THE CRYSTAL STRUCTURE OF 1-VINYLSILATRANE

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I. INTRODUCTION

The 1-vinylsilatrane is a compound with the presence of pentacoordinated silicon[1]. Structural studies of this series of compounds have been reported[2-4]. In the present paper, molecular and crystal structure of 1-vinylsilatrane was determined by direct method with the program system (GC-79) (ALGOL 60) suggested by the author. All the calculations were carried out on the TQ-16 Computer (48 bits, 32 K) produced in China.

II. EXPERIMENTAL

According to its Weissenberg photograph, this compound is orthorhombic, space group $P2_12_12_1$. The crystal data are listed in Table 1.

Intensities were collected on a Philips PW-1100 four-circle diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). A total of 1082 unique reflections were measured ($\theta = 3 \sim 68°$). These included 233 unobserved reflections ($I < 3\sigma(I)$). The intensities were corrected only for the Lorentz and Polarization factors.

The scale factor and over-all temperature factor were determined by Wilson's method.

Table 1

Crystal Data

Molecular Formula: $C_8H_{15}NO_3Si$	M. W. 201
Orthorhombic	Space group $P2_12_12_1$
$a = 15.441$ (3) Å	$V = 987.43$ Å^3
$b = 9.576$ (2)	$D_{obs.} = 1.354$ g · cm^{-3}
$c = 6.678$ (1)	$D_{calc.} = 1.352$ g · cm^{-3}
$Z = 4$	$F_{(000)} = 432$
$\lambda(CuK_\alpha) = 1.5418$ Å	

III. Determination of the Structure

The structure was solved by direct methods and Fourier synthesis, and 169 reflections with $|E| > 1.3$ were used in the calculations. The nine starting phases set were chosen according to the general rule for the selection of them[5]. Some restrictive conditions are laid down for phase calculation by the multi-solution program (GCMS) of the (GC-79) system[6].

Calculations were carried out on the TQ-16 computer. Making use of the phases assigned to the starting set, the phases of other reflections were calculated and refined by the tangent formula. Altogether 161 phases were derived from the first set $\left(\phi_{843} = -\frac{3}{4}\pi,\ \phi_{654} = -\frac{3}{4}\pi,\ \phi_{325} = -\frac{3}{4}\pi\right)$ after seven cycles. The R(karle) was 0.151. The E map was calculated from these phases.

The molecule could not be recognized in the E map because of the symmetrical solution. There was one peak of very high intensity at $x = 0.38$, $y = 0.85$, $z = 0.50$. This symmetrical phenomenon was presumably due to the position of the silicon atom at $z = 0.50$, resulting in a pseudo-mirror plane. Therefore, the high peak was assumed to be the position of the silicon atom. Another four peaks that satisfy the atomic position in molecular structure were selected, and three of them were assumed to be oxygen atoms, and the fourth was considered a nitrogen atom. Fourier synthesis was calculated directly from these five atomic positions. The R value was 0.319. On the electron density map synthesized, another six non-hydrogen atoms were located. The subsequent Fourier synthesis ($R = 0.311$) gave the positions of the two missing non-hydrogen atoms. The coordinate parameters were refined by Fourier approach. The R value was 0.229.

IV. Refinement of the Structure

The atomic parameters were refined by block-diagonal least-squares with the program of (GCLS-BLOCK)[7]. The function minimized was $\sum W_h(|F_o| - |F_c|)^2$, where the weights $W_h = 4I/\sigma^2(I)$. First, overall temperature factor refinement was carried out, and after three cycles, the R value was reduced to 0.158. Next, another two cycles of isotropic refinement gave the result $R = 0.120$, and the final three subsequent cycles of anisotropic refinement reduced the value of R to 0.099.

Difference Fourier synthesis was calculated on the result of the latest anisotropic refinement. All hydrogen atoms were located in the difference map. The isotropic thermal parameters of the hydrogen atoms were assumed to be the same as those of the carbon atoms, to which they are bonded. Two additional cycles of anisotropic refinement (the contributions of the hydrogen atoms were included, but their parameters were kept constant) gave the results $R = 0.089$ for all reflections, and $R = 0.082$ for 835 observed reflections (the fourteen reflections of second extinction were omitted).

Atomic parameters with their estimated standard deviations are listed in Table 2.

Table 2

Atomic Parameters ($\times 10^4$) and Their e. s. d.'s

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Si(1)	3837(1)	8539(2)	4971(3)	36(1)	77(3)	148(5)	3(3)	4(4)	8(8)
O(2)	3161(3)	8539(5)	6061(9)	41(3)	94(9)	290(22)	33(11)	−13(18)	−15(27)
C(3)	3311(7)	1110(9)	6111(16)	66(7)	83(13)	294(39)	−2(22)	57(39)	116(49)
C(4)	3867(7)	1536(8)	4370(18)	86(9)	76(13)	550(58)	2(21)	−146(45)	79(55)
N(5)	4473(4)	425(6)	4026(8)	36(3)	61(8)	120(18)	22(12)	12(18)	96(26)
C(6)	5285(6)	506(11)	5264(21)	49(6)	219(22)	727(74)	1(23)	46(42)	−411(74)
C(7)	5509(5)	9091(9)	5866(13)	41(5)	134(14)	270(32)	−22(17)	11(26)	32(45)
O(8)	4778(3)	8239(5)	6131(8)	47(3)	105(9)	229(18)	−15(11)	−15(17)	39(26)
O(9)	3783(3)	8226(5)	2529(7)	64(4)	93(8)	173(15)	−1(12)	−43(16)	2(23)
C(10)	4017(6)	9236(9)	1070(11)	69(7)	122(14)	139(23)	−30(20)	1(26)	76(36)
C(11)	4697(8)	199(11)	1877(12)	67(8)	177(22)	83(22)	25(29)	114(31)	41(47)
C(12)	3218(5)	6913(8)	5842(12)	42(5)	98(12)	244(28)	−8(16)	12(25)	29(38)
C(13)	2955(5)	5916(11)	4772(18)	53(5)	165(18)	403(46)	7(21)	74(35)	−94(57)

V. Results and Discussion

The bond lengths and angles with ther estimated standard deviations are computed by the (GCSD) program[8] and are listed in Table 3. A perspective view of the molecule is shown in Fig. 1.

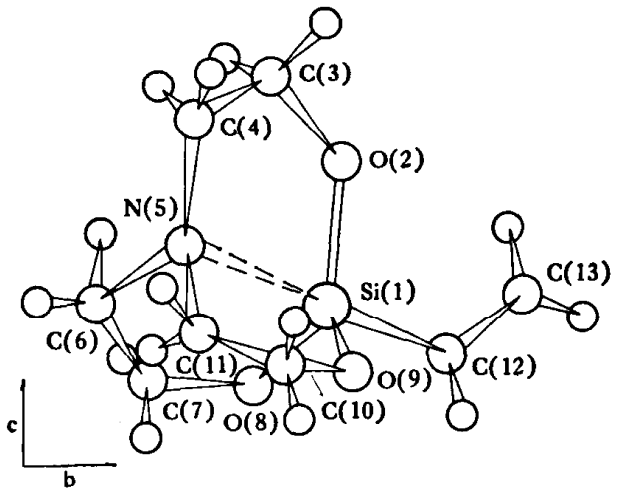

Fig. 1. A perspective view of the 1-vinylsilatrane molecule.

1. *Description of Structure*

(1) The planes formed by C(4), C(6), C(11) and by C(3), C(7), C(10) are inclined to the plane of the oxygens by 0.28° and 0.21° respectively.

(2) The Si atom is inclined toward the C(12), and it is 0.20 Å out of the plane of the oxygens. The N atom is inclined toward the Si atom, and the distance from the N atom to the plane formed by C(4), C(6), C(11) is 0.40 Å. The Si—C(12) is 1.880(8) Å.

(3) In the three five-membered rings, each carbon atom bonded to nitrogen deviates from the least-squares plane formed by the remaining atoms.

(4) The average C—C—O, C—C—N, Si—O—C angles are 111.08, 106.84, and 122.66° respectively. The average Si—O, N—C, C—C, C—O bond lengths are 1.664, 1.477, 1.485 and 1.414 Å respectively. The N--C bond distance is in agreement with that of the standard covalent bond (1.47 Å), but the C—C and C—O bond distances 1.54 and 1.44 Å are shorter than that of the standard covalet bond.

2. *Characteristics of the Si—N Bond*

(1) The molecular geometry at silicon is a distorted form of the double prismatic pyramid. The average angles C—Si—O and O—Si—O are 96.75° and 118.63°. These values are close to the angles of an ideal double prismatic pyramid (90° and 120°).

(2) The angle N—Si—C(12) is 178.72°. Obviously, the atoms N, Si, and C(12) are essentially on a straight line.

(3) The Si—N bond length is 2.150(6)Å. The Si—N bond distance was clearly affected by the electronegative group bonded to the silicon: In β-1-phenylsilatrane, it is 2.156 Å[3]; in 1-m-nitrophenylsilatrane, 2.116 Å[3]; in 1-(r-cyanopropyl)silatrane, 2.164 Å[6]; and in 1-chloromethyl-silatrane, 2.120 Å[4].

(4) The average C—N—C angle (113.03°) is greater than the angle in a tetrahedron, whereas the average C—N—Si angle (105.60°) is less than 109.5°. The average N—Si—O angle is 83.25°, but the average O—Si—C(12) angle is 96.75°. These are explained readily in terms of a transannular Si ← N dative bond.

Table 3

Bond Lengths (Å) and Angles(°) With Their e. s. d.'s

Si—O (2)	1.660 (5)	O(2)—C (3)	1.420 (9)
Si—O (8)	1.659 (5)	O(8)—C (7)	1.418 (10)
Si—O (9)	1.672 (5)	O(9)—C (10)	1.404 (9)
C(3)—C(4)	1.498 (14)	N—C (4)	1.492 (10)
C(6)—C (7)	1.502 (15)	N—C (6)	1.435 (11)
C(10)—C (11)	1.455 (14)	N—C (11)	1.504 (12)
Si—N	2.150 (6)	C(12)—C (13)	1.287 (13)
Si—C (12)	1.880 (8)		
	* * *	* *	
N—Si—O (2)	83.47 (34)	C(4)—N—Si	105.45 (44)
N—Si—O (8)	82.96 (16)	C(6)—N—Si	106.13 (51)
N—Si—O (9)	83.30 (35)	C(11)—N—Si	105.28 (45)
N—Si—C (12)	178.72 (25)	C(4)—N—C(6)	114.37 (68)
O(2)—Si—O(8)	121.01 (35)	C(4)—N—C(11)	110.06 (64)
O(2)—Si—O(9)	117.89 (52)	C(6)—N—C(11)	114.66 (65)
O(8)—Si—O(9)	116.99 (36)	C(3)—C(4)—N	105.84 (79)
O(2)—Si—C(12)	97.52 (35)	C(7)—C(6)—N	107.11 (72)
O(8)—Si—C(12)	95.82 (21)	C(10)—C(11)—N	107.58 (68)
O(9)—Si—C(12)	96.92 (37)	O(2)—C(3)—C(4)	110.54 (68)

Si—O(2)—C(3)	122.57 (39)	O(8)—C(7)—C(6)	110.06 (69)
Si—O(8)—C(7)	122.69 (39)	O(9)—C(10)—C(11)	112.64 (68)
Si—O(9)—C(10)	122.72 (53)	Si—C(12)—C(13)	128.19 (60)

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