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B.A. Trofimov on the 65th Anniversary of His Birth

## *N*-Silatranylmethyl Derivatives of Pyrrole, Indole, and Carbazole

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**Abstract**—Organosilicon derivatives of pyrrole, indole, carbazole, and 2-methylindole containing (MeO)<sub>3</sub>SiCH<sub>2</sub>, Et<sub>3</sub>SiCH<sub>2</sub>, or N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>SiCH<sub>2</sub> group on the nitrogen atom were synthesized. Their structure and stereoelectronic parameters were studied by X-ray diffraction, <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si NMR, IR and UV spectroscopy, and dielcometry, as well as by quantum-chemical calculations.

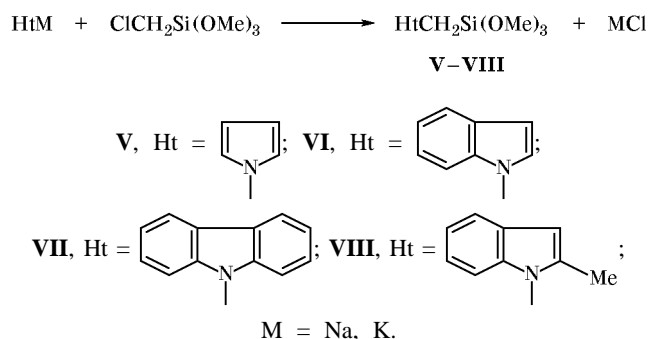
The silatranyl group N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Si (Sa) exhibits a quite strong positive inductive effect [1, 2]; therefore, the +I effect of the SaCH<sub>2</sub> group [1, 3] in silatrane derivatives XCH<sub>2</sub>Sa (where X is an inorganic or organic substituent) is also appreciable. This also follows from the high spectroscopic basicities of compounds of the XCH<sub>2</sub>Sa series (X = F, Cl, Br, I, RO, RS, R<sub>2</sub>N, CH<sub>2</sub>=CH), which are estimated by studying their intermolecular interactions with phenol, and from the low ionization potentials [4]. Owing to the strong electron-donor effect of the silatranyl group π-electron density on the phenyl carbon atoms in 1-phenylsilatrane increases, and the phenyl group therein acts as π-electron donor.

Of specific interest are *N*-silatranylmethylazoles HtCH<sub>2</sub>Sa (Ht is an *N*-azolyl group) where the Sa group is linked to the ring nitrogen atom through a methylene bridge. In the present work we examined the effect of organosilicon substituents, such as SaCH<sub>2</sub>, (MeO)<sub>3</sub>SiCH<sub>2</sub>, and Et<sub>3</sub>SiCH<sub>2</sub>, at the nitrogen atom of pyrrole, indole, carbazole, and 2-methylindole (compounds V–XIII) on the steric and electronic structure and some other properties of these heteroaromatic systems using X-ray diffraction, <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si NMR, IR and UV spectroscopy, and dielcometry. The results are discussed below.

**Methods of synthesis.** *N*-(Trimethoxysilylmethyl) derivatives V–VIII of pyrrole (I), indole (II), carba-

zole (III), and 2-methylindole (IV) were synthesized from the corresponding sodium or potassium salts and chloromethyl(trimethoxy)silane in DMF or xylene in the presence of a catalytic amount of dibenzo-24-crown-8 (Scheme 1).

Scheme 1.



Compounds V–VIII are yellowish readily hydrolyzable liquids. Their yields, boiling points, and elemental analyses are given in Table 1. Compounds VI–VIII have not been reported previously. Only *N*-substituted pyrroles of the general formula HtCH<sub>2</sub>Si(OEt)<sub>3–*n*</sub>Me<sub>*n*</sub> (*n* = 0–3) were described in [5, 6]. *N*-(Trimethoxysilylmethyl)carbazole (VII) was not isolated in the pure state, and it was brought into further syntheses without isolation from the reaction

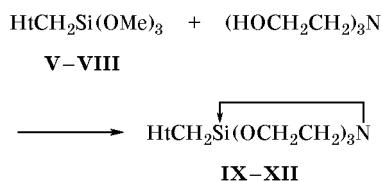
**Table 1.** *N*-Trimethoxysilylmethyl and *N*-(1-silatranylmethyl) derivatives of pyrrole, indole, and carbazole

Comp. no.	Yield, %	bp, °C ( <i>p</i> , mm), or mp, <sup>a</sup> °C	Found, %				Formula	Calculated, %			
			C	H	N	Si		C	H	N	Si
<b>V</b>	79	100–101 (13)	47.36	7.91	6.91	13.65	C <sub>8</sub> H <sub>15</sub> NO <sub>3</sub> Si	47.73	7.51	6.96	13.95
<b>VI</b>	63	150–153 (8)	57.31	6.90	5.61	11.09	C <sub>12</sub> H <sub>17</sub> NO <sub>3</sub> Si	57.34	6.82	5.57	11.17
<b>VIII</b>	60	162–164 (7)	58.62	7.07	4.79	10.52	C <sub>13</sub> H <sub>19</sub> NO <sub>3</sub> Si	58.83	7.22	5.28	10.58
<b>IX</b>	96	203–206 <sup>a</sup>	51.42	7.01	11.32	10.87	C <sub>11</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Si	51.94	7.13	11.01	11.04
<b>X</b>	98	205–206 <sup>a</sup>	59.90	6.35	10.00	9.19	C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> Si	59.91	6.59	9.03	9.95
<b>XI</b>	92	303–305 <sup>a</sup>	63.90	6.94	8.51	7.34	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> Si	64.38	6.26	7.90	7.00
<b>XII</b>	92	230–231 <sup>a</sup>	60.95	7.56	8.67	8.82	C <sub>16</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> Si	60.34	6.97	8.80	8.82
<b>XIII</b>	75	137–138 (30)	67.02	11.16	7.21	14.58	C <sub>11</sub> H <sub>21</sub> NSi	67.62	10.83	7.17	14.37

<sup>a</sup> From chloroform–hexane (1:1).

mixture. By transesterification of compounds **V–VIII** with tris(2-hydroxyethyl)amine in the absence of a catalyst we obtained the corresponding *N*-(1-silatranylmethyl) derivatives **IX–XII** (Scheme 2).

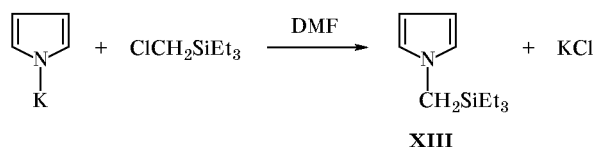
#### Scheme 2.



Silatranyl derivatives **IX–XII** are colorless crystalline substances melting above 200°C; compounds **IX** and **X** readily sublime under reduced pressure (they were purified in this way). The yields, melting points, and analytical data of products **IX–XII** are given in Table 1. They are soluble in tetrahydrofuran, dimethyl sulfoxide, and dimethylformamide.

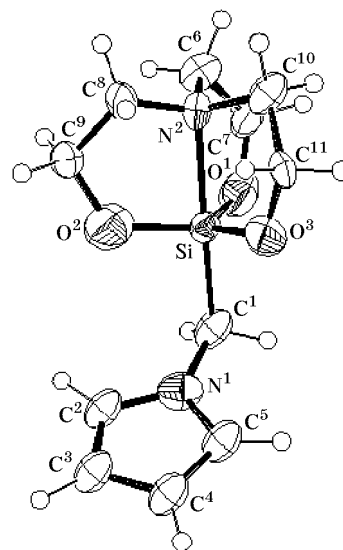
*N*-(Triethylsilylmethyl)pyrrole (**XIII**) was obtained in 75% yield from potassium pyrrolate and chloromethyl(triethyl)silane in DMF in the presence of a catalytic amount of dibenzo-24-crown-8 (Scheme 3).

#### Scheme 3.

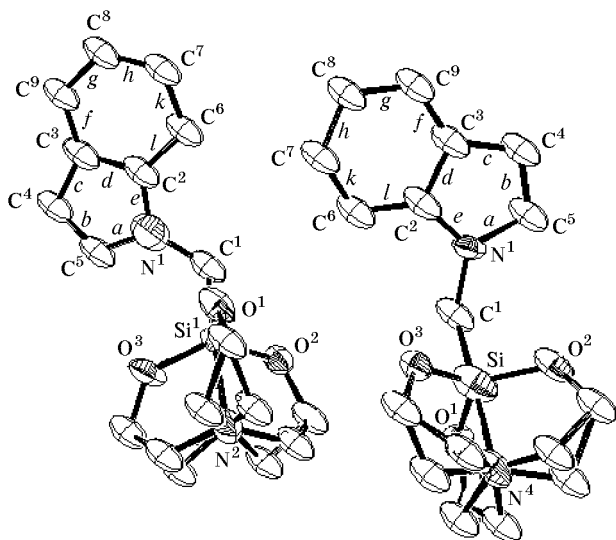


**Molecular structure.** The molecular structures of *N*-(1-silatranylmethyl)pyrrole (**IX**), *N*-(1-silatranylmethyl)indole (**X**), and *N*-(1-silatranylmethyl)carbazole (**XI**) were determined by X-ray analysis [7, 8]

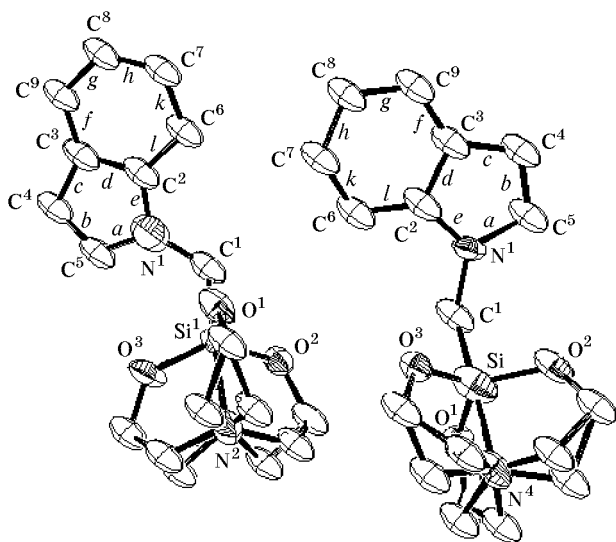
(Figs. 1–3). Table 2 contains the bond lengths and bond angles in the pyrrole ring of molecules **IX–XI**. It should be emphasized that all bonds in the pyrrole ring of **IX** (especially the C<sup>3</sup>–C<sup>4</sup> bond) are shorter than in parent pyrrole (**I**), *N*-methylpyrrole (**XIV**), and compounds **X** and **XI** (Table 2). Leveling of the endocyclic bonds in the pyrrole ring indicates that introduction of a silatranylmethyl group to the nitrogen atom enhances aromatic character of the heteroring. The same follows from the bond angles in the pyrrole ring of **IX**: all these are equal to ~108° [against 106.0–111.1° (α) and 105.3–110.6 (β) in molecule **X** and 106.6–109.4° in **XI**, as well as in **I–III**]. No bond leveling in the pyrrole ring is observed on fusion of one or two benzene rings to the *N*-silatranylmethylpyrrole molecule, i.e., in going to compounds **X** and



**Fig. 1.** Molecular structure of *N*-(1-silatranylmethyl)pyrrole (**IX**) according to the X-ray diffraction data.



**Fig. 2.** Molecular structure of *N*-(1-silatranyl)methylindole (**X**,  $\alpha$ - and  $\beta$ -forms) according to the X-ray diffraction data.



**Fig. 3.** Molecular structure of *N*-(1-silatranyl)methylcarbazole (**XI**) according to the X-ray diffraction data.

**XI.** This indicates a weaker aromatic character of the pyrrole fragment in molecules **X** and **XI**. By contrast, the average carbon–carbon distances in the benzene rings of molecules **X** and **XI**, 1.390 ( $\alpha$ ), 1.386 ( $\beta$ ) and 1.390, 1.393 Å, respectively, are shorter than in benzene. This means that introduction of a silatranyl-methyl group to the nitrogen atom of indole and carbazole increases the aromaticity of the benzene rings therein. The length of the exocyclic  $N^1-C^1$  bond in molecules **IX**, **X**, and **XI** (1.470, 1.470, and 1.467 Å, respectively) approaches the standard N–C

bond length (1.47 Å) (Figs. 1–3). On the other hand, the C–Si bonds in molecules **IX**, **X**, and **XI** (1.902 and 1.91 Å for the  $\alpha$ - and  $\beta$ -forms and 1.897 Å, respectively) are considerably longer than the C–Si bond in trimethoxy(methyl)silane (1.842 Å) where the silicon atom is four-coordinate [9].

The exocyclic N–CH<sub>2</sub> bond in molecule **IX** lies in the plane of the heteroring, whereas the corresponding bond in molecules **X** and **XI** declines from that plane by  $9 \pm 1^\circ$  (in the  $\alpha$ - and  $\beta$ -forms of **X**, the N–CH<sub>2</sub> bond is oriented at opposite sides of the plane of the heterocyclic fragment).

The silicon atom in the silatrane fragment of **IX**, **X**, and **XI** has a trigonal-bipyramid configuration. Its axial apices are occupied by the  $N^2$  and  $C^1$  atoms. The oxygen atoms,  $O^1$ ,  $O^2$ , and  $O^3$  are located in the equatorial plane. The geometric parameters of the silicon polyhedron are typical of silatranes [10, 11].

The axial C–Si–N moiety in **IX–XI** is almost linear: the CSiN angle approaches a value of  $180^\circ$  [ $177.9^\circ$ ,  $176.8^\circ$  ( $\alpha$ ) and  $175.3^\circ$  ( $\beta$ ), and  $177.8^\circ$ , respectively]. The silicon atom is displaced from the axis of the silatrane skeleton: it is located between two oxygen atoms, while the distance to the third oxygen atom is somewhat longer. The C–Si–N fragment in **IX–XI** is almost orthogonal to the HtCH<sub>2</sub> plane. The corresponding dihedral angles are  $77.2^\circ$ ,  $70.5^\circ$  ( $\alpha$ ) and  $83.4^\circ$  ( $\beta$ ), and  $92.8^\circ$ , respectively. Unsymmetrical molecules of *N*-(1-silatranyl)methylindole in crystal exist as two rotational isomers (stable rotamers) in which the N–CH<sub>2</sub>–Si–N fragment appears at different sides of the indole plane. Thus, the presence of two internal rotation axes in molecule **X** gives rise to two mirror configurations, presumably with similar energies.

Almost similar N→Si interatomic distances in molecules **IX–XI** suggest similar effects of the corresponding heterocyclic fragments thereon. Taking into account the correlation observed between the Si–N bond length and constants  $\sigma$  of the substituents on the silicon atom in **IX–XI** and assuming purely inductive interaction between the heterocyclic and silatrane fragments, we estimated the inductive constants  $\sigma_1$  and  $\sigma^*$  of these heterocyclic substituents (Table 3). The constants  $\sigma_R^0$  of the  $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  and  $\text{Si}(\text{OR})_3$  groups (R = Me, Et, CHMe<sub>2</sub>), determined by <sup>13</sup>C NMR spectroscopy, are 0.02 and 0.08, respectively [12, 13]. These values suggest that the  $\pi$ -acceptor power of the silicon atom in the 1-silatranyl group is weaker than in  $\text{Si}(\text{OR})_3$ .

**Dipole moments and quantum-chemical calculations.** Tables 4 and 5 contain the dipole moments  $\mu$

of *N*-trimethoxysilylmethyl (**V**, **VI**, **VIII**) and *N*-sila-tranylmethyl derivatives (**IX–XII**). For comparison, the dipole moments of parent heterocycles **I–IV** and their *N*-methyl derivatives **XIV**, **XV**, and **XVII** are also given. The dipole moments of HtR compounds [R = H, Me, (MeO)<sub>3</sub>SiCH<sub>2</sub>] increase in the following series of Ht: 1-pyrrolyl < 1-indolyl- < 9-carbazolyl < 2-methyl-1-indolyl. The increased dipole moments of *N*-substituted 2-methylindoles **IV**, **VIII**, and **XVII** result from the effect of the 2-methyl group.

The dipole moments of *N*-sila-tranyl derivatives **IX–XII** also depend on the nature of the heterocyclic fragment (Table 5). Unlike compounds **I–VIII** and **XIV–XVII**, the dipole moments of **IX–XII** increase in the series **XI** < **X** < **XII** < **IX**. This may be due to specific character of electronic interactions between molecular fragments or their different steric structures in solution.

With a view to elucidate mutual orientation of the Ht and Sa fragments in isolated molecules **IX–XII**, we performed nonempirical quantum-chemical calculations (HF/6-31G\*) with the use of Gaussian-98 software [18]. Some calculated geometric parameters of compounds **IX–XII** and model methylsilatrane MeSi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (**XVIII**) are collected in Table 6 together with the corresponding X-ray diffraction data for **IX–XI** [7, 8] and **XVIII** [19]. Molecules **IX–XII** are characterized by deviation of the axial C–Si←N fragment from the heteroring plane. The calculated dihedral angle C<sub>Ht</sub>N<sub>Ht</sub>CSi between the axis of the Sa moiety and the heteroring plane in symmetric molecules **IX–XI** is less than 10° (Table 6), which is very consistent with the experimental data. Such molecular structure provides the possibility for overlap of the σ-Si–C orbital (σ<sub>SiC</sub>) with the fragment π-orbital which is transformed via β<sub>1</sub> irreducible representation of the C<sub>2v</sub> π(b<sub>1</sub>) point symmetry group. First of all, this should affect geometric parameters of the axial CSiN fragment. According to the calculations, the Si–C and Si←N bond lengths in molecules **IX**, **XI**, and **XVIII** differ considerably, in keeping with the X-ray diffraction data [7, 8]. The assumption allowing for π(b<sub>1</sub>)–σ<sub>SiC</sub> interaction explains reduction of the μ values in the series **IX** > **X** > **XII** > **XI**. In fact, according to the data of photoelectron spectroscopy [20], the orbital interaction π(b<sub>1</sub>)–σ<sub>SiC</sub> should be the strongest for pyrrole derivative **IX** and the weakest for *N*-substituted carbazole **XI** in which the pyrrole heteroring is fused to benzene rings. The same order of variation, i.e., reduction in going from **IX** to **XII**, is observed for the difference Δμ (Table 6) between the experimental dipole moments and those calculated by the vector additivity scheme (i.e., on the assump-

**Table 2.** Bond lengths *d* (Å) and bond angles ω (deg) in the molecules of *N*-(1-sila-tranylmethyl)pyrrole (**IX**), *N*-(1-sila-tranylmethyl)indole (**X**), and *N*-(1-sila-tranylmethyl)carbazole (**XI**)

Bond or angle	<b>IX</b>	<b>X</b>		<b>XI</b>
		α	β	
N <sup>1</sup> –C <sub>Ht</sub>	1.365	1.370	1.358	1.394
	1.371	1.370	1.410	1.384
C <sup>2</sup> –C <sup>3</sup>	1.361	1.400	1.402	1.414
C <sup>4</sup> –C <sup>5</sup>	1.372	1.362	1.362	1.407
C <sup>3</sup> –C <sup>4</sup>	1.395	1.445	1.471	1.450
N <sup>1</sup> –C <sup>1</sup>	1.470	1.470	1.470	1.467
C <sup>2</sup> N <sup>1</sup> C <sup>5</sup>	108.2	107.4	107.9	108.6
N <sup>1</sup> C <sup>2</sup> C <sup>3</sup>	108.4	109.1	109.1	109.4
N <sup>1</sup> C <sup>5</sup> C <sup>4</sup>	108.3	111.1	110.6	108.8
C <sup>2</sup> C <sup>3</sup> C <sup>4</sup>	108.0	106.3	107.0	106.6
C <sup>3</sup> C <sup>4</sup> C <sup>5</sup>	107.0	106.0	105.3	106.7

**Table 3.** Inductive constants σ<sub>I</sub> and σ\* of substituents in SaX molecules **IX–XI**

Substituent X	σ <sub>I</sub> <sup>a</sup>	σ* <sup>b</sup>
<i>N</i> -Pyrrolyl	0.56	3.09
<i>N</i> -Pyrrolylmethyl	0.29	1.62
<i>N</i> -Indolyl	0.43	2.37
<i>N</i> -Indolylmethyl	0.21	1.20
<i>N</i> -Carbazolyl	0.51	2.82
<i>N</i> -Carbazolylmethyl	0.26	1.46

<sup>a</sup> Calculated from the *l*<sub>Si←N</sub> values.

<sup>b</sup> Calculated by the formula σ\* = 5.53σ<sub>I</sub> [1].

**Table 4.** Dipole moments of *N*-substituted pyrroles, indoles, and carbazoles HtR (benzene, 25°C) [14–17]

Ht	μ, D		
	R = H	R = Me	R = (MeO) <sub>3</sub> SiCXH <sub>2</sub> <sup>a</sup>
<i>N</i> -Pyrrolyl	1.80	1.92	2.68
	1.88 <sup>b</sup>	1.42 <sup>b</sup>	
<i>N</i> -Indolyl	2.05	2.16	3.08
<i>N</i> -Carbazolyl	2.11	–	–
2-Methyl- <i>N</i> -indolyl	2.47	2.52	3.20

<sup>a</sup> Data of this work.

<sup>b</sup> In THF.

**Table 5.** Experimental ( $\mu_{\text{exp}}$ ) and calculated by the vector additivity scheme ( $\mu_{\text{VAS}}$ ) dipole moments of compounds **IX–XII** and energies of ionization from the  $\pi(b_1)$ -MO [IP( $b_1$ )] of heterocycles **I–IV**

Comp. no.	$\mu_{\text{exp}}$ (THF), D	$\mu_{\text{VAS}}$ , <sup>a</sup> D	$\Delta\mu$ , D	IP( $b_1$ ), <sup>b</sup> eV
<b>IX</b>	8.0	6.5	1.5	9.23
<b>X</b>	7.4	6.6	0.8	7.90
<b>XI</b>	6.6	6.5	0.1	7.60
<b>XII</b>	7.3	6.9	0.4	7.65

<sup>a</sup> The  $N_{\text{Ht}}\text{CSi}$  bond angle was assumed to be equal to  $117^\circ$  (see text).

<sup>b</sup> Data of [20].

**Table 6.** Calculated geometric parameters<sup>a</sup> of molecules **IX–XII** and **XVIII**

Comp. no.	Bond lengths $d$ , Å		
	Si←N	Si–C	C–N <sub>Ht</sub>
<b>IX</b>	2.586 (2.089)	1.884 (1.902)	1.456 (1.470)
<b>X</b>	2.588 (2.11)	1.885 (1.91)	1.451 [1.47 ( $\alpha$ )] [1.49 ( $\beta$ )]
<b>XI</b>	2.583 (2.097)	1.885 (1.897)	1.456 (1.47)
<b>XII</b>	2.594	1.887	1.456
<b>XVIII</b>	2.679 (2.175)	1.787 (1.870)	

Comp. no.	Bond and torsion angles, deg		
	NSiC	N <sub>Ht</sub> CSi	C <sub>Ht</sub> N <sub>Ht</sub> CSi
<b>IX</b>	177.3 (177.9)	114.9 (116.9)	82.0 (77.2)
<b>X</b>	175.1 [176.8 ( $\alpha$ ), 175.3 ( $\beta$ )]	117.7 [118.4 ( $\alpha$ ), 117.6 ( $\beta$ )]	40.0 [–70.5 ( $\alpha$ ), 83.4 ( $\beta$ )]
<b>XI</b>	177.1 (177.8)	115.8 (117.5)	86.0 (92.8)
<b>XII</b>	176.5	116.4	85.0

<sup>a</sup> The experimental values (X-ray diffraction) are given in parentheses or brackets.

tion that there is no electronic interaction between the heterocyclic and silatranylmethyl fragments). In the calculations, the dipole moment of the  $\text{CH}_2\text{Sa}$  group was taken equal to that of  $\text{CH}_3\text{Sa}$  (5.46 D, benzene), and it was assumed to be directed from the nitrogen atom to silicon [21, 22]. The smallest  $\Delta\mu$  value was observed for molecule **XI** which is characterized by the highest energy of  $\pi(b_1)$ -MO. The electron-acceptor powers of the heterocyclic substituents are almost similar (Table 3). Therefore, the

inductive effects of the pyrrolyl, indolyl, and carbazolyl groups on the silatrane fragment can also be regarded as approximately similar.

**IR and UV spectra.** The effect of the *N*-silatranylmethyl group on the geometric parameters of the pyrrole ring in compound **IX** is also reflected in the IR spectrum. Absorption bands corresponding to stretching vibrations of the C–C bonds in the pyrrole ring are displaced to higher frequencies (1430, 1486, and  $1552\text{ cm}^{-1}$ ) relative to their position in the spectrum of pyrrole (**I**) (1417, 1468, and  $1529\text{ cm}^{-1}$ ). By contrast, the C–H stretching vibration band of **IX** ( $3092\text{ cm}^{-1}$ ) appears at a lower frequency, as compared to pyrrole ( $3102\text{ cm}^{-1}$ ) and its *N*-methyl ( $3100\text{ cm}^{-1}$ ), *N*-triethylsilylmethyl ( $3101\text{ cm}^{-1}$ ), and *N*-trimethoxysilylmethyl derivatives ( $3100\text{ cm}^{-1}$ ). The observed low-frequency shift ( $\Delta\nu \sim 10\text{ cm}^{-1}$ ) suggests enhanced aromaticity of the pyrrole ring in **IX** due to effect of the  $\text{CH}_2\text{Sa}$  group (cf.  $\nu\text{C–H}$  for pyridine and benzene:  $3036$  and  $3030\text{ cm}^{-1}$ , respectively [23]).

Unlike *N*-silatranylmethylpyrrole (**IX**), the presence of a similar *N*-substituent in indole **X** only slightly changes stretching vibration frequencies of the indole fragment relative to those typical of unsubstituted indole ( $1337$ ,  $1354$ ,  $1459$ , and  $1506\text{ cm}^{-1}$  against  $1336$ ,  $1352$ ,  $1455$ , and  $1505\text{ cm}^{-1}$ ). The low intensity of the C–H stretching vibration bands in the IR spectra of indole and its *N*-silatranylmethyl derivative makes it difficult to estimate the corresponding effect.

In the IR spectrum of *N*-silatranylmethylcarbazole (**XI**), some stretching vibration bands of the carbazole skeleton remain almost the same as in the spectrum of unsubstituted carbazole ( $1326$ ,  $1449$ , and  $1625\text{ cm}^{-1}$  against  $1324$ ,  $1450$ , and  $1626\text{ cm}^{-1}$ ), while the others are displaced on the average by  $9\text{ cm}^{-1}$  to lower frequencies ( $1482$  and  $1591\text{ cm}^{-1}$  against  $1493$  and  $1602\text{ cm}^{-1}$ ).

Thus, the effect of the silatranylmethyl group on the pyrrole fragment in molecules **IX–XI**, observed in the IR spectra, is consistent with the X-ray diffraction data. The results of a more detailed study of the IR spectra of compounds **X** and **XI** with the use of quantum-chemical methods will be reported elsewhere.

In going from pyrrole (**I**) to *N*-trimethoxysilylmethylpyrrole (**V**), *N*-silatranylmethylpyrrole (**IX**), *N*-triethylsilylmethylpyrrole (**XIII**), and finally to *N*-methylpyrrole (**XIV**), the long-wave  $\pi$ - $\pi^*$  absorption band in the electron spectra successively shifts to the red region ( $\Delta\lambda = 1300$ – $1800\text{ cm}^{-1}$  (Table 7). The long-wave absorption maxima of silicon-containing pyrrole derivatives **V**, **IX**, and **XIII** are located in

the same region as those in the spectra of *N*-alkylpyrroles (see also [24]). Taking into account that the I-HOMO of pyrrole is characterized by a node on the nitrogen atom (it does not contribute to the total charge on that atom), displacement of the long-wave absorption maximum in the UV spectra of the examined compounds may be interpreted in terms of variation of the substituent inductive effect.

The long-wave absorption band in the UV spectrum of a solution of carbazole in acetonitrile is located in the region 29 000–32 000 cm<sup>-1</sup>; its most intense vibronic component appears at 31 000 cm<sup>-1</sup>. The corresponding maximum of *N*-ethylcarbazole is displaced by ~700 cm<sup>-1</sup> to lower frequencies [25]. The long-wave absorption maximum of *N*-silatranylmethylcarbazole shifts by 2350 cm<sup>-1</sup> to the red region relative to that of unsubstituted carbazole. Its intensity (both absolute and relative) is greater than those observed for *N*-substituted pyrrole. Unlike pyrrole whose I-HOMO is transformed by the *a*<sub>2</sub> irreducible representation, the I-HOMO of carbazole contributes much to the electron density on the nitrogen atom, i.e., it is π(*b*<sub>1</sub>)-MO. As noted previously, just such fragment orbitals are involved in the π,σ<sub>C-Si</sub> interaction. A conclusion can be drawn that low-energy π-π\* transitions in the UV spectra of pyrrole and carbazole, which have different electronic natures, are differently perturbed by the silatranylmethyl group.

**NMR spectra.** The nature of the heteroring in compounds **IX–XI** insignificantly affects the position of <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si signals from the silatrane moiety in the NMR spectra (Δδ <sup>1</sup>H ~0.2 ppm, Δδ<sub>C</sub> ~1 ppm, Δδ<sub>Si</sub> ~2 ppm; Table 8). In going from *N*-(1-silatranylmethyl)pyrrole (**IX**) to the corresponding indole and carbazole derivatives **X** and **XI**, some deshielding of the bridging methylene protons is observed (Δδ 0.32 ppm); by contrast, the methylene carbon atom becomes more shielded (by ~6 ppm). The <sup>15</sup>N signal from the pyrrole nitrogen atom shifts upfield by about 20 ppm in going from **IX** to **X** and then to **XI**.

The <sup>1</sup>H and <sup>13</sup>C chemical shifts of atoms in the heterocyclic fragment of **IX–XI** almost coincide with those of the corresponding *N*-methyl derivatives **XIV–XVI**. The <sup>15</sup>N signals from the pyrrole nitrogen atom in compounds **IX–XI** are displaced downfield by 9.8, 5.3, and 12 ppm, respectively, relative to those observed in the <sup>15</sup>N spectra of the *N*-methyl analogs. All proton chemical shifts increase in going from compound **IX** to **X** and **XI**. The difference in the chemical shifts of the respective protons is 0.64 ppm for **IX** and **X** and 0.20 ppm for **X** and **XI**. All ring carbon atoms attached to nitrogen are characterized by larger chemical shifts (on the average, by 10–20 ppm)

**Table 7.** Long-wave absorption maxima in the UV spectra of compounds **I**, **V**, **IX**, **XI**, **XIII**, and **XIV**

Comp. no.	ν, cm <sup>-1</sup> (log ε)
<b>I</b>	47 500 (3.81)
<b>V</b>	46 200 (3.82)
<b>IX</b>	45 800 (3.86)
<b>XIII</b>	45 700 (3.86)
<b>XIV</b>	46 250 (3.84)
<b>III</b>	32 260 (3.48), 31 000 (3.60), 29 800 (3.53)
<b>XI</b>	29 800 (3.44), 28 650 (3.54), 27 800 (3.43)

than those of the other carbon atoms. The degree of deshielding increases with increase in the degree of ring fusion in the series **IX** < **X** < **XI** (from 122.50 to 130.13 ppm and from 137.65 to 141.70 ppm).

The differences in the chemical shifts of carbon nuclei in the same positions of the benzene rings in **X** and **XI** are -0.31, -4.62, 2.90, and 1.56 ppm. The <sup>13</sup>C chemical shifts of the benzene carbon atoms in compounds **X** and **XI** and the corresponding *N*-methyl derivatives differ insignificantly.

## EXPERIMENTAL

Single crystals of *N*-(1-silatranylmethyl derivatives **IX–XI**) were preliminarily examined by photometry. A set of reflections (4210, 8907, and 3486 reflections, respectively) was acquired on a Syntex P2<sub>1</sub> automatic four-circle diffractometer (MoK<sub>α</sub> radiation, graphite monochromator; a correction for absorption was introduced). Crystallographic data for compounds **IX–XI**, respectively: *a* = 9.812(4), 14.14(3), 14.371(5) Å; *b* = 11.348(5), 15.05(2), 8.651(4) Å; *c* = 11.168(5), 16.17(3), 14.688(6) Å; β = 99.24(4), 116.0(1), 105.77(3)°; space group *P*2<sub>1</sub>/*c*; *V* = 1227(1), 3093(5), 1757(2) Å<sup>3</sup>; *Z* = 4; *d*<sub>calc</sub> = 1.377(2), 1.307(8), 1.340(2) g/cm<sup>3</sup>. The structures were solved by the direct method and were refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms.

The dielectric permittivities of solutions of **V**, **VI**, and **VIII–XII** in THF were measured on an Epsilon dielcometer (OKBA Joint-Stock Company, Angarsk) at a frequency of 1 MHz (25°C). The densities were determined by the volumetric method, and the refractive indices were measured with the aid of an IRF-454BM refractometer. The dipole moments were calculated by the Onsager formula [30].

The <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13

**Table 8.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectra of *N*-(1-silatranylmethyl)pyrrole (**IX**), *N*-(1-silatranylmethyl)indole (**X**), *N*-(1-silatranylmethyl)carbazole (**XI**), 2-methyl-*N*-(1-silatranylmethyl)indole (**XII**), and their *N*-methyl analogs **XIV**–**XVI** [26–29]

Comp. no.	$^1\text{H}$ , $\delta$ , ppm, $J_{\text{HH}}$ , Hz	$^{13}\text{C}$	$^{15}\text{N}$	$^{29}\text{Si}$
<b>IX</b>	2.83 t $\text{NCH}_2$ , $^3J = 5.9$	40.65 $\text{CH}_2$	–221.6	–78.4
	3.26 s $\text{CH}_2$	51.23 $\text{NCH}_2$		
	3.77 $\text{OCH}_2$ , $^3J = 5.9$	57.31 $\text{OCH}_2$		
	6.01 t 3-H, 4-H, $J = 1.8$	106.03 $\text{C}^3$ , $\text{C}^4$		
	6.71 t 2-H, 5-H, $J = 1.8$	122.50 $\text{C}^2$ , $\text{C}^5$		
		36.27 $\text{CH}_2$		
<b>X</b>	2.64 t $\text{NCH}_2$ , $^3J = 5.8$	50.97 $\text{NCH}_2$	–245.0	–78.3
	3.34 s $\text{CH}_2$	57.20 $\text{OCH}_2$		
	3.67 t $\text{OCH}_2$ , $^3J = 5.8$	98.67 $\text{C}^3$		
	6.34 d 3-H, $^3J = 2.8$	110.39 $\text{C}^7$		
	6.97 d.d 6-H, $^3J = 8.2$ , 7.9	118.05 $\text{C}^6$		
	7.09 d.d 5-H, $^3J = 8.2$ , 7.9	120.09 $\text{C}^4$		
	7.35 d 2-H, $^3J = 2.8$	120.14 $\text{C}^5$		
	7.39 d 7-H, $^3J = 7.9$	128.01 $\text{C}^9$		
	7.52 d 4-H, $^3J = 7.9$	130.13 $\text{C}^2$		
	137.65 $\text{C}^8$			
	34.69 $\text{CH}_2$			
<b>XI</b>	2.75 t $\text{NCH}_2$ , $^3J = 5.9$	51.24 $\text{NCH}_2$	–263.4 –355.4 (silatrane)	–76.6
	3.58 s $\text{CH}_2$	57.24 $\text{OCH}_2$		
	3.69 t $\text{OCH}_2$ , $^3J = 5.9$	110.70 $\text{C}^1$ , $\text{C}^8$		
	7.12 d.d 3-H, $^3J = 7.9$ , 7.7	117.24 $\text{C}^3$ , $\text{C}^6$		
	7.39 d.d 2-H, $^3J = 7.9$ , 7.7	119.53 $\text{C}^4$ , $\text{C}^5$		
	7.59 d 1-H, $^3J = 7.91$	22.33 $\text{C}^{4a}$		
	8.04 d 4-H, $^3J = 7.9$	124.67 $\text{C}^2$ , $\text{C}^7$		
		141.70 $\text{C}^{8a}$		
		–230.9		
<b>XIV</b>	6.06 3-H, 4-H	35.2 $\text{NCH}_3$	–231.4 (neat)	
	6.51 2-H, 5-H ( $\text{CCl}_4$ )	107.7 $\text{C}^3$ , $\text{C}^4$	–231.6 (acetone)	
		121.0 $\text{C}^2$ , $\text{C}^5$		
		32.4 $\text{NCH}_3$		
<b>XV</b>	3.32 $\text{NCH}_3$	100.8 $\text{C}^3$	–250.0 (neat)	
	6.47 3-H	109.0 $\text{C}^7$	–253.6 (DMSO)	
	7.00 5-H	119.1 $\text{C}^4$	–250.3 (neat)	
	7.08 6-H	120.7 $\text{C}^5$		
	7.28 2-H	121.3 $\text{C}^6$		
	7.40 7-H	128.4 $\text{C}^9$		
	7.55 4-H	128.6 $\text{C}^2$		
		136.6 $\text{C}^8$		
	29.7 $\text{NCH}_3$			
<b>XVI</b>	3.74 $\text{NCH}_3$	108.2 $\text{C}^1$ , $\text{C}^8$	–278.0 (acetone)	
	7.21 3-H, 6-H	118.7 $\text{C}^3$ , $\text{C}^6$	–272.7 (DMSO)	
	7.33 1-H, 8-H	120.1 $\text{C}^4$ , $\text{C}^5$	–275.4 (acetone)	
	7.44 2-H, 7-H	122.7 $\text{C}^{4a}$		
	8.07 4-H, 5-H	125.5 $\text{C}^2$ , $\text{C}^7$		
	140.9 $\text{C}^{8a}$			

( $^1\text{H}$ ), 100.61 ( $^{13}\text{C}$ ), 40.56 ( $^{15}\text{N}$ ), and 79.49 MHz ( $^{29}\text{Si}$ ). Compounds **IX–XI** were dissolved in  $\text{CDCl}_3$  with addition of TMS as internal reference. The  $^{29}\text{Si}$  NMR spectra were acquired using INEPT pulse sequence. The  $^{15}\text{N}$  chemical shifts were measured relative to  $\text{MeNO}_2$  from the inverse two-dimensional  $^1\text{H}$ – $^{15}\text{N}$  spectra using the HMBCGP technique. The chemical shifts were determined with an accuracy of 0.01 ( $^1\text{H}$ ), 0.02 ( $^{13}\text{C}$ ), and 0.1 ppm ( $^{15}\text{N}$  and  $^{29}\text{Si}$ ).

**N-(Trimethoxysilylmethyl)pyrrole (V)**. To a solution of 1.74 g (16.5 mmol) of potassium pyrrolate and 0.063 g of dibenzo-24-crown-8 in xylene we added 5 ml of freshly distilled dimethylformamide and then 2.8 g (16.5 mmol) of chloromethyl(trimethoxy)silane. The mixture was stirred for 6 h at 60–90°C, the precipitate was filtered off, and the filtrate was subjected to vacuum distillation.

**N-(Trimethoxysilylmethyl)indole (VIII)** was synthesized in a similar way.

**N-(1-Silatranylmethyl)pyrrole (IX)**. A mixture of 2.44 g (14 mmol) of compound **V** and 2.15 g (14 mmol) of tris(2-hydroxyethyl)amine was stirred for 10 min at 25°C. The colorless precipitate was recrystallized from chloroform–hexane (1:1).

**2-Methyl-N-(1-silatranylmethyl)indole (XII)** was synthesized in a similar way.

**N-(1-Silatranylmethyl)carbazole (XI)**. To a solution of 2.05 g (10 mmol) of potassium carbazolate and 0.063 g of dibenzo-24-crown-8 in 7 ml of freshly distilled dimethylformamide we added 1.72 g (10 mmol) of chloromethyl(trimethoxy)silane. The mixture was stirred for 12 h at 140–150°C, the precipitate was filtered off, and 1.49 g (10 mmol) of tris(2-hydroxyethyl)amine was added. The colorless precipitate was filtered off and recrystallized from DMF.

Compounds **VI** and **X** were synthesized by the procedure described in [31].

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