(3)	868(2)	2667(7)	59(2)
C(20)	3832(3)	1134(2)	2386(5)	45(2)
C(21)	3885(3)	1536(2)	2360(5)	45(2)
C(22)	4426(3)	1774(2)	2689(7)	67(3)
C(23)	4301(5)	2151(2)	2659(9)	86(4)
C(24)	3663(6)	2290(2)	2304(8)	87(4)
C(25)	3122(4)	2058(2)	1993(7)	64(3)
C(26)	3222(3)	1678(2)	2012(5)	42(2)
C(51)	2085(3)	3797(2)	9221(6)	52(2)
C(52)	1573(4)	3501(2)	9563(6)	62(3)
C(53)	1646(6)	3125(3)	9532(8)	96(4)
C(54)	1108(10)	2903(3)	9894(10)	142(7)
C(55)	469(8)	3073(5)	10259(10)	133(7)
C(56)	396(5)	3451(5)	10301(9)	115(5)
C(57)	937(4)	3673(3)	9940(6)	83(4)
C(58)	1036(4)	4071(3)	9957(7)	78(3)
C(59)	602(6)	4362(4)	10331(10)	118(5)
C(60)	893(7)	4713(4)	10251(13)	130(6)
C(61)	1562(8)	4787(3)	9948(13)	151(8)
C(62)	1950(6)	4510(3)	9570(9)	98(4)
C(63)	1713(4)	4145(2)	9582(6)	66(3)
C(64)	3291(3)	3692(2)	7648(6)	47(2)
C(65)	3467(3)	3316(2)	8119(6)	49(2)
C(66)	3300(4)	2961(2)	7760(8)	65(2)
C(67)	3491(4)	2664(2)	8365(9)	79(3)
C(68)	3831(4)	2707(2)	9310(8)	76(3)
C(69)	4017(4)	3053(2)	9656(7)	64(3)
C(70)	3829(3)	3356(2)	9048(6)	48(2)
C(71)	3993(3)	3758(2)	9191(6)	47(2)
C(72)	4362(3)	3939(2)	9966(6)	56(2)
C(73)	4445(4)	4320(2)	9905(7)	67(3)
C(74)	4171(4)	4507(2)	9050(8)	67(3)
C(75)	3809(3)	4333(2)	8265(7)	61(3)
C(76)	3704(3)	3947(2)	8349(6)	48(2)
C(100)	3028(4)	988(2)	-355(8)	78(3)
C(101)	2575(5)	1785(2)	-361(7)	77(3)
C(200)	1763(4)	3433(2)	7063(7)	71(3)
C(201)	2075(4)	4245(2)	7121(7)	73(3)

Equivalent isotropic displacement U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

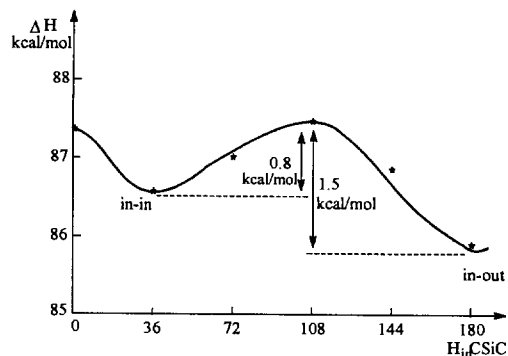


Fig. 5. The variation of the $H_{in}CSiC$ dihedral angle during the transformation of the in-in conformer (c) to the in-out conformer (a). The in-out conformers (a180 and a116) can transform to the in-in state (c47) relatively easily, by an expense of 1.5 kcal/mol.

When one of the fluorenyl groups is substituted by a R' group ($R' = Me, Me_3Si, Me_2SiCl, Me_2SiF$ [10]), the conformation **c** is of course unfavorable for steric reasons; thus, the conformation of these derivatives is probably mainly **a**. This is also in this case corroborated by the 1H -NMR spectra which exhibit for both the Me and proton on the fluorenyl very large differences with those of $Me_2Si(CHR_2)_2$: the Me lies in a normal range (0 to 30 ppm [10]), as expected, since they are close to only one fluorenyl group. On the other hand, the CHR_2 proton is high field shifted by about 1 to 1.5 ppm (2.65–3.17 ppm instead of 4–4.20 ppm). This is of course due to its position close to the other fluorenyl group.

Such a conformation change between $Me_2Si(CHR_2)_2$ and $Me_2Si(CHR_2)(CR'R)_2$ appears normal, arising from the small gap in energy between the two conformers. Thus, the present calculations provide a better understanding of shifts observed in 1H -NMR for these compounds.

3. Experimental section

Bis(9-fluorenyl)dimethylsilane was prepared by the method described in Ref. [10]. Suitable crystals for the X-ray diffraction were grown by slowly evaporating a solution in diethyl ether.

3.1. X-ray data collection and structure analysis

The crystal data and refinement results are listed in Table 1. All data were collected at room temperature (293K) by using a Siemens P4 PC diffractometer and graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, with variable scan speed (4–60°/min). Three standard reflections were measured after every 97 reflections. In view of the small absorption coefficient, no absorption corrections have been made. The data were

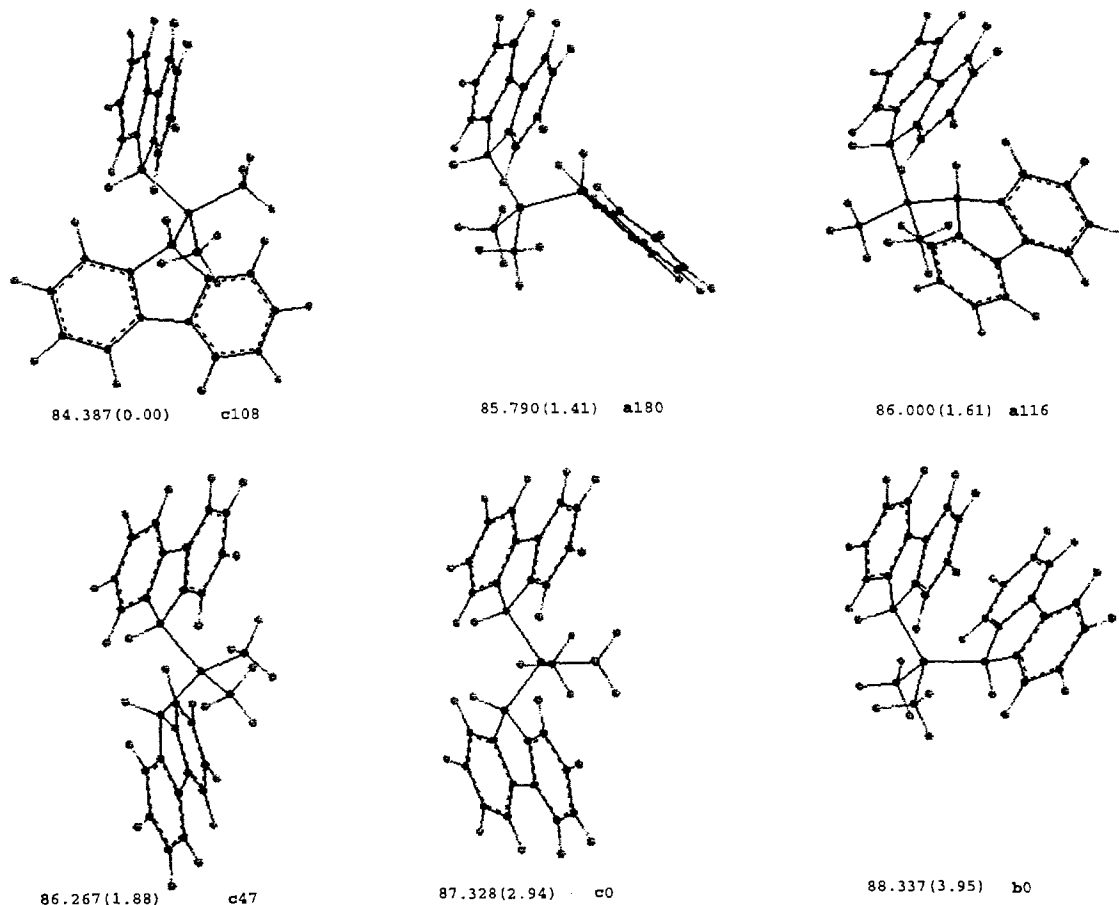


Fig. 6. The full optimized structures of the conformers encountered during the partial optimizations which lead to the data of Fig. 4 and Fig. 5. The heat of formation for each individual and the relative values (kcal/mol) are indicated along with the code which shows the actual values attained by the HC(fluorenyl) ... C(fluorenyl)H dihedral angles.

refined with Siemens SHELXTL PLUS (PC version) set of programs and the structure was solved by direct methods and refined by the full matrix least squares method. The hydrogen atoms were introduced at fixed positions.

3.2. Calculation details

All the calculations were performed within the Spartan 4.0 package [17]. First a very crude estimate of the possible conformers was determined by the Coordinate Drive facility in the Molecular Mechanics module (MM2 Force Field). Only the two H–C(fluorenyl)–C(fluorenyl)–H dihedrals were varied from 0 to 180°. The conformations thus obtained were subjected to RHF/AM1 optimizations, first maintaining the dihedral constraints and then repeating the calculation on the new geometries but relaxing these constraints. The constrained optimizations were exited when the drop in the energy was less than 0.001 kcal/mol and the gradient was smaller than 0.0001. For the unrestricted optimizations the tolerance in the displacement of atoms was

also considered in addition to the above two and taken as 0.0001. No convergence problems were encountered.

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