BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1557—1563 (1968)

The Crystal and Molecular Structure of 1,1′-Bis(pentamethyldisilanyl)-ferrocene, $(\pi\text{-}C_5H_4Si(CH_3)_2Si(CH_3)_3)_2Fe$

Ken HIROTSU, Taiichi HIGUCHI and Akira SHIMADA

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka

(Received January 22, 1968)

Crystals of 1,1′-bis(pentamethyldisilanyl)ferrocene, $(\pi\text{-}C_5H_4Si(CH_3)_2Si(CH_3)_3)_2Fe$, are monoclinic, with $a=6.84$, $b=30.87$, $c=12.67$ Å and $\beta=96.80°$. The space group is $P2_1/n$ and there are four molecules in a unit cell. The structure was solved by Patterson and minimum functions, and further refined by Fourier and difference syntheses, and finally by a least-squares method. The final R value is 14.4% for 883 observed reflections. The two cyclopentadienyl rings are planar, approximately parallel to each other, separated by 3.28 Å and deviated by about 6° from the fully *eclipsed* configuration. The molecular configuration is *gauche* with respect to the two side-chains. The mean values of the bond distances are found to be Fe-C(cyclopentadienyl rings)= 2.05, C-C=1.45, C(cyclopentadienyl rings)-Si=1.87, C(methyl groups)-Si=1.90 and Si-Si= 2.34 Å. All intermolecular separations correspond to the normal van der Waals interactions.

Since the molecular structure of ferrocene had been determined, several of its derivatives have also been studied by means of X-rays to elucidate the spacial configurations of the two cyclopentadienyl rings in the molecules. It was found that in some of the molecules the *staggered* configurations of rings are maintained, while in others, intermediate configurations, between *staggered* and *eclipsed*, are preferred. The differences in these ring configurations might be very interesting.

1,1′-Bis(pentamethyldisilanyl)ferrocene was investigated in order to determine which ring configuration it takes in the crystalline state. Moreover, the present molecule has one substituent (pentamethyldisilanyl group) on each ring, and therefore the configuration of the substituents in the molecule and their arrangement in the crystal would be another interest.

Experimental

The crystals were kindly prepared and supplied by Professor Makoto Kumada of Kyoto University.[1] The specimens, which are suitable for X-ray work, were crystallized from ethanol solution in the form of ferrocene-like orange-yellow plates, elongated along the a axis, with the (010) plane developed. The crystals sublime gradually in air. Multiple Weissenberg intensity data were collected with Ni-filtered Cu$K\alpha$ radiation on the b and the c axes for zero layers, and on the a axis for zero and first layers. 1285 reflections were observed; 402 were too weak to be measured. Intensities were estimated visually with calibrated intensity scales. No correction was applied to absorption and extinction. All intensity data exhibit a high background due to strong fluorescence by the iron atoms. Atomic scattering factors for iron were used after being corrected for the effect of dispersion. After the Lorentz

TABLE 1. CRYSTAL DATA (λ, Cu$K\alpha$=1.5418 Å)

1,1′-bis(pentamethyldisilanyl)ferrocene
$C_{20}H_{38}Si_4Fe$; MW=446.7 mp=58—59°C
Monoclinic
$a=6.84$, $b=30.87$, $c=12.67$ Å $\beta=96.80°$
$Dm=1.01\ \mathrm{g\cdot cm^{-3}}$, $Dc(\text{with } Z=4)=1.02\ \mathrm{g\cdot cm^{-3}}$
$\mu=64.2\ \mathrm{cm^{-1}}$ (Cu$K\alpha$)
Space group is $P2_1/n$.

---

[1] M. Kumada, K. Mimura, M. Ishikawa and K. Shiina, *Tetrahedron Letters*, **1965**, 83.

and the polarization corrections were made, intensities were placed on a common relative scale. The crystal data are given in Table 1.

Structure Determination

At first, the structure projected along the *a* axis was sought by means of the Patterson and minimum functions. The iron atom and two silicon atoms directly bonded to the cyclopentadienyl rings were easily located. The first Fourier synthesis based on these three atoms revealed the iron and all the four silicon atoms clearly, while the positions of carbon atoms were not resolved. They were found and refined by a combination of successive Fourier and difference syntheses, molecular geometry being taken into consideration. The analysis of the *c* axis projection was also done in a similar way to the *a* axis projection.

Refinements were carried out by means of a least-squares method, using all the reflection data. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where w (weights) were set equal to unity for all reflections. After four cycles of the refinement, the discrepancy index R was 14.4% for the observed reflections only.

Table 2 gives the final positional and isotropic thermal parameters, and their e. s.d.'s obtained from the last cycle of the least-squares refinement.

TABLE 2. ATOMIC PARAMETERS
Atomic parameters and estimated standard deviations

	x $10^4\sigma(x)$	y $10^4\sigma(y)$	z $10^4\sigma(z)$	B $10^2\sigma(B)$
Fe	0.1886(10)	0.1481(1)	0.1938(3)	3.72(12)
Si(1)	0.0321(19)	0.0480(2)	0.2933(6)	4.11(20)
Si(2)	0.1080(19)	0.2570(2)	0.1180(6)	3.86(19)
Si(3)	−0.0836(20)	−0.0173(2)	0.2147(6)	4.33(20)
Si(4)	0.1810(19)	0.3241(2)	0.1965(6)	4.25(20)
C(1)	0.0779(56)	0.0857(7)	0.1852(18)	3.37(58)
C(2)	0.2667(57)	0.0897(7)	0.1384(18)	3.77(59)
C(3)	0.2427(62)	0.1233(8)	0.0512(20)	5.46(69)
C(4)	0.0393(61)	0.1364(8)	0.0466(20)	4.99(69)
C(5)	−0.0617(60)	0.1158(8)	0.1250(20)	4.74(66)
C(6)	0.1970(61)	0.2140(8)	0.2167(20)	5.20(69)
C(7)	0.3870(60)	0.1962(8)	0.2242(21)	5.69(68)
C(8)	0.3967(61)	0.1660(8)	0.3130(21)	5.05(67)
C(9)	0.1959(60)	0.1645(8)	0.3495(20)	5.62(69)
C(10)	0.0840(59)	0.1950(8)	0.2880(20)	4.80(66)
C(11)	−0.1645(60)	0.0727(8)	0.3742(21)	6.07(69)
C(12)	0.2741(62)	0.0357(8)	0.3808(21)	6.45(69)
C(13)	−0.1567(60)	−0.0547(8)	0.3236(20)	5.26(69)
C(14)	0.1192(59)	−0.0454(8)	0.1413(20)	5.45(68)
C(15)	−0.2917(62)	−0.0055(8)	0.1179(21)	7.25(68)
C(16)	−0.1653(61)	0.2536(8)	0.0754(21)	5.84(68)
C(17)	0.2382(64)	0.2513(8)	−0.0068(20)	4.87(69)
C(18)	0.0900(58)	0.3699(8)	0.1017(20)	4.71(65)
C(19)	0.4485(59)	0.3264(8)	0.2394(20)	6.40(69)
C(20)	0.0217(61)	0.3303(8)	0.3157(20)	6.11(69)

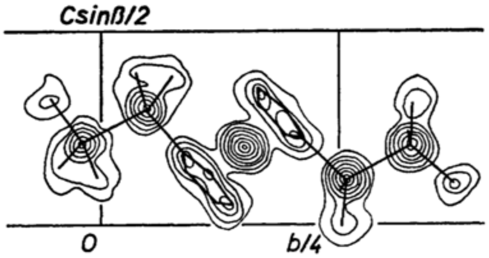

Fig. 1. Electron density projected along the *c* axis, contours are drawn in an arbitrary scale.

The observed and calculated structure factors are listed in Table 7.[*1] Figure 1 shows the electron-density map along the *a* axis.

Discussion

The views of the molecule perpendicular to and parallel to the cyclopentadienyl rings are given in Fig. 2. The best planes through the cyclopentadienyl rings are given in Table 4, together with the deviations of the atoms from these planes. These two planes are nearly parallel (the angle between them is 1.02°) to each other and the spacing between them is 3.28 Å, which may be compared with 3.32, 3.32 and 3.30 Å found in ferrocene,2) biferrocenyl3) and diferrocenyl ketone,4) respectively. Si(1) and Si(2) lies 0.05 Å above and below each of the best planes of the cyclopentadienyl rings to which they are attached, with respect to the Fe atom. The angle between plane 1 (see Fig. 2B) and the plane through Si(1), Si(3) and C(1) is 88.7°, while plane 2 and the plane through Si(2), Si(4) and C(6) makes an angle of 92.0°. Therefore, Si(3) lies on the plane which is normal to plane 1 and passes through C(1) and Si(1). This relation also holds for Si(4). Figure 3 shows one half of a molecule viewed along the Si(1)–Si(3) bond and the other half of the molecule viewed along the Si(2)–Si(4) bond. The conformation around the Si(1)–Si(3) and Si(2)–Si(4) bonds is *staggered*, though the dihedral angles seem to be a little different. From the above results, this molecule has roughly a twofold axis through the Fe atom, parallel to both cyclopentadienyl rings.

Ferrocene derivatives with one substituent on each ring have three possible configurations (*cis*, *trans* or *gauche*). It is well shown in Fig. 2A that

---

[*1] The complete data of the F_o-F_c table are kept as Document No. 6802 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥ 600 for photoprints. Pay by check or money order, payable to: Chemical Society of Japan.

2) J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.*, **9**, 373 (1956).

3) A. C. MacDonald and J. Trotter, *ibid.*, **17**, 872 (1964).

4) J. Trotter and A. C. MacDonald, *ibid.*, **21**, 359 (1966).

TABLE 3. BOND DISTANCES, BOND ANGLES AND NON-BONDED INTERATOMIC DISTANCES IN A MOLECULE
e. s. d. values in parenthesis

Bond distances		Å
Fe-C(1)	2.07	(0.02)
Fe-C(2)	2.03	(0.02)
Fe-C(3)	2.04	(0.03)
Fe-C(4)	2.05	(0.03)
Fe-C(5)	2.08	(0.04)
Fe-C(6)	2.06	(0.02)
Fe-C(7)	2.02	(0.03)
Fe-C(8)	2.03	(0.04)
Fe-C(9)	2.03	(0.03)
Fe-C(10)	2.06	(0.03)
C(1)-C(2)	1.49	(0.05)
C(2)-C(3)	1.51	(0.03)
C(3)-C(4)	1.44	(0.06)
C(4)-C(5)	1.42	(0.04)
C(5)-C(1)	1.48	(0.05)
C(6)-C(7)	1.40	(0.06)
C(7)-C(8)	1.46	(0.04)
C(8)-C(9)	1.50	(0.05)
C(9)-C(10)	1.39	(0.04)
C(10)-C(6)	1.39	(0.04)
Si(1)-Si(3)	2.34	(0.01)
Si(2)-Si(4)	2.33	(0.01)
Si(1)-C(1)	1.85	(0.02)
Si(2)-C(6)	1.88	(0.03)
Si(1)-C(11)	1.94	(0.03)
Si(1)-C(12)	1.92	(0.04)
Si(3)-C(13)	1.91	(0.03)
Si(3)-C(14)	1.96	(0.03)
Si(3)-C(15)	1.80	(0.04)
Si(2)-C(16)	1.89	(0.04)
Si(2)-C(17)	1.91	(0.03)
Si(4)-C(18)	1.91	(0.03)
Si(4)-C(19)	1.85	(0.04)
Si(4)-C(20)	1.97	(0.03)

Bond angles		(°)
C(1)-Fe-C(2)	42.6	(1.1)
C(2)-Fe-C(3)	43.6	(1.2)
C(3)-Fe-C(4)	41.4	(1.3)
C(4)-Fe-C(5)	40.4	(1.2)
C(5)-Fe-C(1)	41.7	(1.2)
C(6)-Fe-C(7)	40.3	(1.3)
C(7)-Fe-C(8)	42.2	(1.3)
C(8)-Fe-C(9)	43.4	(1.3)
C(9)-Fe-C(10)	39.8	(1.2)
C(10)-Fe-C(6)	39.4	(1.2)

Bond angles		(°)
C(1)-C(2)-C(3)	108.9	(2.4)
C(2)-C(3)-C(4)	104.1	(2.6)
C(3)-C(4)-C(5)	113.0	(2.8)
C(4)-C(5)-C(1)	107.7	(2.6)
C(5)-C(1)-C(2)	106.2	(2.4)
C(6)-C(7)-C(8)	105.1	(2.7)
C(7)-C(8)-C(9)	107.4	(2.6)
C(8)-C(9)-C(10)	105.6	(2.6)
C(9)-C(10)-C(6)	109.8	(2.8)
C(10)-C(6)-C(7)	111.9	(2.8)
C(2)-C(1)-Si(1)	125.3	(2.1)
C(5)-C(1)-Si(1)	128.4	(2.2)
C(1)-Si(1)-C(11)	109.4	(1.4)
C(1)-Si(1)-C(12)	110.0	(1.4)
C(1)-Si(1)-Si(3)	107.7	(1.0)
C(11)-Si(1)-C(12)	112.1	(1.4)
C(11)-Si(1)-Si(3)	110.0	(1.0)
Si(3)-Si(1)-C(12)	107.5	(1.1)
Si(1)-Si(3)-C(15)	108.3	(1.1)
Si(1)-Si(3)-C(13)	108.5	(1.1)
Si(1)-Si(3)-C(14)	111.1	(1.0)
C(15)-Si(3)-C(13)	111.2	(1.5)
C(15)-Si(3)-C(14)	108.2	(1.4)
C(13)-Si(3)-C(14)	109.6	(1.4)
C(10)-C(6)-Si(2)	124.9	(2.4)
C(7)-C(6)-Si(2)	123.2	(2.4)
C(6)-Si(2)-C(17)	109.9	(1.4)
C(6)-Si(2)-C(16)	112.6	(1.4)
C(6)-Si(2)-Si(4)	108.0	(1.1)
C(17)-Si(2)-Si(4)	109.8	(1.1)
C(17)-Si(2)-C(16)	107.5	(1.4)
Si(4)-Si(2)-C(16)	109.1	(1.1)
Si(2)-Si(4)-C(20)	107.7	(1.0)
Si(2)-Si(4)-C(18)	110.7	(1.0)
Si(2)-Si(4)-C(19)	108.4	(1.1)
C(18)-Si(4)-C(20)	104.0	(1.4)
C(19)-Si(4)-C(20)	112.8	(1.4)
C(18)-Si(4)-C(19)	113.2	(1.4)

Non-bonded interatomic distances		Å
C(1)-C(9)	3.24	(0.04)
C(2)-C(8)	3.28	(0.04)
C(3)-C(7)	3.21	(0.04)
C(4)-C(6)	3.32	(0.04)
C(5)-C(10)	3.28	(0.04)
Fe-Si(1)	3.55	(0.01)
Fe-Si(2)	3.52	(0.01)

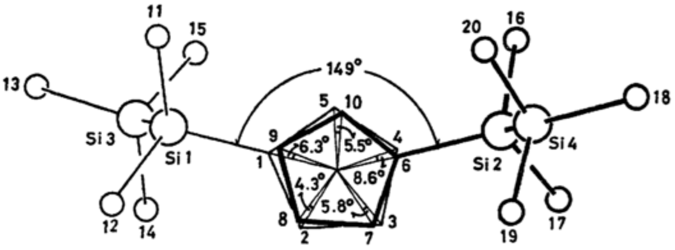

Fig. 2A. View of the molecule along the normal to the mean plane of the rings.

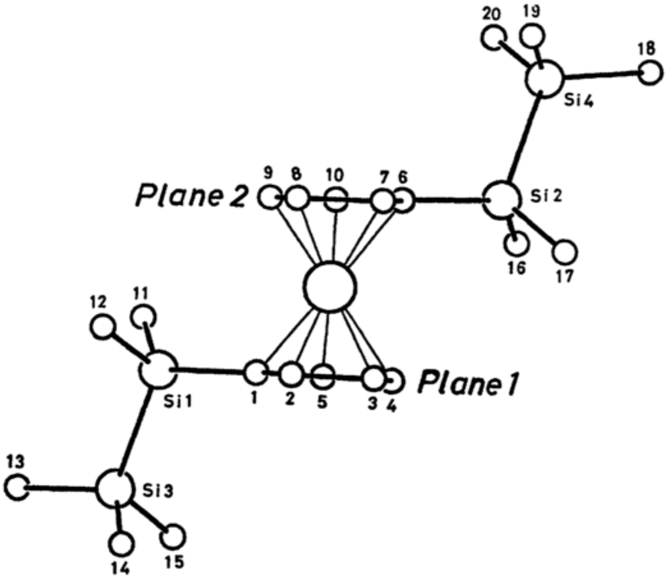

Fig. 2B. View of the molecule along the plane 1.

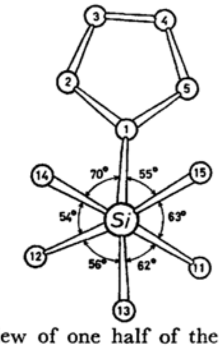

Fig. 3A. View of one half of the molecule along the Si(1)-Si(3) bond without Fe atom.

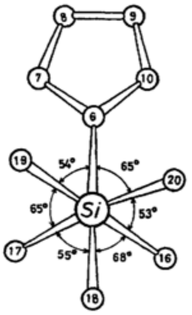

Fig. 3B. View of the other half of the molecule along the Si(2)-Si(4) bond without Fe atom.

TABLE 4. LEAST SQUARES PLANES OF THE RINGS

Plane 1 defined by C(1), C(2), C(3), C(4), C(5): $0.3878X+Y+0.8626Z=-4.8146$		Plane 2 defined by C(6), C(7), C(8), C(9), C(10): $0.4135X+Y+0.8788Z=-9.4048$	
Deviations of atoms from plane 1		Deviations of atoms from plane 2	
C(1)	0.005	C(6)	0.020
C(2)	−0.012	C(7)	−0.029
C(3)	0.015	C(8)	0.027
C(4)	−0.013	C(9)	−0.017
C(5)	0.005	C(10)	−0.001
*Si(1)	−0.047	*Si(2)	0.050

Atoms with * were not included in calculation of the plane.

TABLE 5. CONFIGURATIONS OF CYCLOPENTADIENYL RINGS IN SOME OF FERROCENE DERIVATIVES

Compound	Ring configuration	Reference
Ferrocene	*Staggered*	Dunitz, Orgel & Rich (1956)
Ferrocenedisulfonyl chloride	*Staggered*	Starovskii & Struchkov (1963)[5]
Biferrocenyl	$\varphi^* = 17°$	MacDonald & Trotter (1964)
Diethyldiferrocenyl	$\varphi = 4°$	Kaluski & Struchkov (1964)[6]
Diferrocenyl ketone	$\varphi = 5°$	Trotter & MacDonald (1966)
α-Keto-1,5-tetramethylene ferrocene	$\varepsilon^{**} = 8.9°$	Fleischer & Hawkinson (1967)[7]
1,1′-Bis(pentamethyldisilanyl)ferrocene	$\varphi = 6°$	This paper

* The angle φ was defined as the angle between the projection of the Fe–C bonds on the mean plane of a cyclopentadienyl rings.

** The angle ε was defined as the angle between the lines passing through the nearly superimposed atoms and the midpoint of the opposite sides of the rings.

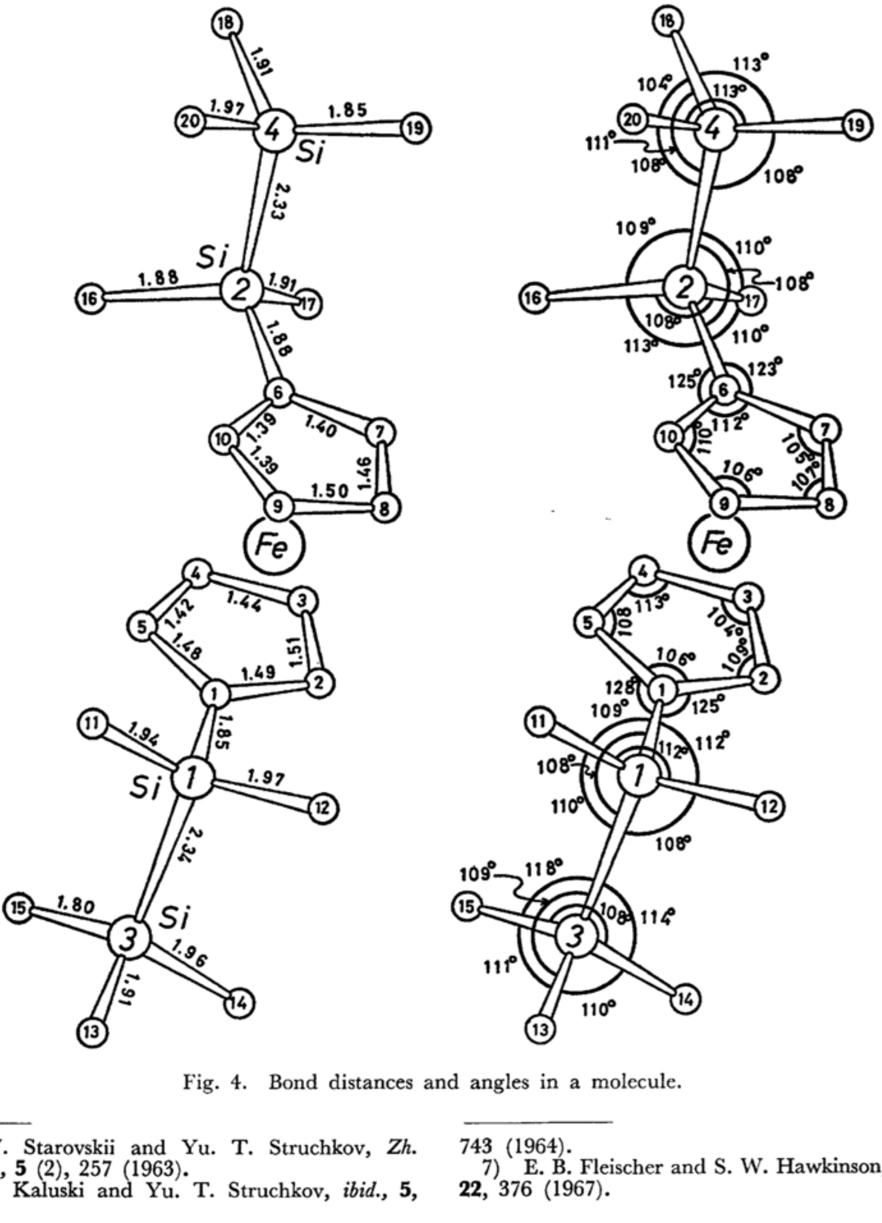

Fig. 4. Bond distances and angles in a molecule.

---

5) O. V. Starovskii and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **5** (2), 257 (1963).

6) Z. L. Kaluski and Yu. T. Struchkov, *ibid.*, **5**, 743 (1964).

7) E. B. Fleischer and S. W. Hawkinson, *Acta Cryst.*, **22**, 376 (1967).

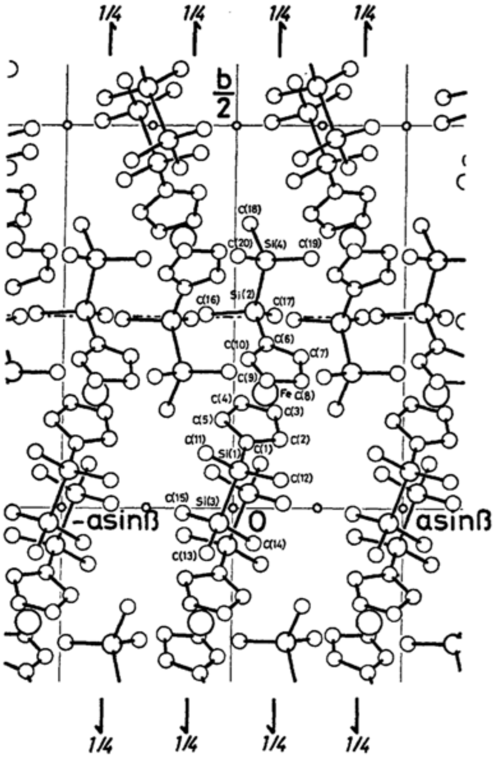

Fig. 5. Arrangement of the molecules along the *c* axis.

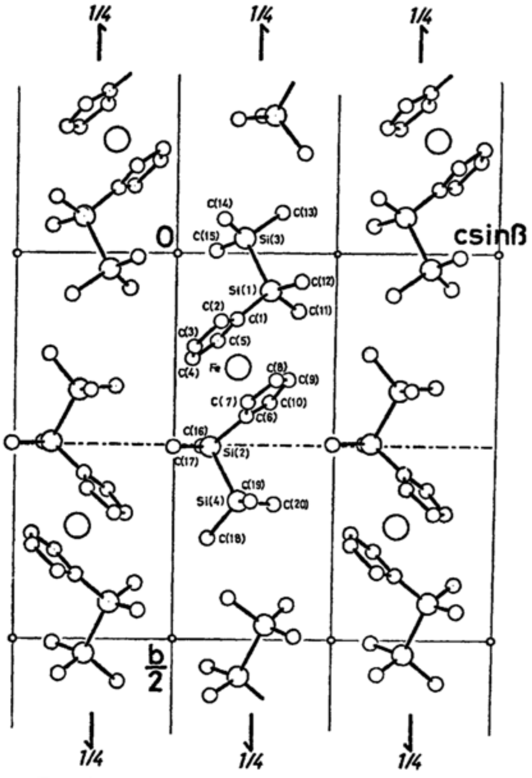

Fig. 6. Arrangement of the molecules along the *a* axis.

the present molecule has the *gauche* form. The angle between the projection of C(1)-Si(1) bond and that of C(6)-Si(2) on the mean plane of five-membered rings is 149°.

The angles φ between the Fe-C bonds projected on the mean plane of the rings are:

C(1)-Fe-C(9)	6.3°
C(2)-Fe-C(8)	4.3°
C(3)-Fe-C(7)	5.8°
C(4)-Fe-C(6)	8.6°
C(5)-Fe-C(10)	5.5°

The average value 6.1° shows that the configuration is almost the *eclipsed* one. Table 5 shows the ring configurations of ferrocene and its derivatives. These results may indicate that in ferrocene and its derivatves the *staggered* position is preferred owing to a small *inter-ring* separation, but this orientation will be easily rotated by stronger intermolecular forces until the *inter-ring* repulsion and intermolecular forces become comparable. In this compound, the substituent on each ring occupies the larger portion of the molecule and the ring configuration will be greatly affected by the arrangement of the substituents. Consequently, a stronger

TABLE 6. INTERMOLECULAR DISTANCES LESS THAN 4.2 Å

The reference molecule 1 lies at *x*, *y*, *z*.

from Atom	to Atom	in molecule at	*d*
(molecule 1)			
C(20)	C(19)	2	3.95 Å
C(7)	C(11)	3	4.17
C(12)	C(11)	3	4.09
C(14)	C(11)	3	4.19
C(14)	C(15)	3	3.93
C(17)	C(16)	3	4.01
C(20)	C(20)	4	3.89
C(17)	C(18)	5	3.97
C(3)	C(15)	6	3.99
C(12)	C(15)	6	4.02
C(11)	C(9)	7	3.85
C(11)	C(10)	7	4.15
C(13)	C(8)	7	3.90
C(13)	C(9)	7	4.07
C(10)	C(12)	8	4.07
C(14)	C(4)	9	4.04

Molecule 1 at	x,	y,	z
2 at	$-x$,	$-y$,	$-z$
3 at	$1+x$,	y,	z
4 at	$-1-x$,	$-y$,	$-z$
5 at	$-x$,	$-y$,	$1-z$
6 at	$1/2+x$,	$1/2-y$,	$-1/2+z$
7 at	$-1/2+x$,	$1/2-y$,	$-1/2+z$
8 at	$-1/2+x$,	$1/2-y$,	$1/2+z$
9 at	$1/2+x$,	$1/2-y$,	$1/2+z$

intermolecular force than the *inter-ring* repulsion may force such an arrangement as $\varphi=6.1°$.

The bond distances and angles are listed in Table 3 and shown in Fig. 4. The average C(Cp[*2])-C(Cp) bond distances is 1.45 Å (the average e.s.d. value is 0.05 Å), which is comparable to the values observed in the many ferrocene derivatives. The mean bond angle in the five-membered rings is 108.0±2.6°. The distortion in some bond angles from 108° is not significant. The mean Fe-C (Cp) distance, 2.05±0.03 Å, is consistent with those found in ferrocene derivatives. The average bond angle of C(Cp)-C(Cp)-Si is 125.4±2.3°. The average Si-C(Cp) distance, 1.87±0.03 Å is quite consistent with that of phenylsilane,8) 1.84±0.005 Å. The Si-Si bond distances (2.34 and 2.33 Å) are normal values. The average value of Si-C (methyl group) bonds is 1.90±0.03 Å, which is normal. The average angle around Si atoms is 109.5°, equal to the tetrahedral angle.

The average isotropic temperature factor of carbon atoms is 5.35 Å^2, which is relatively high in view of the fact that the absorption effect might be expected to reduce the temperature factors a little. This shows, together with the comparatively small density (*Dm* is 1.02 g·cm^{-3}), that thermal vibration in this molecule is considerable. The average isotropic temperature factor of Cp-carbons is 4.87 Å^2, and that of methyl carbons 5.84 Å^2. It may be significant that the difference between them is fairly large.

The mode of packing of the molecules in the crystal can be seen in Figs. 5 and 6. Molecules are packed with their long axes arranged along the *b* axis. Sets of molecules related by a twofold screw axis have approximately hexagonal packing. Most of the closest contacts are either of the CH_3---CH_3 or CH_3---CH(Cp) type. All shorter intermolecular distances (<4.2 Å) are given in Table 6.

The authors wish to express their appreciation to Professor Makoto Kumada and Dr. Mitsuo Ishikawa of Kyoto University for kindly supplying the samples for this study, to Dr. Kazumi Nakatsu of our laboratory and Dr. Noritake Yasuoka of Osaka University for their electronic computer programs, and to the Oki Electric Industry Co., Ltd., and the Japan Information Processing Service Co., Ltd., for the use of electronic computers. The present study was partly supported by a Scientific Reserch Grant from the Ministry of Education.

[*2] Cp is cyclopentadienyl.