

Journal of Organometallic Chemistry, 197 (1980) 275–283
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CRYSTAL STRUCTURES OF *m*-TRIFLUOROMETHYLPHENYLSILATRANONE AND *p*-FLUOROPHENYLSILATRANONE

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(Received April 8th, 1980)

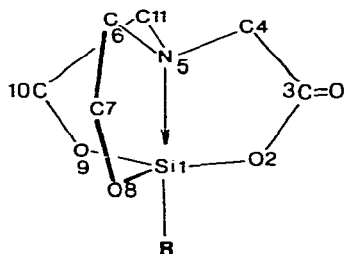
Summary

The crystal structures of two silatranone derivatives are reported. The close N → Si approach (2.106(3) Å in *m*-trifluoromethylphenyl-, and 2.129(3) Å in *p*-fluorophenyl-silatranone) indicates strong dative acceptor bonds. For various silatrane derivatives and inverse relation has been revealed between the mean group electronegativity of the substituent R attached to silicon and the N → Si dative bond distance. In both structures there are long (1.72 Å) Si—O bonds in the Si—O—CO moiety. The *m*-trifluoromethylphenyl derivative contains a disordered CF₃ group.

Introduction

In an earlier paper [1] we reported the preparation of novel type silatrane derivatives, 2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-3-ones (“silatranones”) (Fig. 1). The presence of a five-coordinated silicon in these compounds was proved by NMR studies and potentiometric titrations.

The aim of the present X-ray study was to reveal the effect of the carbonyl group in the silatrane skeleton upon the molecular geometry. The silatranone structure is shown in Fig. 1.



I: R = *m*-CF₃-Ph-

II: R = *p*-F-Ph-

Fig. 1. The structural formula of silatranones with the numbering of atoms.

Experimental

Unit cell determination and intensity data collection were performed on a computer controlled Enraf-Nonius CAD4 diffractometer at room temperature. Crystal data and data collection parameters are shown in Table 1.

Structural solution and refinement

Both structures were solved by Multan (supplied by Enraf-Nonius with the SDP-34 program package) and Fourier methods. The structures were refined by full-matrix least-squares with anisotropic temperature factors for the non-hydrogen atoms (except for fluorine atoms in molecule I). Several attempts have been made to refine I as an ordered crystal structure. Three fluorine atoms were located in a Fourier map but refinement resulted in unusually high isotropic temperature factors for them. Subsequent difference Fourier calculations revealed further five strong peaks in the vicinity of C(19), each higher than $1 \text{ e}/\text{\AA}^3$. These were also included in the calculations, with multiplicities proportional to their peak heights in the difference map. Multiplicities of all eight fluorine atoms were refined freely and they behaved well during refinement (the sum of the refined multiplicities was 3.05). Least-squares parameters, the weighting scheme used and final *R* values are given in Table 1. Atomic scattering factors and anomalous dispersion coefficients were taken from [2].

The final atomic parameters for the non-hydrogen atoms (except disordered fluorine atoms) are given in Tables 2 and 3, the parameters of the disordered fluorine atoms in Table 4 and the calculated hydrogen positions in Table 5. All calculations were performed by using the E.N. SDP-34 program package and local programs on a PDP 11/34 computer.

Discussion

Both structures are built up from monomeric silatranone molecules (Fig. 2). Bond lengths and angles are shown in Table 6.

The lengths of the N → Si donor-acceptor bonds are 2.106(3) (I) and

TABLE 1
CRYSTAL DATA, DATA COLLECTION AND LEAST-SQUARES PARAMETERS

	Compound I	Compound II
Empirical formula	C ₁₃ H ₁₄ O ₄ NSiF ₃	C ₁₂ H ₁₄ O ₄ NSiF
Formula weight	333.3	283.3
Cell constants <i>a</i> (Å)	11.555 (2)	12.696 (3)
<i>b</i>	13.492 (2)	13.927 (6)
<i>c</i>	10.328 (8)	14.405 (3)
β (°)	114.54 (3)	—
<i>V</i> (Å ³)	1464.7 (2.0)	2547.1 (2.2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>Z</i>	4	8
Density (calc) (Mg/m ³)	1.512	1.478
Wavelength (Mo-K α), Å		0.71073
μ (Mo-K α) (mm ⁻¹)	0.22	0.21
Approx. crystal size (mm)	0.20 × 0.25 × 0.28	0.05 × 0.15 × 0.25
2 Θ range		3 < 2 Θ < 50°
Scan width		(0.35 + 0.35 tan Θ)
Max. scan time (min)		1
Scan technique		Θ -2 Θ
Number of reflexions collected	2503	2199
Number of reflexions with zero intensity	0	1108
Number of reflexions used in least-squares	2215 [<i>I</i> ≥ 2 σ (<i>I</i>)]	1390 [<i>I</i> ≥ 1 σ (<i>I</i>)]
Number of variables	212	172
Weighting scheme		$w = 4F_0^2 / \sigma(F_0^2)^2$
	$[\sigma(F_0^2) = \{\sigma(I)^2 + (\rho I)^2\}^{1/2} / LD]$	
<i>p</i> used in the weighting scheme	0.04	0.01
<i>R</i> _{obs}	0.075	0.070
<i>R</i> _{wO}	0.092	0.040
<i>R</i> _{tot}	0.083	0.138 ^a

^a Including zero-intensity reflexions.

2.129(3) Å (II), respectively. The former is the second closest N...Si approach found in silatranes so far (the length of the N → Si link in 1-chlorosilatrane [12] is 2.023 Å). The carbonyl oxygen O(12) probably has little effect, if any, on the N → Si bond distance, which seems to depend primarily on the electron-withdrawing properties of R. The N → Si distance is inversely proportional to the mean electronegativity of R. The group electronegativity was approximated by calculating the geometric mean of the electronegativities given by Sanderson [3] for the atoms forming the group. These data are given in Table 7 and the graph of the observed N → Si distances against the mean group electronegativity, \bar{X}_R is shown in Fig. 3. Contrary to the fact that this rough approximation neglects the structure of R, and in addition to this, different crystalline forms

TABLE 2

FINAL ATOMIC COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS (EXCEPT DIS-ORDERED FLUORINE ATOMS) AND MEAN TEMPERATURE FACTORS FOR COMPOUND I

	x	y	z	$B_{eq} (\text{\AA}^2)$
Si(1)	7624(1)	935(1)	2206(1)	2.83(2)
O(2)	6873(3)	2051(3)	1593(3)	3.59(7)
O(8)	8771(3)	879(3)	3810(4)	3.93(7)
O(9)	6805(3)	-44(3)	1382(3)	3.91(7)
O(12)	5585(4)	3263(3)	1611(4)	5.4(1)
N(5)	6425(4)	925(3)	3283(4)	3.28(8)
C(3)	6100(4)	2492(4)	2083(5)	3.6(1)
C(4)	6018(4)	1955(4)	3306(5)	4.0(1)
C(6)	7216(5)	509(5)	4695(6)	4.7(1)
C(7)	8552(6)	880(5)	5076(6)	4.5(1)
C(10)	5897(5)	-500(4)	1788(6)	4.4(1)
C(11)	5345(4)	285(4)	2389(6)	3.9(1)
C(13)	8643(4)	1066(4)	1189(5)	3.2(1)
C(14)	9883(4)	1442(4)	1840(5)	3.9(1)
C(15)	10594(5)	1602(4)	1051(6)	4.7(1)
C(16)	10109(5)	1394(5)	-388(6)	5.2(1)
C(17)	8880(5)	1015(5)	-1038(6)	4.8(1)
C(18)	8179(5)	852(4)	-260(6)	4.0(1)
C(19)	11940(6)	2005(6)	1836(7)	10.3(2)

(e.g. 1-phenylsilatrane modifications) may have dative bonds of different length, the N \rightarrow Si distances may be estimated for a given R.

The carbonyl group in the silatrane skeleton affects its geometry quite uniformly in both compounds. A remarkable feature of the structures are the long

TABLE 3

FINAL ATOMIC COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS AND MEAN TEMPERATURE FACTORS FOR COMPOUND II

	x	y	z	$B_{eq} (\text{\AA}^2)$
Si(1)	2009(1)	1697(1)	1164(1)	2.41(2)
F	-1504(2)	-770(2)	2651(2)	6.04(6)
O(2)	1171(1)	2572(2)	763(2)	2.74(5)
O(8)	2695(2)	1894(2)	2120(2)	3.27(5)
O(9)	2380(2)	925(2)	359(1)	3.08(5)
O(12)	882(2)	3951(2)	38(2)	3.83(6)
N(5)	3151(2)	2610(2)	539(2)	2.42(6)
C(3)	1485(3)	3395(2)	386(2)	2.94(8)
C(4)	2662(3)	3563(3)	455(2)	2.95(9)
C(6)	4060(3)	2577(3)	1183(3)	3.23(8)
C(7)	3599(3)	2503(3)	2149(2)	3.53(8)
C(10)	3252(3)	1097(3)	-247(2)	3.33(9)
C(11)	3360(3)	2163(3)	-381(2)	3.16(8)
C(13)	928(3)	933(2)	1673(2)	2.50(7)
C(14)	123(3)	608(3)	1097(2)	2.93(8)
C(15)	-698(3)	39(3)	1416(3)	3.36(9)
C(16)	-698(3)	-204(3)	2340(3)	3.38(9)
C(17)	66(3)	83(3)	2941(2)	3.76(9)
C(18)	881(3)	652(3)	2604(3)	3.26(8)

TABLE 4

FINAL ATOMIC COORDINATES ($\times 10^3$), ISOTROPIC TEMPERATURE FACTORS, MULTIPLICITIES AND C—F DISTANCES FOR THE DISORDERED FLUORINE ATOMS (COMPOUND I)

	x	y	z	B (Å ²)	mult.	C—F (Å)
F(1)	1261(1)	198(1)	113(1)	7.2(2)	0.62	1.27(1)
F(2)	1213(1)	260(1)	289(1)	5.7(2)	0.48	1.30(1)
F(3)	1272(1)	118(1)	281(1)	6.9(2)	0.48	1.52(1)
F(4)	1178(1)	294(1)	223(1)	6.7(3)	0.33	1.37(2)
F(5)	1230(1)	253(1)	88(1)	8.2(4)	0.34	1.41(1)
F(6)	1250(1)	193(1)	308(1)	9.1(4)	0.32	1.18(1)
F(7)	1168(1)	311(1)	108(1)	9.2(3)	0.24	1.65(2)
F(8)	1276(2)	144(2)	191(3)	9.0(6)	0.24	1.23(2)

TABLE 5

THE CALCULATED HYDROGEN ATOMIC COORDINATES ($\times 10^3$) AND C—H DISTANCES (Å)

	Compound I ($\overline{B}_H = 4.5 \text{ \AA}^2$)				Compound II ($\overline{B}_H = 4.3 \text{ \AA}^2$)			
	x	y	z	C—H	x	y	z	C—H
H(4a)	504	196	320	1.09	287	400	107	1.11
H(4b)	663	228	431	1.08	298	393	-16	1.10
H(6a)	685	76	547	1.10	457	196	102	1.03
H(6b)	717	-30	466	1.09	455	323	110	1.10
H(7a)	866	162	550	1.08	421	220	263	1.12
H(7b)	923	40	588	1.09	340	321	241	1.09
H(10a)	515	-84	86	1.09	313	74	-92	1.10
H(10b)	635	-107	258	1.09	399	81	5	1.10
H(11a)	462	71	155	1.08	279	242	-89	1.09
H(11b)	490	-5	304	1.10	415	235	-62	1.10
H(14)	1026	159	290	1.01	14	82	40	1.05
H(15)					-129	-22	97	1.06
H(16)	1061	154	-97	1.01				
H(17)	854	84	-208	1.01	3	-13	366	1.07
H(18)	727	58	-77	1.03	147	88	305	1.04

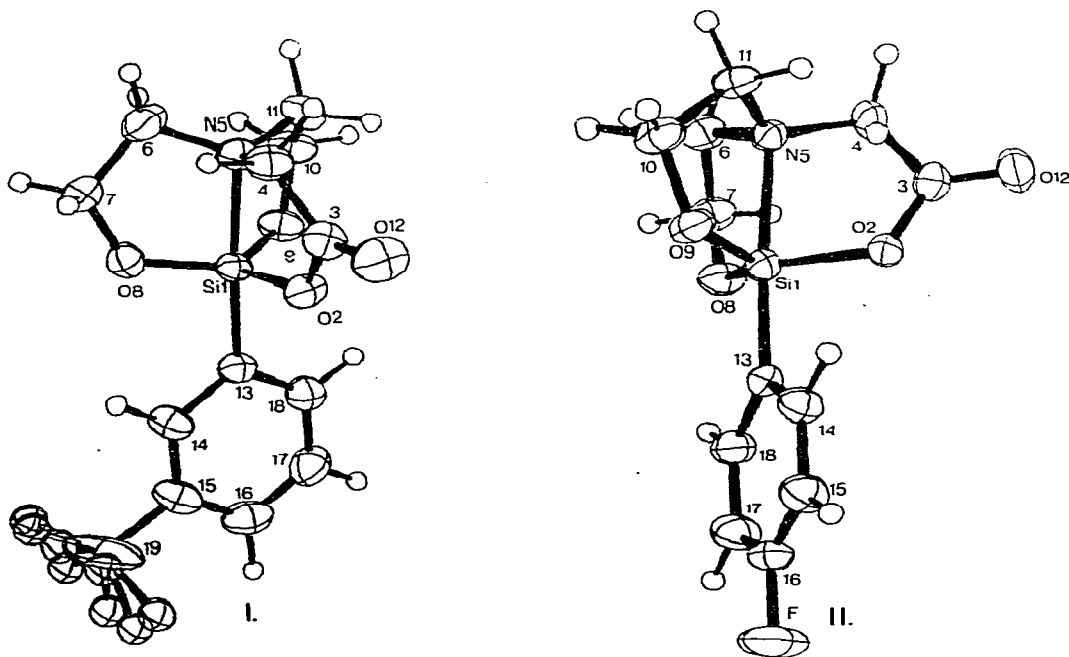


Fig. 2. Molecular diagrams of the title compounds with the numbering of atoms (bare numbers denote carbon atoms).

TABLE 6
 BOND DISTANCES (Å) and ANGLES (°)

	I	II		I	II
Si(1)—N(5)	2.106(3)	2.129(3)	C(4)—N(5)	1.471(7)	1.470(4)
Si(1)—O(2)	1.722(4)	1.718(2)	C(6)—N(5)	1.473(6)	1.481(4)
Si(1)—O(8)	1.638(3)	1.652(2)	C(11)—N(5)	1.482(6)	1.488(4)
Si(1)—O(9)	1.643(4)	1.651(2)	C(13)—C(14)	1.400(7)	1.393(5)
Si(1)—C(13)	1.884(4)	1.885(3)	C(13)—C(18)	1.395(5)	1.397(5)
O(2)—C(3)	1.336(5)	1.329(4)	C(14)—C(15)	1.394(6)	1.387(5)
O(8)—C(7)	1.431(4)	1.428(4)	C(15)—C(16)	1.381(6)	1.373(5)
O(9)—C(10)	1.421(6)	1.430(4)	C(16)—C(17)	1.391(8)	1.360(5)
C(3)—O(12)	1.196(6)	1.199(4)	C(17)—C(18)	1.376(6)	1.391(5)
C(3)—C(4)	1.492(6)	1.517(5)	C(15)—C(19)	1.525(8)	—
C(6)—C(7)	1.512(8)	1.514(5)	C(16)—F	—	1.367(4)
C(10)—C(11)	1.498(7)	1.503(5)			

	I	II		I	II
N(5)—Si(1)—C(13)	174.6(3)	176.2(2)	C(3)—C(4)—N(5)	108.2(6)	106.4(5)
N(5)—Si(1)—O(2)	81.9(2)	81.7(2)	C(7)—C(6)—N(5)	106.1(7)	106.0(5)
N(5)—Si(1)—O(8)	84.2(3)	83.9(2)	C(10)—C(11)—N(5)	106.1(6)	106.5(5)
N(5)—Si(1)—O(9)	84.5(3)	84.1(2)	C(4)—N(5)—C(6)	114.5(6)	114.1(4)
O(2)—Si(1)—O(8)	119.0(3)	119.3(2)	C(4)—N(5)—C(11)	111.6(6)	112.4(4)
O(2)—Si(1)—O(9)	114.8(3)	113.7(2)	C(6)—N(5)—C(11)	114.2(6)	113.9(4)
O(8)—Si(1)—O(9)	122.5(3)	122.9(2)	Si(1)—N(5)—C(4)	106.7(4)	106.6(3)
O(2)—Si(1)—C(13)	93.8(3)	94.6(2)	Si(1)—N(5)—C(6)	104.6(5)	104.3(3)
O(8)—Si(1)—C(13)	97.9(3)	98.8(2)	Si(1)—N(5)—C(11)	104.1(4)	104.3(3)
O(9)—Si(1)—C(13)	98.4(3)	96.5(2)	Si(1)—C(13)—C(14)	121.6(6)	119.1(4)
Si(1)—O(2)—C(3)	124.4(5)	124.3(4)	Si(1)—C(13)—C(18)	121.9(6)	124.2(4)
Si(1)—O(8)—C(7)	123.2(5)	123.2(4)	C(13)—C(14)—C(15)	120.6(7)	122.7(5)
Si(1)—O(9)—C(10)	122.1(5)	122.7(4)	C(14)—C(15)—C(16)	121.5(8)	117.5(6)
O(2)—C(3)—O(12)	122.0(7)	122.4(5)	C(15)—C(16)—C(17)	118.1(8)	123.0(6)
O(2)—C(3)—C(4)	113.1(7)	113.7(5)	C(16)—C(17)—C(18)	120.5(9)	118.4(6)
O(8)—C(7)—C(6)	108.1(7)	108.9(5)	C(17)—C(18)—C(13)	122.5(8)	121.8(6)
O(9)—C(10)—C(11)	108.1(7)	108.3(5)	C(14)—C(13)—C(18)	116.8(7)	116.7(5)
			C(14)—C(15)—C(19)	117.6(8)	—
			C(16)—C(15)—C(19)	120.9(8)	—
			C(15)—C(16)—F	—	117.4(5)
			C(17)—C(16)—F	—	119.6(6)

TABLE 7

 N → Si DISTANCES AND MEAN GROUP ELECTRONEGATIVITIES OF R IN VARIOUS SILA-
 TRANES $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$

R	$d(\text{N} \rightarrow \text{Si})$ (Å)	\bar{X}_R	Ref.
C_2H_5	2.21	3.62	4
$\alpha\text{-C}_6\text{H}_5$	2.193(5)	3.68	5
$\text{ClCH}_2\text{CH}_2\text{CH}_2$	2.18	3.74	6
CH_3	2.175(4)	3.61	7
$\beta\text{-C}_6\text{H}_5$	2.156(4)	3.68	8
$\gamma\text{-C}_6\text{H}_5$	2.132(4)	3.68	9
$p\text{-FC}_6\text{H}_4^a$	2.129(3)	3.84	this work
ClCH_2	2.120	3.92	10
$m\text{-NO}_2\text{C}_6\text{H}_4$	2.116(8)	3.95	11
$m\text{-CF}_3\text{C}_6\text{H}_4^a$	2.106(3)	4.07	this work
Cl	2.023	4.93	12

^a $\text{RSi}(\text{OCOCH}_2)(\text{OCH}_2\text{CH}_2)_2\text{N}$

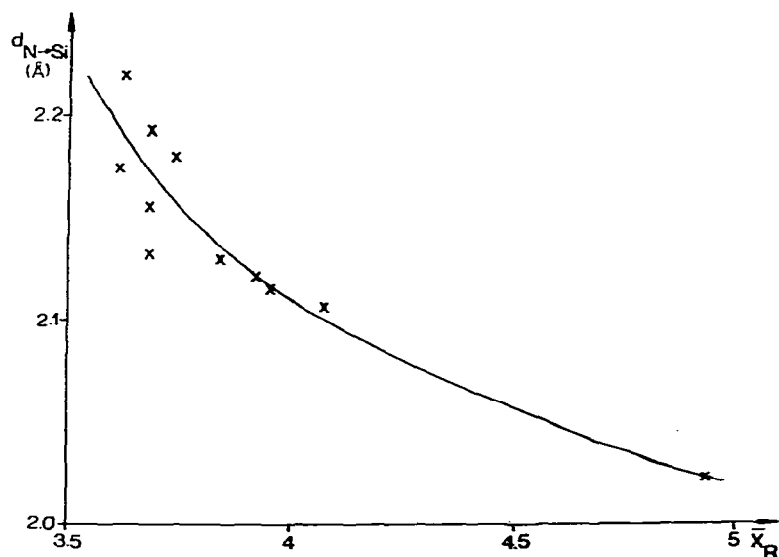


Fig. 3. The $N \rightarrow Si$ dative bond lengths plotted against the mean-group electronegativity of R.

Si(1)—O(2) bonds (1.72 Å). Only two crystal structures possessing similar Si—O—CO-moieties have been reported so far. While in silicon tetraacetate [13] the length of the Si—O bonds is normal, the corresponding Si—O distance in *O*-trimethylsilyl-*N*-phenylcarbamate is 1.70 Å [14]. The carbonyl group seems to reduce the interaction between O(2) and Si and also affects the O(2)—C(3) bond, which is nearly 0.1 Å shorter than the corresponding O(8)—C(7) and O(9)—C(10) bonds. Nevertheless the C=O double bond is well localized.

The silicon atom deviates from the plane of the three equatorial oxygen atoms by 0.186(1) in I and 0.196(1) Å in II in opposite direction to the nitro-

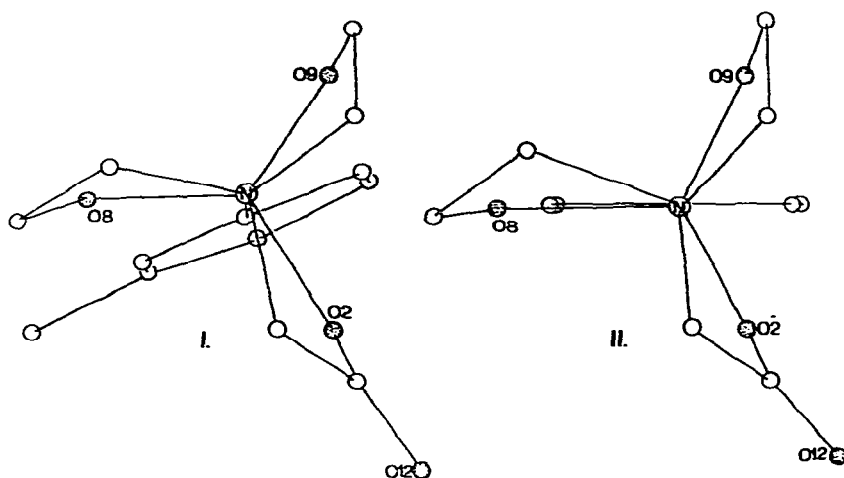


Fig. 4. The structures as viewed down the $N \rightarrow Si$ axis. (Hydrogen and fluorine atoms are omitted for clarity.)

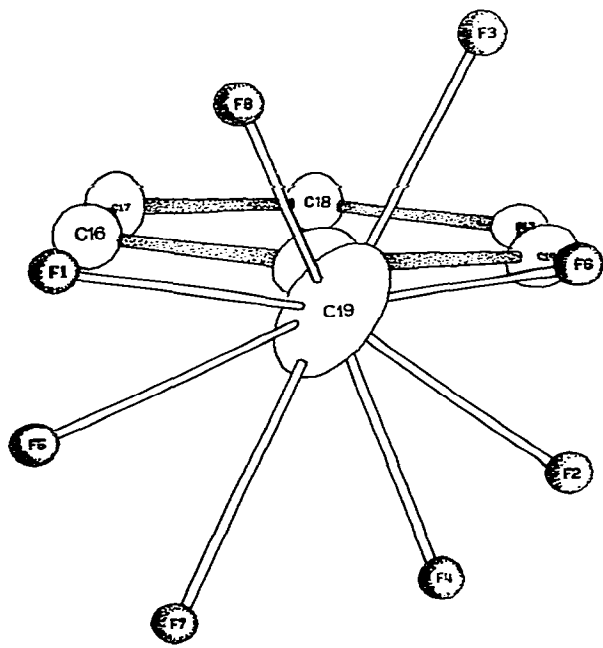


Fig. 5. The disordered CF_3 -group and the phenyl carbon atoms (compound I).

gen. The distances of N(5) from the plane of the adjacent carbon atoms are 0.385(4) (I) and 0.386(2) Å (II).

Fig. 4 depicts the structures as viewed down the $\text{N} \rightarrow \text{Si}$ axis. The relative positions of the phenyl rings with respect to the silatrane skeleton are different in these molecules. The $\text{C}(18)\text{—C}(13)\text{—Si}(1)\text{—O}(8)$ dihedral angles are $160.4(8)$ (I) and $-2.4(5)^\circ$ (II).

The disorder of the fluorine atoms in compound I is presumably due to a rotational oscillation about the $\text{C}(15)\text{—C}(19)$ bond coupled with a high amplitude out-of-plane motion of C(19). As shown in Fig. 5 the distribution of the fluorine atoms has an approximate eight-fold symmetry, F(1) and F(6) being nearly coplanar with the phenyl ring. The C—F distances are subject to large errors, the mean C—F distances is 1.27(6) Å. The long C—F distances are found along the direction of the out-of-plane motion of C(19) while short ones are perpendicular to it.

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