THE CRYSTAL STRUCTURES OF HETEROCYCLIC COMPOUNDS OF SILICON.

III. CRYSTAL AND MOLECULAR STRUCTURES OF 2,2-DIPHENYL-2-SILA-1-OXA-1,2-DIHYDRONAPHTHALENE AND 2,2-DICHLORO-3-TRICHLOROSILYL-2-SILA-1-OXA-1,2-DIHYDRONAPHTHALENE

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UDC 548.737

An x-ray structural study of two organosilicon compounds, 2,2-diphenyl-2-sila-1-oxa-1,2-dihydronaphthalene (I) and 2,2-dichloro-3-trichlorosilyl-2-sila-1-oxa-1,2-dihydronaphthalene (II), has been carried out. The structures were determined by the direct method and refined by the method of least squares in the anisotropic (I) and isotropic (II) approximations from three-dimensional sets of diffractometric data as far as R-factors of 8.6 and 15.5% for compounds I and II respectively. Both molecules are characterized by a planar conformation of the naphthalene unit, and the intracyclic Si−C bond lengths (1.838 and 1.82 Å for compounds I and II, respectively) are slightly shorter than the standard value of 1.87 Å.

INTRODUCTION

The present paper describes a continuation of earlier studies involving the determination of the structures of heterocyclic compounds of silicon [1, 2]. Compounds I and II were synthesized as follows. Firstly, the gas-phase reaction of benzofuran with trichlorosilane at a temperature of 640°C and a contact time of approximately 30 sec gave 2,2-dichloro-2-sila-1-oxa-1,2-dihydronaphthalene (III) in up to 70% yield (bp = 113°C at 16 mm Hg, mp = 12°C). At the same time the reaction products also contained compound II (bp = 180°C at 1 mm Hg, mp = 73°C), in quantities not exceeding 5%. Treatment of compound III with phenylmagnesium bromide gave compound I in yields of up to 85% (bp = 188°C at 1.5 mm Hg, mp = 84°C). The compounds obtained were characterized by infrared, Raman, PMR, and ^{13}C NMR spectroscopy [3, 4].

EXPERIMENTAL

The unit cell parameters of compounds I and II were determined from KFOR diffraction patterns and refined on automatic four-circle Hilger−Watts (I) and Syntex P$\bar{1}$ (II) diffractometers.

	I	II
a, Å	10.598(3)	24.760(5)
b, Å	10.661(3)	15.705(4)
c, Å	14.659(4)	7.126(3)
γ, deg	104.30(3)	
M	300	350.5
V, Å^3	1604.9	2771.2
d_{calc}, g/cm^3	1.25	1.69
Z	4	8
Space group	$P2_1/1b$	$Pbam$

The three-dimensional sets of experimental data for compounds I and II were obtained on the above diffractometers using monochromatic molybdenum radiation, by the standard $\theta/2\theta$ scanning method.

Translated from Zhurnal Strukturnoi Khimii, Vol. 23, No. 1, pp. 140-147, January-February, 1982. Original article submitted November 26, 1980.

TABLE 1. Coordinates of the Atoms in the Molecule of Compound I*

Atom	x	y	z	Atom	x	y	z
Si	—0,0700(2)	0,1593(2)	0,8422(2)	C(10)	—0.1059(8)	0,2626(8)	1,0147(6)
O	0,0547(5)	0,2908(5)	0,8330(4)	C(11)	—0.1752(9)	0,2837(10)	1,0913(6)
C(1)	0,0098(9)	0,0272(8)	0,8630(7)	C(12)	—0,3075(9)	0,2363(10)	1,0934(6)
C(2)	0,1387(9)	0,0550(8)	0,8671(6)	C(13)	—0.3727(9)	0,1661(10)	1,0230(7)
C(3)	0,2273(7)	0,1812(8)	0,8513(6)	C(14)	—0,3028(8)	0,1430(9)	0,9444(6)
C(4)	0,3633(8)	0,1961(11)	0,8532(7)	C(15)	—0,1674(7)	0,1395(7)	0,7359(5)
C(5)	0,4477(8)	0,3105(11)	0,8383(7)	C(16)	—0,2490(8)	0,2288(9)	0,7180(6)
C(6)	0,4033(9)	0,4216(11)	0,8204(7)	C(17)	—0.3165(9)	0,2177(10)	0,6341(7)
C(7)	0,2692(8)	0,4099(9)	0,8181(6)	C(18)	—0,3063(10)	0,1231(11)	0,5713(7)
C(8)	0,1853(7)	0.2929(8)	0,8349(5)	C(19)	—0,2273(9)	0,0408(10)	0,5881(7)
C(9)	—0,1679(8)	0.1917(8)	0,9404(6)	C(20)	—0,1567(8)	0,0520(8)	0,6692(6)

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* The standard deviations of the coordinates of the atoms are given in brackets.

TABLE 2. Coordinates and Individual Temperature Factors of the Basis Atoms in the Structure of Compound II

Atom	Molecule A				Molecule B			
	x	y	z	B_j	x	y	z	B_j
Si(1)	0,2091(3)	0,5110(5)	0,5000	3,8(2)	0,0267(3)	0,1755(5)	0	3,3(1)
Si(2)	0,3281(3)	0,4264(6)	0,5000	4,5(2)	—0,0523(3)	0,3397(5)	0	3,9(2)
O(1)	0,1481(7)	0,4733(11)	0,5000	3,9(4)	0,0916(7)	0,1647(10)	0	3,9(4)
Cl(1)	0,2167(3)	0,5862(4)	0,2746(10)	7,4(1)	—0,0037(2)	0,1156(3)	0,2265(8)	5,7(1)
Cl(2)	0,3619(4)	0,3096(6)	0,5000	6,9(2)	—0,1122(3)	0,2535(6)	0	6,4(2)
Cl(3)	0,3553(4)	0,4882(6)	0,2756(14)	11,2(3)	—0,0618(3)	0,4149(5)	0,2273(11)	7,3(2)
C(1)	0,2556(10)	0,4203(15)	0,5000	3,2(5)	0,0139(10)	0.2888(16)	0	3,5(5)
C(2)	0,2303(11)	0,3411(18)	0,5000	5,2(6)	0.0575(9)	0,3405(14)	0	2,8(4)
C(3)	0,1715(11)	0,3271(17)	0,5000	4,1(5)	0,1138(9)	0.3157(15)	0	3,1(5)
C(4)	0,1525(10)	0,2414(17)	0,5000	3,8(5)	0,1552(10)	0,3771(16)	0	3,6(5)
C(5)	0,0995(10)	0,2216(16)	0,5000	3,5(5)	0,2091(11)	0,3539(18)	0	4,3(6)
C(6)	0,0630(11)	0,2900(18)	0,5000	4.3(6)	0,2237(11)	0,2662(19)	0	4,7(7)
C(7)	0,0783(12)	0,3756(19)	0,5000	4,9(7)	0,1863(11)	0,2003(17)	0	4,1(6)
C(8)	0,1329(11)	0,3909(17)	0,5000	3,7(6)	0,1300(11)	0,2299(17)	0	4,4(6)

DETERMINATION AND REFINEMENT OF THE STRUCTURES

The structure of compound I was determined by the direct method using 1179 independent reflections with $I \geq 3\sigma(I)$. The method of successive approximation of electron density series made it possible to determine the coordinates of all the atoms other than hydrogen, with allowance for which the R-factor was 16.2% (for $B_{total} = 3.47$ Å^2).

The refinement of the structure of compound I was carried out first in the isotropic approximation with allowance for Cruickshank's weighting factors [5] in the last stages, as far as a R-factor of 11.6%. The refinement was then continued in the block-diagonal anisotropic approximation. The final R-factor was 8.6%, and the corresponding coordinates of the atoms are given in Table 1. (The individual anisotropic temperature corrections and the parameters of the ellipsoids of the thermal vibrations can be obtained from the authors.)

The determination of the structure of compound II was carried out in the same way as for compound I, using 1100 reflections with $I \geq 3\sigma(I)$. The structure of compound II was refined by the method of least squares in the isotropic approximation with allowance for obvious geometric considerations in the first stages (the C–C bond lengths and CCC valence angles in the benzene fragments were assumed to be equal to 1.40 Å and 120°, respectively). These restrictions were removed in the last stages of the refinement. The final R-factor was 15.5%, and the corresponding coordinates of the atoms and the individual isotropic temperature factors for the two independent molecules are given in Table 2.

The calculations were carried out on M-222 and BESM-4 computers using the automated sets of programs "Rentgen-70" and "Kristall."

TABLE 3. Bond Lengths (Å) in the Molecule of Compound I

Bond	*d*	Bond	*d*
Si—C(1)	1,838(5)	C(9)—C(10)	1,394(7)
Si—C(9)	1,856(5)	C(10)—C(11)	1,391(8)
Si—C(15)	1,852(4)	C(11)—C(12)	1,368(7)
Si—O	1,677(3)	C(12)—C(13)	1,359(7)
C(1)—C(2)	1,326(7)	C(13)—C(14)	1,423(8)
C(2)—C(3)	1,457(7)	C(14)—C(9)	1,397(6)
C(3)—C(4)	1,411(7)	C(15)—C(16)	1,410(8)
C(3)—C(8)	1,391(7)	C(16)—C(17)	1,417(7)
C(4)—C(5)	1,340(6)	C(17)—C(18)	1,389(9)
C(5)—C(6)	1,402(8)	C(18)—C(19)	1,377(10)
C(6)—C(7)	1,397(7)	C(19)—C(20)	1,393(8)
C(7)—C(8)	1,363(6)	C(20)—C(15)	1,376(7)
C(8)—O	1,380(5)		

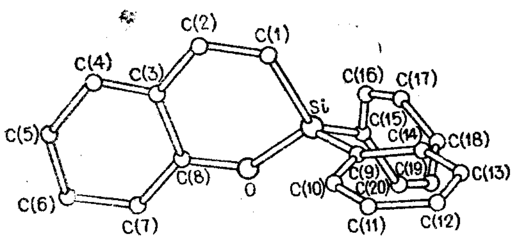

Fig. 1. Structure of the molecule of compound I.

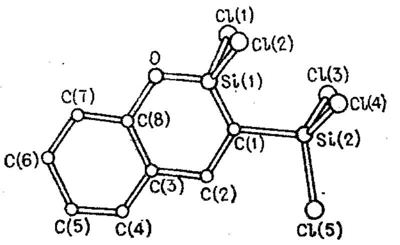

Fig. 2. Structure of the molecule of compound II.

GEOMETRY OF THE MOLECULES AND DISCUSSION OF RESULTS

The numbering of the atoms and the conformation of the molecules compounds I and II are given in Figs. 1 and 2 (for compound II, one of the two crystallographically nonequivalent molecules is shown). The individual values of the bond lengths and valence angles are given in Tables 3 and 4 for compound I and in Tables 5 and 6 for compound II. In the discussion of the bond lengths and valence angles in compound II, the values averaged over the two independent molecules are used.

It should be noted that at the present time the number of published papers devoted to the structure of heterocyclic compounds of silicon is extremely small (an exception is provided by papers on the determination ofthe structures of siloxanes). Compounds in which the silicon atom is included in a system of the naphthalene type are shown in Fig. 3. The structures of these compounds have been established by x-ray structural analysis (with the exception of compound III, for which structural studies have not been carried out, since it is a liquid under normal conditions).

To explain the structures of compounds of this type, containing silicon atoms having unoccupied d-orbitals and unsaturated fragments or atoms with unshared electron pairs, the concepts of $p_\pi - d_\pi$ interaction is usually introduced, or alternatively the explanation is based on the manifestation of the inductive effect [6]. The problem of $p_\pi - d_\pi$ interaction is at present the subject of lively discussion (see for example [7-11]), but in experimental work devoted to this problem it has not been shown sufficiently convincingly that the results obtained are due to the effect of $p_\pi - d_\pi$ interaction, and that another alternative explanation cannot be given for the facts observed. The number of correct quantum-chemical calculations with an expanded spd basis is extremely small, and the interpretation of the data obtained is often extremely ambiguous [7, 12].

The compounds I and II which we studied are analogs of naphthalene, differing from the latter in that the C−C multiple bond has been replaced by an Si−O bond. Since the Si−O bond is also a multiple bond [13], it is possible in principle for it to take part in conjugation with the phenyl ring and the alkene bond, with the use of the unoccupied 3d-orbitals of the silicon atom and the formation of a system of the aromatic type.

The existence of aromaticity is generally accompanied by a planar conformation of the corresponding fragments, and also by equalization of the bond orders in them.

The molecules of compounds I and II have planar conformations, and the molecule of compound II is ideally planar from symmetry requirements (the independent molecules are situated in planes m with z = 0 and $^1/_2$),

TABLE 4. Valence Angles ω (deg) in the Molecule of Compound I

Angle	ω	Angle	ω
C(1)SiO	103,7(2)	C(3)C(8)O	121,4(3)
C(1)SiC(9)	113,3(2)	C(8)OSi	126,3(3)
C(1)SiC(15)	113,6(2)	SiC(9)C(10)	119,8(4)
C(9)SiC(15)	110,6(2)	SiC(9)C(14)	122,1(4)
C(9)SiO	105,5(2)	C(9)C(10)C(11)	121,4(5)
C(15)SiO	109,3(2)	C(10)C(11)C(12)	119,5(5)
SiC(1)C(2)	118,7(4)	C(11)C(12)C(13)	121,4(5)
C(1)C(2)C(3)	126,3(5)	C(12)C(13)C(14)	119,6(5)
C(2)C(3)C(4)	120,5(5)	C(13)C(14)C(9)	120,0(5)
C(2)C(3)C(8)	123,3(5)	C(14)C(9)C(10)	118,0(5)
C(3)C(4)C(5)	122,2(5)	SiC(15)C(16)	119,8(4)
C(4)C(3)C(8)	116,2(4)	SiC(15)C(20)	122,6(4)
C(4)C(5)C(6)	120,8(5)	C(15)C(16)C(17)	121,4(5)
C(5)C(6)C(7)	118,4(5)	C(16)C(17)C(18)	118,3(4)
C(6)C(7)C(8)	119,8(5)	C(17)C(18)C(19)	120,2(4)
C(7)C(8)C(3)	122,7(5)	C(18)C(19)C(20)	119,8(5)
C(7)C(8)O	115,9(5)	C(19)C(20)C(15)	122,2(5)
C(20)C(15)C(16)	117,3(5)		

and in the molecule of compound I the dihedral angle between the condensed rings of the naphthalene unit, which are planar to within 0.03 Å, is only 1.4°. Thus the conformations of these molecules are identical to that found for naphthalene and its deuterium-substituted analog [14, 15]. The geometry of the molecules of compounds I and II is extremely similar to that found in another heterocyclic compound of silicon, 3-bromo-2,2-diphenyl-2-sila-Δ3-1-tetralone (IV) (see Fig. 3) [17]. The molecule of compound IV is planar to within 0.046 Å, and the dihedral angle between the condensed rings of the tetralone fragment is 0.48°, whereas the tetrahydronaphthalene fragment of the molecule of compound V is nonplanar and is bent along the line joining the carbon atoms in positions 1 and 4 of the heterocyclic ring, by 53.04°. It should be noted that whereas in compound IV the silicon atom is joined to carbon atoms in the sp^2 state, in compound V the silicon atom in the heterocyclic ring is joined to sp^3 hybridized carbon atoms.

Thus the planar conformation of the molecules of compounds I and II is in principle favorable for the production of a closed conjugation chain in the system $-C_{sp^2}-O-Si-C_{sp^2}-$. For the bond lengths in the heterocyclic ring in this case we should expect an increase in the multiplicities of the single bonds Si−C and C−O and a decrease in the multiplicity of the alkene bond C=C.

The intracyclic bond lengths Si−C in compounds I and II (1.838 and 1.82 Å, respectively) are shorter than those found in compounds IV and V and in 1-sila-2,8-dioxa-5-methyl-5-azacyclo-octane-spiro[2']silachromene (VI) [18], where they are equal to 1.889, 1.883, and 1.851 Å, respectively, and shorter than the standard length of the Si−C single bond, 1.87 Å [19, 20]. It is known that the presence of electronegative substituents on the silicon atom leads to a decrease in the length of the Si−C bonds. Thus the shortest Si−C distances were observed in compound II, where the Si atom is joined to Cl atoms, which have a higher electronegativity than the phenyl substituents (in compounds I, IV, and V) or the diethanolamine substituent (in compound VI).

Calculations (see, for example, [10, 21]) have shown that electronegative substituents on silicon atoms facilitate the $p_\pi-d_\pi$ interaction of the unoccupied 3d-orbitals with the π-systems of unsaturated fragments or the unshared electron pairs of neighboring atoms, decreasing the effective dimensions of the diffuse d-orbitals. Moreover, electronegative substituents show an inductive effect, which may also lead to a decrease in the distances to other substituents on the silicon atom.

In fact, in compounds such as, for example, SiH_3F and $SiHF_3$, increase in the number of F atoms leads to a decrease in the Si−H distances from 1.485 to 1.455 Å [22, 23], although $p_\pi-d_\pi$ interaction between the Si and H atoms is impossible. In this case we are apparently dealing with the purely inductive influence of the F atoms. On the other hand, the replacement of three phenyl groups by fluorine atoms in the molecule of tetraphenylsilane leads to a decrease in the Si−C distances from 1.876 Å [24] to 1.828 Å [25]. In the structure of N-(tert-butylphenylfluorosilyl)-N-(phenyldifluorosilyl)-2,4,6-trimethylaniline, the Si−C distance in the phenyldifluorosilyl group, 1.828 Å, is 0.03 Å shorter than the analogous distance in the tert-butylphenylfluorosilyl group [26]. A similar regular feature can be observed in the structures of 2,2-diphenyl- and 2-fluoro-2-naphthyl-2-sila-1,2,3,4-tetrahydronaphthalene (on the introduction of the F atom, the distance $Si-C_{sp^2}$ decreases from 1.871 to 1.85 Å) [17, 27] and in various other structures. In all these cases, the effects of $p_\pi-d_\pi$ interaction and the inductive influence of the electronegative substituents can appear simultaneously. It should

TABLE 5. Bond Lengths d (Å) in the Structure of Compound II

Bond	Molecule A, d	Molecule B, d	d_{av}	Bond	Molecule A, d	Molecule B, d	d_{av}
Si(1)—Cl(1)	2,002(8)	2,014(7)	2,008(5)	C(3)—C(4)	1,425(37)	1,407(34)	1,416(25)
Si(1)—O(1)	1,622(19)	1,616(19)	1,619(13)	C(3)—C(8)	1,384(38)	1,407(36)	1,396(26)
Si(1)—C(1)	1,832(25)	1,808(26)	1,820(18)	C(4)—C(5)	1,350(36)	1,383(38)	1,367(26)
Si(2)—C(1)	1,797(25)	1,823(26)	1,810(18)	C(5)—C(6)	1,404(38)	1,424(41)	1,414(28)
Si(2)—Cl(2)	1,989(11)	2,008(12)	1,999(8)	C(6)—C(7)	1,397(41)	1,390(40)	1,394(29)
Si(2)—Cl(3)	2,016(13)	2,018(9)	2,017(8)	C(7)—C(8)	1,374(40)	1,468(38)	1.421(23)
C(1)—C(2)	1,393(36)	1,352(33)	1,373(24)	C(8)—O(1)	1,348(30)	1,398(31)	1,373(22)
C(2)—C(3)	1,472(38)	1,447(32)	1,460(25)				

TABLE 6. Valence Angles ω (deg) in the Structure of Compound II

Angle	Molecule A, ω	Molecule B, ω	ω_{av}
Cl(1)Si(1)O(1)	108,1(5)	108,1(4)	108,1(3)
Cl(1)Si(1)C(1)	114,1(5)	113,7(5)	113,9(4)
Cl(1)Si(1)Cl(1′)	106,7(4)	106,5(4)	106,6(3)
C(1)Si(1)O(1)	107,4(10)	107,3(11)	107,4(7)
Si(1)O(1)C(8)	126,2(17)	125,9(16)	126,1(12)
Si(1)C(1)Si(2)	124,6(14)	128,1(14)	126,4(10)
Si(1)C(1)C(2)	114,8(19)	115,5(19)	115,2(13)
O(1)C(8)C(7)	116,2(24)	113,2(22)	114,7(16)
O(1)C(8)C(3)	121,8(24)	119,9(22)	120,9(16)
C(1)Si(2)Cl(2)	111,5(6)	110,4(5)	111,0(4)
C(1)Si(2)Cl(3)	110,6(9)	111,9(9)	111,3(6)
Cl(2)Si(2)Cl(3)	108,2(4)	107,8(4)	108,0(3)
Cl(3)Si(2)Cl(3′)	107,1(4)	106,7(4)	106,9(3)
Si(2)C(1)C(2)	120,5(19)	116,5(19)	118,5(13)
C(1)C(2)C(3)	126,8(24)	128,0(21)	127,4(16)
C(2)C(3)C(4)	118,2(23)	118,2(21)	118,2(16)
C(2)C(3)C(8)	123,1(24)	123,4(21)	123,3(16)
C(3)C(4)C(5)	119,3(24)	117,9(24)	118,6(17)
C(4)C(5)C(6)	122,2(24)	122,0(25)	122,1(17)
C(5)C(6)C(7)	118,6(26)	118,8(26)	118,7(18)
C(6)C(7)C(8)	119,3(26)	116,0(24)	117,7(18)
C(7)C(8)C(3)	122,1(26)	126,9(24)	124,5(18)
C(8)C(3)C(4)	118,7(24)	118,4(22)	118,6(16)

be noted that in the structure of compound I, the intracyclic distance Si–C, 1.838 Å, is shorter by more than 3σ than the normal value of 1.87 Å, in spite of the fact that the silicon atom is joined to phenyl substituents, whose electronegativity, and hence inductive effect, is relatively slight. Moreover, the Si–C(1) distance is shorter than the distances Si–C(9) and Si–C(15) 1.856 and 1.852 Å, respectively, and the reason for the decrease in length cannot be the thermal motion of the carbon atoms, since the individual isotropic factors for the atoms C(1), C(9), and C(15) differ little. Thus in compound I it is possible in principle to have an increase in the multiplicity of the Si–C(1) bond as a result of the participation of the unoccupied 3d-orbitals of the silicon atom in bonding.

The Si–C distances in compound II (average value 1.81 Å) are even shorter, compared with the normal value, and this decrease in length can be expplained on the basis of the inductive influence of the Cl atoms, which is superimposed on the effect of $p_\pi - d_\pi$ interaction. The change in the valence angles at the Si atoms can also be related to the inductive influence of the substituents. Thus the intracyclic angle C(1)SiO at the Si atom in compound I, 103.7°, is smaller, and the exocyclic angle C(9)SiC(15), 110.6°, is larger, compared with the analogous values in compound II, equal to 108.1 and 106.1°, respectively. The data obtained show good agreement with Bent's views [28] regarding the rehybridization of an atom having electronegative substituents.

Analysis of the bond lengths in the heterocyclic ring of the molecule of compound I shows that with the slight increase in the multiplicity of the Si–C(1) bond, the multiplicities of the bonds C(1)–C(2) and C(8)–O did not change, and the multiplicity of the Si–O bond even decreased. Thus the distance Si–O 1.677 Å is greater than the normal value 1.63-1.64 Å [13]. The bond length C(1)–C(2) 1.326 Å coincides within the limits of experimental accuracy with the standard value of the C=C double bond length 1.33 Å. The C–O distance in compound I, 1.380 Å, is close to those found in salicyclic acid, 1.36 Å [29], phloroglucinol dihydrate, 1.37 Å [30], β-naphthol, 1.39 Å [31], and 3,4-dimethylphenol, 1.39 Å [32].

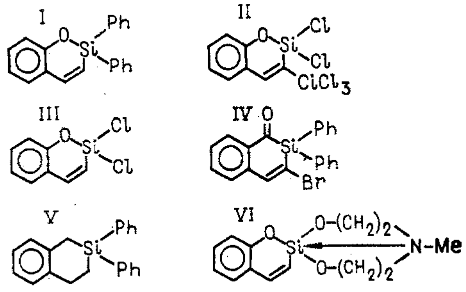

Fig. 3. Silicon compounds of the naphthalene type for which structural studies have been carried out.

In compound II, in addition to the above-mentioned decrease in the length of the Si–C bond, a slightly shortened Si–O distance, 1.62 Å, was found. In addition, the distance C(1)–C(2), 1.373 Å, is longer than that in compound I and is close to those found in aromatic compounds. In addition to these changes, however, the C–O bond length in compound II, 1.37 Å, coincides with that found in compound I and other related compounds.

Thus for compounds I and II it is possible to state that there is planar conformation of the molecules and a decrease in the length of the intracyclic Si–C bonds; both of these factors may indicate the existence of $p_\pi - d_\pi$ interaction with the participation of the 3d-orbitals of the silicon atom and the π-electrons of the alkene bond. In the molecule of compound II, judging from the structural data, this interaction takes place to a greater extent as a result of the presence of the electronegative chlorine atoms. Moreover, in compound II there is an increase in the length of the alkene bond C(1)–C(2).

To determine the nature of the C(1)–C(2) bond, the bromination of compounds I and III and 2,2-dimethyl-2-sila-1-oxa-1,2-dihydronaphthalene (VII) was studied. The bromination of compounds I and VII involves the attachment of a Br_2 molecule across the double bond with the formation of the 3,4-dibromo-1,2,3,4-tetrahydro-derivative. Even during the synthesis, however, HBr begins to be liberated from the reaction mixture, and the 3-bromo-1,2-dihydro-derivative is formed (the position of the Br atom was established from the infrared spectra). It should be noted that the dibromo-derivative can be isolated from the reaction mixture and characterized spectroscopically [33, 34]. Similar behavior is shown by the bond between the carbon atoms in positions 9 and 10 in the phenanthrene molecule, which is extremely reactive, and similar in character to the alkene bond [35]. In the analogous reaction of compound III with Br_2, an intermediate product cannot be isolated. The reaction gave only 2,2-dichloro-3-bromo-2-sila-1-oxa-1,2-dihydronaphthalene. Thus the study of the chemical properties show that the C(1)–C(2) bond in compound III (and hence in compound II) is closer in character to the bonds in aromatic compounds, compared with the analogous bond in compound I, confirming in principle the results of the structural study.

In the molecule of compound I, the phenyl fragments C(9)...C(14) and C(15)...C(20) are planar within the limits of experimental accuracy, and the dihedral angles between their planes and the plane of the naphthalene unit are 69.1 and 61.1°, respectively.

The packing of the molecules in the structure of compound I involves van der Waals bonds, and the shortest contacts correspond to C...C interactions and are equal to 3.56-3.64 Å, which coincides with twice the van der Waals radius of the C atom. The distances between the other atoms are greater than the sums of the van der Waals radii of the corresponding atoms. In the structure of compound II there are a number of intermolecular contacts shorter than the sums of the van der Waals radii. Contacts of this kind are formed between the following atoms: Cl...Cl', Cl...O', and Cl...C', related by the symmetry operation (x, y, 1 – z), and are equal to 3.20-3.21, 2.93-3.38, and 3.13-3.21 Å, respectively, whereas the sums of the van der Waals radii of the corresponding atoms are 3.56, 3.30, and 3.58 Å [36, 37]. The C...C and Si...C distances, 3.61-3.80 and 3.65-3.84 Å, respectively, correspond to normal intermolecular contacts; the other contacts are greater than the sums of the corresponding van der Waals radii.

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