Crystal and Molecular Structure of 2,2,3,3,7,7-Hexafluoro-2,3,7-trisilanorborn-5-ene

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Crystals of the title compound are monoclinic, space-group $P2_1/c$, with $a = 6{\cdot}293(9)$, $b = 11{\cdot}44_4(1_5)$, $c = 13{\cdot}99_2(1_5)$ Å, $\beta = 120{\cdot}7(2)°$. The structure was solved by direct methods from diffractometer data and refined by least-squares to R 0·050 for 1368 independent reflections. The molecule has a virtual mirror plane of symmetry.

ONE of the products of the reaction between silicon difluoride and acetylene[1] is a crystalline substance of formula $C_4H_4Si_3F_6$, which, largely on the basis of its ^{19}F n.m.r. spectrum, has been identified as 2,2,3,3,7,7-hexafluoro-2,3,7-trisilanorborn-5-ene (I). We now report a crystal-structure determination the results of

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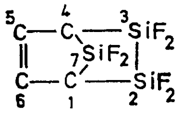
[1] C. S. Liu, J. L. Margrave, J. C. Thompson, and P. L. Timms, *Canad. J. Chem.*, 1972, **50**, 459.

which confirm the original assignment of the molecular structure.



(I)

(Note the systematic numbering differs from the arbitrary crystallographic numbering)

EXPERIMENTAL

The compound was prepared by reaction between silicon difluoride and acetylene, and purified by exhaustive vacuum-line distillation between −30 and −15 °C. The white elongated crystals obtained were stable at room temperature in the absence of air and water and sublimable under vacuum. Because of the volatility and reactivity of the compound D_m was not determined.

Crystal Data.—$C_4H_4F_6Si_3$, $M = 250{\cdot}32$, Monoclinic, $a = 6{\cdot}293(9)$, $b = 11{\cdot}44_4(1_5)$, $c = 13{\cdot}99_2(1_5)$ Å, $\beta = 120{\cdot}7(2)^\circ$, $U = 866{\cdot}4 \pm 3{\cdot}3$ Å^3, $D_c = 1{\cdot}92$, $Z = 4$. Space-group $P2_1/c$ (No. 14). Mo-K_α radiation, $\lambda = 0{\cdot}7107$; μ(Mo-K_α) = 4·4 cm^{-1}.

Crystallographic Measurements.—The crystal used for structure analysis was sublimed *in vacuo* into a Lindeman glass capillary. The crystal was elongated along *a* (*ca.* 3 mm) and showed the forms {100} and {011}. The *X*-ray diffraction data were measured on a four-circle automatic diffractometer, by use of zirconium-filtered Mo-K_α radiation, in the θ—2θ scan mode. A 2° peak base-width was scanned, increasing with 2θ,[2] using a scan rate of 2° min^{-1} with backgrounds measured for 20 s per reflection. A standard reflection (200) was measured every sixty reflections, its gradual decrease in intensity during data collection was used to rescale all the data, by use of a linear interpolation procedure. Data collection was interrupted after two days because of problems with the diffractometer, at which time the intensity of the standard reflection had decreased to 45% of its original value. By the time the technical problems were solved the crystal had decomposed further, and data collection was not resumed. The measured data extended to $2\theta = 65^\circ$ in the layers for $h = 0$—5 with part of the layer $h = 6$ also collected. Only one quadrant of reciprocal space was examined. Of the 1938 independent reflections measured, 1368 were considered observed on the intensity criterion that $I \geqslant 3\sigma(I)$. For estimating $\sigma(I)$, counting statistics and an Abrahams factor of 0·008 were used.[3] No corrections for absorption were applied. The cell dimensions were obtained by a least-squares refinement of the 2θ values of axial reflections measured on both the positive and negative side of $2\theta = 0$.

Structure Determination.—The structure was solved by direct methods, by use of the symbolic addition procedure. A total of 183 reflections were found to have $E > 1{\cdot}5$. After assignment of signs to three origin-determining reflections, three additional reflections were given phases of either 0 or π, and signs were generated from the tangent formula. Of the eight possible sets, the one with the lowest R_K (16%)[4] was found to give an E map which revealed the whole structure. Anisotropic refinement for the thirteen non-hydrogen atoms converged to R 0·055. A difference Fourier synthesis at this stage showed the four highest peaks in positions expected for hydrogen atoms. The temperature factors of the hydrogen atoms were kept equal to those of the carbon atoms to which they were attached, but the hydrogen positional co-ordinates were not refined. The refinement finally converged to R 0·050.

The atomic form-factor curves used were evaluated from Hartree–Fock wavefunctions, using coefficients given in ref. 5. For the hydrogen atoms, the curve used was taken from ref. 6. For calculating the silicon contributions, the scattering curve of Si was adjusted to include the real part of the anomalous scattering contribution (+0·1e). The imaginary part (+0·1e) was also included in the calculations, these values being taken from ref. 7.

The positional co-ordinates of the atoms and the temperature factors are given in Tables 1 and 2 respectively.

TABLE 1

Atomic fractional co-ordinates * with standard deviations in parentheses

	X/a	Y/b	Z/c
Si(1)	6657(3)	1493(1)	1519(1)
Si(2)	5963(3)	3473(1)	1037(1)
Si(3)	1512(3)	2011(1)	−219(1)
F(1)	7704(7)	769(3)	886(3)
F(2)	8418(6)	1155(3)	2777(3)
F(3)	6599(7)	3838(3)	114(3)
F(4)	7287(7)	4421(3)	1972(3)
F(5)	2227(7)	1826(3)	−1144(2)
F(6)	−1341(6)	1790(3)	−807(3)
C(1)	3385(9)	1157(4)	1068(4)
C(2)	3055(10)	1955(5)	1856(4)
C(3)	2687(10)	3078(5)	1585(4)
C(4)	2583(10)	3420(4)	508(4)
H(1)	315(9)	40(4)	113(4)
H(2)	328(10)	169(5)	260(4)
H(3)	266(10)	359(5)	207(4)
H(4)	198(9)	408(4)	27(4)

* Non-hydrogen atoms × 10^4, hydrogen atoms × 10^3.

The bond lengths and angles in the molecule appear in Tables 3 and 4. The least-squares refinement program used was XFLS.[8] The bond lengths and angles with deviations were obtained by use of ORFFE.[9] Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20321 (3 pp., 1 microfiche).*

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies).

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[3] S. C. Abrahams and J. L. Bernstein, *Acta Cryst.*, 1965, **18**, 926.

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[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 215.

[8] R. D. Ellison, XFLS, an Extensively Modified Version of ORFLS, Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., unpublished.

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TABLE 2

Anisotropic temperature factors * and their standard deviations (in parentheses), $\times 10^4$. (Hydrogen temperature factors kept equal to the temperature factors of carbon atoms to which they are attached)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	319(5)	42(1)	55(1)	0(2)	66(2)	2(1)
Si(2)	306(5)	40(1)	64(1)	−16(2)	70(2)	2(1)
Si(3)	302(5)	59(1)	39(1)	−33(2)	51(2)	−2(1)
F(1)	520(16)	66(3)	102(3)	12(5)	158(6)	−6(2)
F(2)	431(14)	81(3)	60(2)	29(5)	42(5)	10(2)
F(3)	530(17)	77(3)	118(3)	−9(6)	178(7)	21(3)
F(4)	442(15)	58(2)	95(3)	−43(5)	61(5)	−17(2)
F(5)	568(16)	84(3)	54(2)	−28(5)	118(5)	−6(2)
F(6)	314(12)	102(3)	67(2)	−45(5)	43(4)	6(2)
C(1)	321(20)	41(3)	46(3)	−20(6)	59(6)	3(2)
C(2)	336(20)	69(4)	46(3)	−12(8)	71(6)	4(3)
C(3)	336(21)	65(4)	57(3)	−13(8)	89(7)	−14(3)
C(4)	325(19)	40(3)	53(3)	0(6)	63(6)	4(3)

* In the form: $T = \exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

TABLE 3

Bond lengths (Å) with standard deviations. As the hydrogen thermal parameters were not refined, the standard deviations of the C–H bonds are based solely upon positional uncertainty, and are hence underestimated

Si(1)–Si(2)	2·342(3)	Si(3)–C(1)	1·850(5)
Si(1)–F(1)	1·582(4)	Si(3)–C(4)	1·841(5)
Si(1)–F(2)	1·576(4)	C(1)–C(2)	1·527(7)
Si(1)–C(1)	1·859(6)	C(2)–C(3)	1·326(7)
Si(2)–F(3)	1·591(4)	C(3)–C(4)	1·526(7)
Si(2)–F(4)	1·572(4)	C(1)–H(1)	0·90(5)
Si(2)–C(4)	1·862(6)	C(2)–H(2)	1·03(5)
Si(3)–F(5)	1·586(4)	C(3)–H(3)	0·89(5)
Si(3)–F(6)	1·567(5)	C(4)–H(4)	0·84(5)

TABLE 4

Bond angles (°) with standard deviations

F(1)–Si(1)–Si(2)	114·5(1_5)	Si(3)–C(1)–C(2)	97·6(3)
F(2)–Si(1)–Si(2)	118·7(1_4)	Si(1)–C(1)–C(2)	99·6(3)
F(2)–Si(1)–C(1)	110·8(2)	Si(1)–C(1)–Si(3)	105·4(3)
F(1)–Si(1)–C(1)	114·0(2)	H(1)–C(1)–Si(1)	112(3)
Si(2)–Si(1)–C(1)	95·2(1_6)	H(1)–C(1)–Si(3)	124(3)
F(1)–Si(1)–F(2)	103·9(2)	H(1)–C(1)–C(2)	115(3)
Si(1)–Si(2)–F(3)	113·6(1_5)	C(3)–C(4)–Si(3)	98·1(3)
Si(1)–Si(2)–F(4)	119·1(1_8)	C(3)–C(4)–Si(2)	98·7(4)
Si(1)–Si(2)–C(4)	95·1(1_6)	Si(3)–C(4)–Si(2)	105·7(3)
F(3)–Si(2)–C(4)	113·3(2)	H(4)–C(4)–Si(2)	109(4)
F(4)–Si(2)–C(4)	111·4(2)	H(4)–C(4)–Si(3)	127(3)
F(3)–Si(2)–F(4)	104·4(2)	H(4)–C(4)–C(3)	114(3)
F(5)–Si(3)–F(6)	106·1(2)	C(1)–C(2)–C(3)	116·2(4)
F(5)–Si(3)–C(1)	114·7(2)	C(1)–C(2)–H(2)	124(3)
F(6)–Si(3)–C(1)	114·5(2)	C(3)–C(2)–H(2)	120(3)
F(6)–Si(3)–C(4)	115·5(2)	C(2)–C(3)–C(4)	116·4(4)
F(5)–Si(3)–C(4)	113·1(2)	C(2)–C(3)–H(3)	119(4)
C(1)–Si(3)–C(4)	93·0(2)	C(4)–C(3)–H(3)	124(3)

DISCUSSION

Description of the Structure.—The structure is clearly that of a molecular crystal, there being no close intermolecular contacts. There is a virtual mirror plane through Si(3) and the mid-points of Si(1)–Si(2) and C(2)–C(3). This is illustrated[10] in Figure 1, which also shows the arbitrary crystallographic numbering system.

Table 5 shows the results of a best least-squares molecular fit calculation[11] between the molecule and its mirror image. The greatest deviations from mirror symmetry occur at the fluorine atoms, which, being on the outside of the molecule, are more susceptible to the influence of intermolecular forces. The carbon–silicon framework is symmetrical to within 1σ of the positional co-ordinates. The deviations of the hydrogen-atom positions from this symmetry are probably not significant owing to the large estimated error associated with their positions. There appear to be no close H–F, H–Si, or F–C contacts. All bond lengths appear to be within accepted limits. The distances C(1)–C(2) [1·527(7) Å] and C(3)–C(4) [1·526(7) Å] are slightly longer than =C–CH$_3$ in propene (1·51 Å), and longer than analogous bonds in *anti*-7-norbornenyl-*p*-bromobenzoate (1·51 and 1·52 Å) whose structure has been reported.[12]

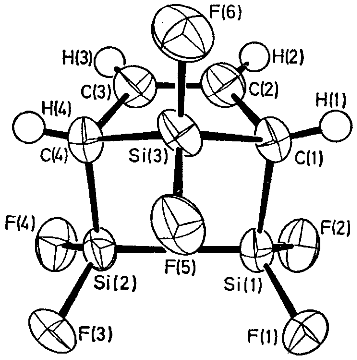

FIGURE 1 Plane view of the molecule, showing the approximate mirror plane of symmetry and the arbitrary crystallographic numbering system. The ellipsoids are drawn to include 50% probability. Hydrogen atoms are drawn as spheres on an arbitrary scale (ORTEP ref. 10)

TABLE 5

Best molecular fit (least-squares) between the molecule and its mirror image. (Hydrogen atoms not included in calculation)

Matched atoms		
Molecule	Mirror image	Distance (Å)
Si(1)	Si(2)	0·001
Si(2)	Si(1)	0·004
Si(3)	Si(3)	0·004
F(1)	F(3)	0·034
F(2)	F(4)	0·019
F(3)	F(1)	0·028
F(4)	F(2)	0·012
F(5)	F(5)	0·059
F(6)	F(6)	0·031
C(1)	C(4)	0·007
C(2)	C(3)	0·017
C(3)	C(2)	0·012
C(4)	C(1)	0·009
Unmatched atoms		
H(1)	H(4)	0·074
H(2)	H(3)	0·142
H(3)	H(2)	0·142
H(4)	H(1)	0·072

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[10] C. K. Johnson, ORTEP: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., 1964.

[11] S. C. Nyburg, unpublished program.

[12] A. C. MacDonald and J. Trotter, *Acta Cryst.*, 1965, **19**, 456.

The mean Si–F bond length is 1·573 Å, which is close to that found for other $-SiF_2$ groups in *e.g.* SiH_2F_2 [13] and Me_3SiHF_2.[14,15]

However, for each SiF_2 group one Si–F bond is longer than the other. Significantly Si(2)–F(3) is longer than Si(2)–F(4), and Si(3)–F(5) is longer than Si(3)–F(6). The difference between Si(1)–F(1) and Si(1)–F(2) is less marked. For the pseudo-mirror related groups $Si(1)F_2$ and $Si(2)F_2$, the longer Si–F bonds [Si(1)–F(1) and Si(2)–F(3)] are those lying closest to the plane Si(1),-Si(2),C(3),C(2) (see Figure 2). Similarly, the longer of the two Si(3)–F bonds is that lying closest to the plane Si(3),C(2),C(3). Unfortunately structural data for geminally substituted norbornenes are not available, so it is not possible to correlate bond lengths with chemical reactivity. However the extensive studies of substituted norbornenes have indicated that solvolytic reactions, for example, may go through a carbonium ion stabilised by interaction of the conventionally labelled C(7) atom [our Si(3)] with the double bond. The observed variation of Si–F bond lengths may perhaps indicate a small ground-state interaction between the silicon atoms and the double bond.

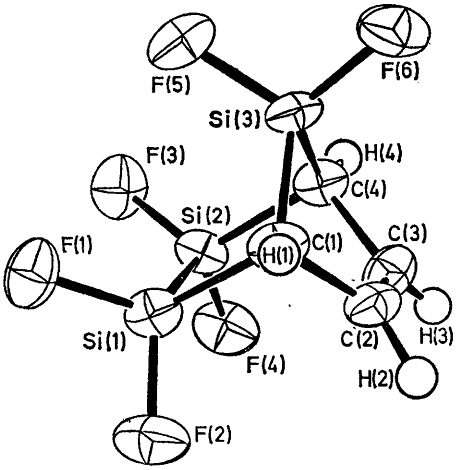

FIGURE 2 Lateral view of the molecule showing the large bend at C(1) and C(4) of the Si(1), Si(2), C(1)—(4) ring

Concerning the bond angles: it might be expected that the less than tetrahedral angle C(1)–Si(3)–C(4) (93·0°) would lead to an increase of the F(5)–Si(3)–F(6) angle beyond the normal tetrahedral value. Instead, this latter angle is also decreased (106·1°). Similar observations can be made for the angles around Si(1) and Si(2). The angles within the rings of the C–Si skeleton of the molecule are also smaller than normal sp^3 or sp^2 values, but this is not unexpected in such a strained ring system.

Bridged molecules of this type may be described in terms of a number of five- or six-membered buckled rings. The equation of the planes of parts of these rings, and the angles between the planes are given in Table 6.

TABLE 6

Equations of best least-squares planes in the form $AX + BY + CZ = D$, where X, Y, and Z are the co-ordinates in Å referred to the unit cell axes. Deviations (Å) of relevant atoms from the planes are given in square brackets

	A	B	C	D
Plane (1):				
Si(1), Si(2), C(1), C(2)	0·3379	−0·2224	−0·9145	−1·0050
[Si(1) 0·002, Si(2) −0·002, F(1) 1·259, F(2) −1·225, F(3) 1·279, F(4) −1·217, C(1) −0·002, C(2) 0·002]				
Plane (2):				
Si(3), C(1), C(4)	0·9859	−0·0034	−0·1675	1·1288
[F(5) 1·281, F(6) −1·237]				
Plane (3):				
C(1)—(4)	−0·8414	−0·1654	−0·5145	−2·0274
[C(1) −0·003, C(2) 0·006, C(3) −0·006, C(4) 0·003, H(1) 0·26, H(2) −0·08, H(3) −0·10, H(4) 0·20]				

Angles (°) between planes:

1—2	119·1
1—3	102·9
2—3	138·0

The symmetrical structure of the molecule established in this study is in agreement with the deductions previously drawn from the ^{19}F n.m.r. spectrum.[1] There is as yet insufficient structural information for this type of compound to be able to make any correlations between ^{19}F–^{19}F coupling constants and the molecular structural parameters. The value of J[F(5)–F(6)] of 56 Hz at an angle of 106·1° is considerably larger than J[F(1)–F(2)], J[F(3)–F(4)] of 31 Hz where the angle is 104°. However, there may be no simple relationship between the coupling constants and molecular angular parameters as is apparently the case in a number of cyclic fluorocarbon derivatives.[16]

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[1/2159 *Received*, 16*th November*, 1971]

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[16] K. L. Williamson and B. A. Braman, *J. Amer. Chem. Soc.*, 1967, **89**, 6183.