ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 12, pp. 2468–2477. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.D. Sheludyakov, N.E. Kuz'mina, A.M. Abramkin, A.A. Korlyukov, D.E. Arkhipov, S.V. Loginov, D.A. Cheshkov, P. A. Storozhenko, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 12, pp. 2019–2028.

Synthesis and Structure of *N*-(2-Silatranylethyl)imidazoles

V. D. Sheludyakov[a], N. E. Kuz'mina[b], A. M. Abramkin[a], A. A. Korlyukov[c], D. E. Arkhipov[c], S. V. Loginov[a], D. A. Cheshkov[a], and P. A. Storozhenko[a]

[a] *State Research Institute of Chemistry and Technology of Organometallic Compounds, sh. Entuziastov 38, Moscow, 105118 Russia*
e-mail: vdsh2004@yandex.ru

[b] *Medical Equipment Scientific Appraisal Center, Moscow, Russia*

[c] *Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

Received June 27, 2011

Abstract—Organosilicon imidazole derivatives containing a 2-silatranylethyl [$N(CH_2CH_2O)_3Si(CH_2)_2$] group on the nitrogen atom were synthesized, and their steric and electronic structures, including the nature of interaction between the imidazole and silatrane fragments, were studied by X-ray analysis and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.

DOI: 10.1134/S1070363211120085

This work continues our studies on the synthesis and reactivity of new *N*-[2-(trimethoxysilyl)ethyl]-substituted diazoles. While studying chemical properties of *N*-[2-(trimethoxysilyl)ethyl]diazoles obtained by nucleophilic addition of diazoles to trimethoxysilanes [1], they were converted into the corresponding silatranes taking into account high stability of the silatrane structure and potential biological activity of new compounds possessing diazole and silatrane fragments. The goal of the present work was to synthesize *N*-(2-silatranylethyl) derivatives of imidazole, *N*-(2-silatranylethyl)imidazole (**VIII**), 2-methyl-*N*-(2-silatranylethyl)imidazole (**IX**), 2-ethyl-*N*-(2-silatranylethyl)imidazole (**X**), 4-methyl-*N*-(2-silatranylethyl)imidazole (**XI**), 5-methyl-*N*-(2-silatranylethyl)imidazole (**XII**), and *N*-(2-silatranylethyl)-benzimidazole (**XIII**) and examine their structure.

Silatranes constitute a unique class of heterocyclic compounds containing a five-coordinate silicon atom. Their specificity is reflected in steric structure of their molecules and electron density distribution therein, which determines geometric and spectral parameters of silatranes [2–4]. An important structural problem is to find correlations between the structure and spectral parameters of newly synthesized silatranes.

Compounds **VIII–XIII** were synthesized from the corresponding trimethoxysilanes via transetherification. They were isolated as colorless crystalline substances, which are soluble in water, alcohols, acetone, chloroform, dimethyl sulfoxide, and other organic solvents; silatrane derivatives **VIII–XIII** readily sublime under reduced pressure. Their structure was proved by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The molecular and crystalline structures of compounds **VIII–X** and **XIII** were determined by X-ray analysis. The principal crystallographic data and refinement parameters are collected in Table 1, and the bond lengths and bond angles in molecules **VIII–X** and **XIII** are given in Tables 2–5 (Figs. 1–4).

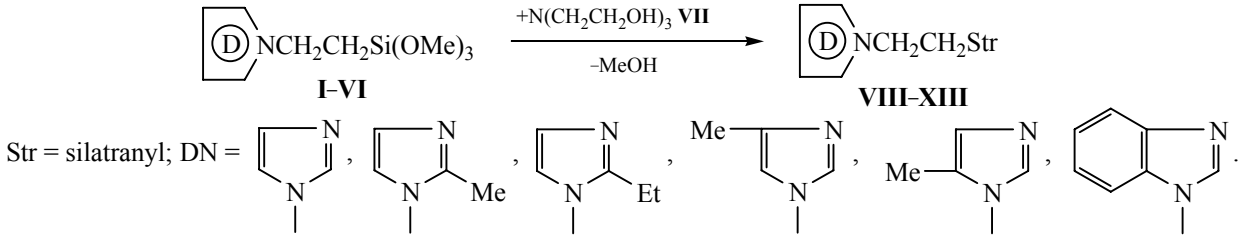

Table 1. Crystallographic and structure refinement parameters of compounds **VIII**–**X** and **XIII**

Parameter	**VIII**	**IX**	**X**	**XIII**
Formula	$C_{11}H_{19}N_3O_3Si$	$C_{12}H_{21}N_3O_3Si$	$C_{13}H_{23}N_3O_3Si$	$C_{15}H_{21}N_3O_3Si$
Molecular weight	269.38	283.41	297.43	319.44
Temperature, K	120	120	120	120
Crystal system	Rhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	8	4	4	4
a, Å	11.1310(16)	6.6508(5)	6.560(2)	6.8417(11)
b, Å	13.0921(19)	10.1463(8)	10.169(4)	17.729(3)
c, Å	17.121(3)	19.9315(16)	21.527(7)	13.068(2)
α, deg	90.00	90.00	90.00	90.00
β, deg	90.00	95.5800(10)	97.837(5)	103.781(2)
γ, deg	90.00	90.00	90.00	90.00
V, Å^3	2495.1(6)	1338.62(18)	1422.5(8)	1539.4(4)
d_{calc}, g cm^{-3}	1.434	1.406	1.389	1.378
μ, cm^{-1}	1.94	1.84	1.77	1.69
F(000)	1152	608	640	680
$2\theta_{max}$, deg	60	60	60	60
Total reflection number	26830	20289	14173	13525
Number of independent reflections (R_{int})	3623	3915 (0.0373)	4101	4487 (0.0455)
Number of reflections with $I > 2\sigma(I)$	2435	2608	2151	2551
Number of refined parameters	163	201	182	199
R_1	0.0440	0.0506	0.0525	0.0633
wR_2	0.0894	0.1053	0.0985	0.1274
GOOF	1.027	1.031	0.995	1.089
Residual electron density, e Å^{-3} (d_{min}/d_{max})	0.428/–0.335	0.942/–0.795	0.510/–0.413	0.484/–0.423

In the molecular structure of *N*-(2-silatranylethyl) imidazoles the most interesting are geometric parameters of the silatranyl fragment, for they provide information on transannular interaction between the silicon and nitrogen atoms and hybridization of their valence orbitals, as well as on the effect of the imidazole ring on the structure of the silatrane skeleton.

It is generally believed that transannular interaction between silicon and nitrogen atoms involves partial transfer of the nitrogen lone electron pair to the $3p_z$ orbital of sp^2-hybridized silicon atom [5]. The C–Si–N bond is a three-center four-electron hypervalent bond. The interatomic $Si^1\cdots N^1$ distances in molecules **VIII**–**X** and **XIII** are fairly similar (2.109–2.112 Å), and they are considerably shorter than the sum of the corresponding van der Waals radii (3.5 Å [5]); the N^1–C bond lengths (1.466–1.482 Å) approach standard value for C_{sp^3}–N^+ bond (1.499 Å [6]), indicating effective transannular interaction. As a result, the Si^1–O (1.662–

Table 2. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of *N*-(2-silatranylethyl)-1*H*-imidazole (**VIII**)

Bond	*d*	Bond	*d*
Si^1–O^2	1.6687 (12)	N^2–C^9	1.350 (2)
Si^1–O^1	1.6712 (12)	N^2–C^{11}	1.374 (2)
Si^1–O^3	1.6771 (12)	N^2–C^8	1.471 (2)
Si^1–C^7	1.9007 (16)	N^3–C^9	1.314 (2)
Si^1–N^1	2.1125 (14)	N^3–C^{10}	1.374 (2)
O^1–C^1	1.4318 (19)	C^1–C^4	1.520 (2)
O^2–C^2	1.422 (2)	C^2–C^5	1.521 (2)
O^3–C^3	1.4237 (19)	C^3–C^6	1.518 (2)
N^1–C^5	1.476 (2)	C^7–C^8	1.516 (2)
N^1–C^4	1.477 (2)	C^{10}–C^{11}	1.370 (2)
N^1–C^6	1.482 (2)		
Angle	ω	Angle	ω
$O^1C^1C^4$	108.59 (13)	$C^9N^2C^8$	125.96 (14)
$O^2C^2C^5$	108.77 (13)	$C^9N^2C^{11}$	106.74 (14)
$O^3C^3C^6$	108.45 (13)	$C^{11}N^2C^8$	126.87 (14)
$N^1C^4C^1$	105.95 (13)	$C^9N^3C^{10}$	104.09 (14)
$N^1C^5C^2$	106.17 (13)	$C^1O^1Si^1$	122.31 (10)
$N^1C^6C^3$	106.08 (13)	$C^2O^2Si^1$	121.94 (10)
$C^8C^7Si^1$	111.40 (11)	$C^3O^3Si^1$	122.50 (10)
$N^2C^8C^7$	115.92 (13)	$C^7Si^1N^1$	178.74 (7)
$N^3C^9N^2$	113.04 (15)	$O^1Si^1C^7$	96.00 (7)
$C^{11}C^{10}N^3$	111.05 (15)	$O^1Si^1N^1$	83.99 (6)
$C^{10}C^{11}N^2$	105.07 (15)	$O^1Si^1O^3$	119.90 (6)
$C^4N^1C^6$	112.76 (13)	$O^2Si^1C^7$	96.61 (6)
$C^4N^1Si^1$	105.79 (10)	$O^2Si^1N^1$	84.49 (6)
$C^5N^1C^4$	113.34 (13)	$O^2Si^1O^1$	118.11 (6)
$C^5N^1C^6$	113.98 (13)	$O^2Si^1O^3$	118.91 (6)
$C^5N^1Si^1$	104.84 (10)	$O^3Si^1C^7$	94.97 (7)
$C^6N^1Si^1$	105.06 (10)	$O^3Si^1N^1$	83.95 (6)

Table 3. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of 2-methyl-1-(2-silatranylethyl)-1*H*-imidazole (**IX**)

Bond	*d*	Bond	*d*
Si^1–O^1	1.6713 (15)	N^2–C^9	1.362 (3)
Si^1–O^2	1.6762 (14)	N^2–C^{11}	1.379 (3)
Si^1–O^3	1.6724 (14)	N^2–C^8	1.474 (2)
Si^1–C^7	1.886 (2)	N^3–C^9	1.324 (3)
Si^1–N^1	2.1104 (17)	N^3–C^{10}	1.382 (3)
O^1–C^1	1.427 (2)	C^1–C^4	1.5379 (18)
O^2–C^2	1.421 (2)	C^2–C^5	1.5360 (18)
O^3–C^3	1.415 (2)	C^3–C^6	1.5171 (18)
N^1–C^5	1.4622 (17)	C^7–C^8	1.525 (3)
N^1–C^4	1.4766 (17)	C^9–C^{12}	1.487 (3)
N^1–C^6	1.4829 (17)	C^{10}–C^{11}	1.359 (3)
Angle	ω	Angle	ω
$O^1Si^1O^2$	119.15 (8)	$C^2O^2Si^1$	122.43 (13)
$O^1Si^1O^3$	118.46 (8)	$C^3O^3Si^1$	123.08 (12)
$O^2Si^1O^3$	119.10 (8)	$C^5N^1C^4$	114.95 (17)
$O^1Si^1C^7$	95.80 (9)	$C^5N^1C^6$	111.76 (18)
$O^2Si^1C^7$	95.03 (8)	$C^4N^1C^6$	111.43 (17)
$O^3Si^1C^7$	97.32 (8)	$C^5N^1Si^1$	106.50 (13)
$O^1Si^1N^1$	84.12 (6)	$C^4N^1Si^1$	105.57 (12)
$O^2Si^1N^1$	84.09 (7)	$C^6N^1Si^1$	105.89 (12)
$O^3Si^1N^1$	83.64 (6)	$C^9N^2C^{11}$	106.94 (17)
$C^7Si^1N^1$	178.94 (8)	$C^9N^2C^8$	127.97 (18)
$C^1O^1Si^1$	121.70 (12)	$C^{11}N^2C^8$	126.50 (17)
$C^9N^3C^{10}$	104.91 (17)	$O^1C^1C^4$	108.77 (16)
$O^2C^2C^5$	109.58 (16)	$O^3C^3C^6$	109.77 (16)
$N^1C^4C^1$	104.20 (16)	$N^1C^5C^2$	106.16 (16)
$N^1C^6C^3$	105.74 (16)	$C^8C^7Si^1$	117.90 (14)
$N^2C^8C^7$	111.34 (16)	$N^3C^9N^2$	111.66 (18)
$N^3C^9C^{12}$	125.46 (19)	$N^2C^9C^{12}$	122.88 (18)
$C^{11}C^{10}N^3$	110.69 (19)	$N^2C^{11}C^{10}$	105.79 (19)

Table 4. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of 2-ethyl-1-(2-silatranylethyl)-1*H*-imidazole (**X**)

Bond	*d*	Bond	*d*
$Si^1–O^3$	1.6616 (16)	$N^3–C^9$	1.319 (3)
$Si^1–O^1$	1.6621 (15)	$N^3–C^{10}$	1.377 (3)
$Si^1–O^2$	1.6669 (15)	$N^4–C^4$	1.467 (3)
$Si^1–C^7$	1.874 (2)	$N^4–C^6$	1.469 (3)
$Si^1–N^4$	2.1111 (19)	$N^4–C^5$	1.474 (3)
$O^1–C^1$	1.413 (3)	$C^1–C^4$	1.514 (3)
$O^2–C^2$	1.417 (2)	$C^2–C^5$	1.507 (3)
$O^3–C^3$	1.410 (2)	$C^3–C^6$	1.510 (3)
$N^2–C^9$	1.347 (3)	$C^7–C^8$	1.511 (3)
$N^2–C^{11}$	1.373 (3)	$C^9–C^{12}$	1.499 (3)
$N^2–C^8$	1.465 (3)	$C^{10}–C^{11}$	1.351 (3)
$C^{12}–C^{13}$	1.507 (3)		
Angle	ω	Angle	ω
$O^3Si^1O^1$	118.16 (8)	$C^4N^4C^6$	113.19 (17)
$O^3Si^1O^2$	119.48 (8)	$C^4N^4C^5$	113.29 (17)
$O^1Si^1O^2$	118.83 (8)	$C^6N^4C^5$	113.46 (16)
$O^3Si^1C^7$	96.81 (9)	$C^4N^4Si^1$	104.74 (12)
$O^1Si^1C^7$	96.45 (9)	$C^6N^4Si^1$	105.64 (13)
$O^2Si^1C^7$	95.53 (9)	$C^5N^4Si^1$	105.47 (13)
$O^3Si^1N^4$	83.57 (7)	$O^1C^1C^4$	107.64 (17)
$O^1Si^1N^4$	83.97 (8)	$O^2C^2C^5$	108.59 (17)
$O^2Si^1N^4$	83.68 (7)	$O^3C^3C^6$	108.93 (17)
$C^7Si^1N^4$	179.21 (9)	$N^4C^4C^1$	105.81 (17)
$C^1O^1Si^1$	121.90 (13)	$N^4C^5C^2$	106.01 (17)
$C^2O^2Si^1$	122.45 (13)	$N^4C^6C^3$	105.86 (16)
$C^3O^3Si^1$	122.77 (13)	$C^8C^7Si^1$	117.25 (15)
$C^9N^2C^{11}$	106.62 (18)	$N^2C^8C^7$	112.24 (17)
$C^9N^2C^8$	129.06 (18)	$N^3C^9N^2$	112.43 (19)
$C^{11}N^2C^8$	124.03 (18)	$N^3C^9C^{12}$	124.7 (2)
$C^9N^3C^{10}$	104.27 (18)	$N^2C^9C^{12}$	122.83 (19)
$C^{11}C^{10}N^3$	110.8 (2)	$C^{10}C^{11}N^2$	105.9 (2)
$C^9C^{12}C^{13}$	113.48 (19)		

Table 5. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of 1-(2-silatranylethyl)-1*H*-benzimidazole (**XIII**)

Bond	*d*	Bond	*d*
$Si^1–O^1$	1.6681 (17)	$N^2–C^9$	1.353 (3)
$Si^1–O^2$	1.6678 (17)	$N^2–C^{11}$	1.378 (3)
$Si^1–O^3$	1.6700 (17)	$N^2–C^8$	1.472 (3)
$Si^1–C^7$	1.884 (2)	$N^3–C^9$	1.315 (3)
$Si^1–N^1$	2.109 (2)	$N^3–C^{10}$	1.390 (3)
$O^1–C^1$	1.417 (3)	$C^1–C^4$	1.520 (3)
$O^2–C^2$	1.420 (3)	$C^2–C^5$	1.525 (4)
$O^3–C^3$	1.422 (3)	$C^3–C^6$	1.511 (4)
$N^1–C^5$	1.479 (3)	$C^7–C^8$	1.521 (3)
$N^1–C^4$	1.474 (3)	$C^{10}–C^{15}$	1.394 (3)
$N^1–C^6$	1.476 (3)	$C^{10}–C^{11}$	1.412 (3)
$C^{11}–C^{12}$	1.383 (3)	$C^{12}–C^{13}$	1.378 (3)
$C^{13}–C^{14}$	1.403 (3)	$C^{14}–C^{15}$	1.374 (3)
Angle	ω	Angle	ω
$O^1Si^1O^2$	118.35 (9)	$C^2O^2Si^1$	122.50 (16)
$O^1Si^1O^3$	119.81 (9)	$C^3O^3Si^1$	122.55 (15)
$O^2Si^1O^3$	118.63 (9)	$C^5N^1C^4$	114.2 (2)
$O^1Si^1C^7$	95.80 (10)	$C^5N^1C^6$	113.01 (19)
$O^2Si^1C^7$	96.50 (10)	$C^4N^1C^6$	113.3 (2)
$O^3Si^1C^7$	95.64 (10)	$C^5N^1Si^1$	104.88 (15)
$O^1Si^1N^1$	84.15 (8)	$C^4N^1Si^1$	105.11 (14)
$O^2Si^1N^1$	84.16 (8)	$C^6N^1Si^1$	105.25 (15)
$O^3Si^1N^1$	83.75 (8)	$C^9N^2C^{11}$	106.6 (2)
$C^7Si^1N^1$	179.26 (10)	$C^9N^2C^8$	126.9 (2)
$C^1O^1Si^1$	122.35 (15)	$C^{11}N^2C^8$	126.4 (2)
$C^9N^3C^{10}$	103.7 (2)	$O^1C^1C^4$	108.7 (2)
$O^2C^2C^5$	108.47 (19)	$O^3C^3C^6$	108.85 (19)
$N^1C^4C^1$	106.0 (2)	$N^1C^5C^2$	105.64 (19)
$N^1C^6C^3$	105.8 (2)	$C^8C^7Si^1$	112.25 (17)
$N^2C^8C^7$	115.6 (2)	$N^3C^9N^2$	114.7 (2)
$N^3C^{10}C^{15}$	129.9 (2)	$C^{12}C^{11}C^{10}$	122.4 (2)
$N^3C^{10}C^{11}$	110.2 (2)	$C^{11}C^{12}C^{13}$	116.7 (2)
$C^{15}C^{10}C^{11}$	119.7 (2)	$C^{12}C^{13}C^{14}$	121.7 (2)
$N^2C^1C^{12}$	132.7 (2)	$C^{15}C^{14}C^{13}$	121.6 (2)
$N^2C^{11}C^{10}$	104.8 (2)	$C^{14}C^{15}C^{10}$	117.8 (2)

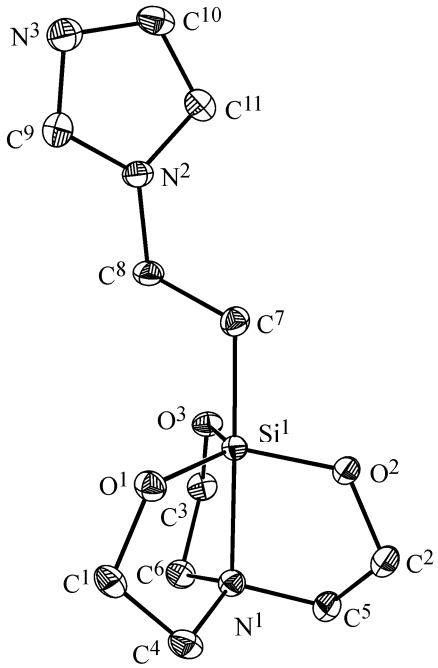

Fig. 1. Structure of the molecule of 1-(2-silatranylethyl)-1*H*-imidazole (**VIII**) according to the X-ray diffraction data.

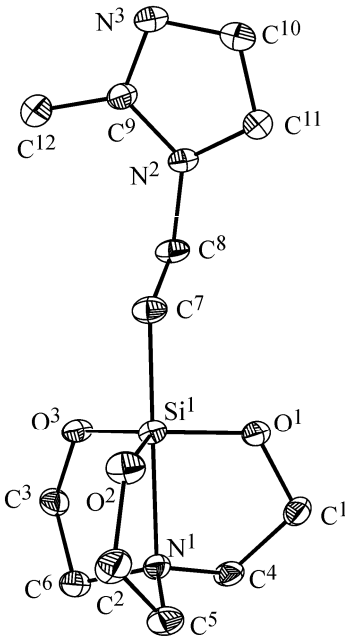

Fig. 2. Structure of the molecule of 2-methyl-1-(2-silatranylethyl)-1*H*-imidazole (**IX**) according to the X-ray diffraction data.

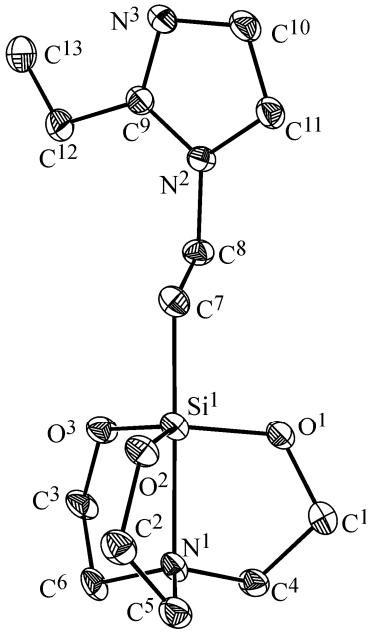

Fig. 3. Structure of the molecule of 2-ethyl-1-(2-silatranylethyl)-1*H*-imidazole (**X**) according to the X-ray diffraction data.

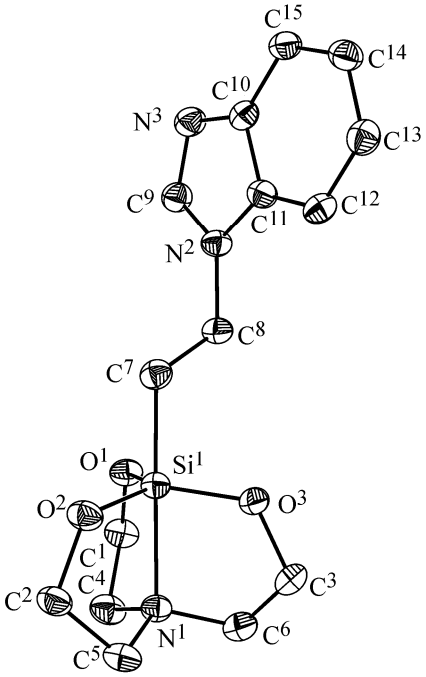

Fig. 4. Structure of the molecule of 1-(2-silatranylethyl)-1*H*-benzimidazole (**XIII**) according to the X-ray diffraction data.

1.676 Å) and $Si^1–C^7$ bonds (1.874–1.901 Å) in the examined molecules are slightly longer than average Si–O and Si–C_{sp^3} bonds in tetrahedral silicon compounds (1.631 and 1.863 Å, respectively [6]).

The silicon polyhedron adopts a distorted trigonal bipyramid configuration with three oxygen atoms located in the equatorial plane and C^7 and N^1 atoms in axial positions. The $C^7Si^1N^1$ bond angle approaches

180° (Tables 2–5). The C^7–Si^1–N^1 axis is almost orthogonal to the equatorial plane: the dihedral angle between the equatorial plane and the plane passing through the C^7, Si^1, and N^1 atoms is 90.2, 90.3, 89.9, and 90.1° in molecules **VIII**–**X** and **XIII**, respectively.

Deviation of the Si^1 atom from the equatorial plane (Δ) characterizes change of its hybridization [5] and is 0.171, 0.176, 0.182, and 0.173 Å in molecules **VIII**–**X**, and **XIII**, respectively. Thus the silicon atom in **X** is characterized by the maximal change toward sp^3 hybridization. Therefore, the Si^1–O (1.662–1.667 Å) and Si^1–C^7 bonds (1.874 Å) in molecule **X** are slightly shorter than analogous bonds in **VIII**, **IX**, and **XIII** and are most similar to those typical of tetrahedral silicon compounds.

The O–C bonds in the silatrane fragment (1.415–1.432 Å) are slightly longer than standard O–C bond in C–O–Si–X_3 systems (1.416 Å [6]), and the C–C bond lengths in the silatrane fragment an in the exocyclic N-ethyl bridge (C^7–C^8) range from 1.510 to 1.525 Å, which is typical of standard C_{sp^3}–C_{sp^3} bond (1.513 Å [6]). These data suggest that the negative charge on the silicon atom is delocalized only over the SiO_3 fragment as a result of transannular N→Si interaction.

The bond lengths in the imidazole rings, N^2–C^9 (1.347–1.353 Å), N^3–C^9 (1.314–1.324 Å), N^3–C^{10} (1.374–1.390 Å), C^{10}–C^{11} (1.351 Å), and C^{11}–N^2 (1.373–1.379 Å) approach the corresponding standard values (1.349, 1.313, 1.376, 1.360, and 1.370 Å, respectively [6]). There is no clear correlation between electronic properties of substituent in the imidazole ring and geometric parameters of the latter. Presumably, geometric parameters of the imidazole ring are influenced not only by inductive effect of the substituent therein but also by polarization effect of the silatranyl group which act in opposite directions.

The C^8–N^2 bond length (1.465–1.474 Å) approaches average C_{sp^3}–N_{sp^3} bond length (1.469 Å [6]). The shortest C^8–N^2 (1.465 Å) and C^7–C^8 bonds (1.510 Å) were found in molecule **X**. Somewhat shorter bonds in the exocyclic N-ethyl bridge in molecule **X** as compared to **VIII**, **IX**, and **XIII** may be due to inductive effect of the 2-ethylimidazole (the presence of ethyl group maximally enhances electron-donor properties of the heteroring).

A specific structural feature of the examined compounds is coplanar orientation of the exocyclic N-ethyl bridge to the axial axis of the silicon trigonal bipyramid: the N^1, Si^1, C^7, C^8, and N^2 atoms deviate from the plane by 0.017, 0.068, 0.023, and 0.031 Å for compounds **VIII**–**X** and **XIII**, respectively. This plane in molecules **IX**, **X**, and **XIII** is almost orthogonal to the imidazole ring plane (the dihedral angles are 93.1, 98.3, and 85.4°, respectively), whereas the corresponding dihedral angle in molecule **VIII** is 50.6°.

The observed distortion of steric structure of molecule **VIII** may be caused by polarization effect which is known to be important in silatranes [2]. Excess charges in the silatrane fragment induce a dipole moment in the substituent which in turn is involved in electrostatic interaction with the negative charge on the former [2].

Polarization effects were studied by analyzing interatomic contacts in the crystalline structure of compounds **VIII**–**X** and **XIII**. The existence of shortened contacts (shorter than the sum of the corresponding van der Waals atoms according to Pauling; r = 1.2, 1.4, 1.5, and 1.7 Å for H, O, N, and C, respectively [7]) indicates specific interactions that are appreciably stronger than conventional van der Waals interactions.

No shortened intramolecular contacts were found for molecules **VIII**–**X** and **XIII** having a staggered conformation. On the other hand, a number of various shortened intermolecular contacts were revealed (Table 6): C–H···O between hydrogen atom in the imidazole ring and oxygen atom in the silatrane fragment of the neighboring molecule; C–H···O between hydrogen and oxygen atoms in the neighboring silatrane fragments; C–H···N between hydrogen atom in the silatrane fragment and nitrogen atom in the imidazole ring of the neighboring molecule; C–H···C between hydrogen atom in the imidazole ring and carbon atom in the silatrane fragment of the neighboring molecule; C–H···C between hydrogen and carbon atoms in the neighboring imidazole rings; and C–H···C between hydrogen and carbon atoms in the neighboring silatrane fragments.

The efficiency of intermolecular non-valence interactions (δ, %) involving a hydrogen atom in a hydrocarbon fragment and a heteroatom B (B = O, N, C) was estimated by calculating the relative deviation of the H···B distance (r_{HB}) from the sum of the van der Waals radii of hydrogen atom and atom B (Σr_{vdW}):

$$\delta = \Delta r/\Sigma r_{vdW},\ \Delta r = \Sigma r_{vdW} - r_{HB}.$$

Table 6. Shortened intramolecular contacts in the crystalline structures of compounds **VIII–X** and **XIII**

A–H (x, y, z) ··· B	Position B	r_{HB}, Å	Δ, %	r_{AB}, Å
	VIII			
C^9–H···O^1	$x - 0.5, y, 0.5 - z$	2.515	3.27	3.453
C^1–H···N^3	$-0.5 - x, y + 0.5, z$	2.569	4.85	3.491
	IX			
C^6–H···O^1	$x - 1, y, z$	2.489	4.27	3.425
C^{11}–H···O^2	$x + 1, y, z$	2.554	1.77	3.464
C^3–H···C^1	$-x, 1 - y, -z$	2.881	0.66	3.661
C^7–H···C^5	$1 - x, y + 0.5, 0.5 - z$	2.646	8.76	3.408
C^3–H···C^6	$-x, 1 - y, -z$	2.757	4.93	3.591
C^5–H···C^7	$1 - x, 1 - y, 0.5 - z$	2.776	4.28	3.408
C^{12}–H···C^9	$2 - x, 2 - y, -z$	2.839	2.10	3.527
	X			
C^6–H···O^1	$x + 1, y, z$	2.565	1.35	3.483
C^{13}–H···N^2	$-x, 1 - y, 1 - z$	2.673	1.00	3.513
C^1–H···N^3	$x, y - 1, z$	2.658	1.55	3.586
C^7–H···C^5	$1 - x, 0.5 + y, 0.5 - z$	2.790	3.79	3.477
C^5–H···C^7	$1 - x, y - 0.5, 0.5 - z$	2.838	2.14	3.477
C^{13}–H···C^9	$-x, 1 - y, 1 - z$	2.677	7.69	3.529
C^4–H···C^{10}	$x + 1, y - 1, z$	2.834	2.28	3.772
C^4–H···C^{13}	$x, y - 1, z$	2.855	1.55	3.562
	XIII			
C^{15}–H···O^2	$x - 0.5, -0.5 - y, z + 0.5$	2.560	1.54	3.237
C^9–H···O^3	$x - 1, y, z$	2.508	3.54	3.409
C^{12}–H···N^3	$x + 1, y, z$	2.595	3.89	3.455
C^2–H···C^5	$2 - x, -y, -z$	2.851	1.69	3.776
C^6–H···C^{10}	$1 - x, -y, 1 - z$	2.795	3.62	3.741
C^5–H···C^{13}	$1.5 - x, y + 0.5, 0.5 - z$	2.813	3.00	3.757
C^5–H···C^{14}	$1.5 - x, y + 0.5, 0.5 - z$	2.834	2.28	3.786

While determining the nature of A–H···B interactions, we kept in mind that hydrogen bond shortens not only H···B contact but also A···B distance; shortening of the latter is insignificant if hydrogen bond is weak (the A···B distance is slightly shorter than Σr_{vdW} for A and B), whereas it exceeds 0.3 Å if hydrogen bond is strong [8]. The nature of A–H···B interaction characterized by an A···B distance of 3.2–4.0 Å is generally interpreted as electrostatic [9]. In our case, all A···B distances are longer than Σr_{vdW} for A and B atoms: $r_{C\cdots O}$ = 3.237–3.483 Å (Σr_{vdW} = 3.1 Å [7]), $r_{C\cdots N}$ = 3.491–3.586 Å

(Σr_{vdW} = 3.2 Å [7]), $r_{C\cdots C}$ = 3.408–3.786 Å (Σr_{vdW} = 3.4 Å [7]). Therefore, C–H···B interactions were considered to be electrostatic.

Comparison of non-valence interactions occurring in the crystalline structures of compounds **VIII**–**X** and **XIII** shows radical difference of structure **VIII**. The latter lacks electrostatic interactions between silatrane fragments of neighboring molecules, and electrostatic interactions exist only between imidazole and silatrane fragments. The strongest electrostatic interaction is observed between the imidazole N^3 atom and hydrogen atom in the silatrane OCH_2 group of the neighboring molecule (δ 4.85%). Analogous interaction in crystalline structure **X** is considerably weaker (δ 1.55%), and it is absent in structures **IX** and **X**. A correlation was found between the efficiency of $N^3\cdots H$ intermolecular electrostatic interaction and deviation of the imidazole ring plane from orthogonal orientation with respect to the plane including the exocyclic N-ethyl bridge and axis of the silicon trigonal bipyramid (**VIII**, 39.4°; **IX**, 8.3°; **X**, 3.1°; **XIII**, 4.6°). We can presume that steric structure of *N*-(2-silatranylethyl)imidazole molecules is distorted as a result of intermolecular electrostatic interaction involving the N^3 atom in the imidazole ring and hydrogen atom in the silatrane OCH_2 fragment in neighboring molecules.

Electrostatic interactions between silatrane fragments of neighboring molecules (five of the seven observed) predominate in the crystalline structure of **IX**. The shortest contact in the crystalline structure of **X** is that between the hydrocarbon fragments in neighboring imidazole rings (δ 7.69%); next in efficiency are electrostatic interactions between hydrocarbon moeties in neighboring silatrane fragments (δ 3.79%). Among seven kinds of intermolecular interactions in the crystalline structure of **XIII**, five are electrostatic interactions between aromatic system and silatrane fragment of neighboring molecules, one is interaction between two aromatic systems, and one is between neighboring silatrane fragments. The latter is the least effective (δ 1.69%). It should be noted that crystalline structures in which electrostatic interaction between two silatrane fragments is lacking or ineffective are characterized by minimal deviation of the silicon polyhedron from regular trigonal bipyramid. This means that intermolecular polarization effect of the silatranyl group distorts the shape of the silicon polyhedron to a stronger extent than does intermolecular polarization effect of the imidazole ring.

The spectral parameters of compounds **VIII**–**XIII** are determined by transannular Si···N interaction in the silatrane fragment and inductive and polarization effects of the imidazole and silatrane fragments. Electron density transfer from the nitrogen atom to silicon leads to enhanced shielding of the silicon nucleus in the examined *N*-(2-silatranylethyl)imidazoles as compared to analogous *N*-[2-(trimethoxysilyl)ethyl]imidazoles [1], so that the ^{29}Si signal is displaced from δ_{Si} –45.2 to –47.0 to the range –71.7 to –73.0 ppm. The shift of the ^{29}Si signal of compounds **VIII**, **IX**, and **XIII** is insignificant (δ_{Si} –72.8, –72.1, and –73.0 ppm, respectively) as compared to that observed for **X**–**XII** (δ_{Si} –71.7, –71.8, and –71.8 ppm, respectively). This is very consistent with variation of the efficiency of electrostatic interactions involving the imidazole ring and SiO_3 moiety in the silatrane fragment in these compounds. Presumably, effective participation of the silatrane oxygen atoms in intermolecular electrostatic interaction with hydrogen atom in the imidazole ring reduces electronegativity of the former; as a result, electronic shielding of the silicon nucleus increases.

Enhanced electronic shielding of Si nucleus due to transannular interaction between the silicon and nitrogen atoms induces downfield shift of signals from α-methylene protons in the exocyclic N-ethyl bridge in the ^1H NMR spectra of the examined *N*-(2-silatranylethyl)imidazoles from δ 1.07–1.24 to 0.88–1.07 ppm {cf. the data for the corresponding *N*-[2-(trimethoxysilyl)ethyl]imidazoles [1]}. Inductive effect of the silatranyl substituent almost does not affect the position of signals from the β-methylene protons: δ (β-CH_2) 3.85–4.26 and 3.82–4.24 ppm for *N*-(2-silatranylethyl)- and *N*-[2-(trimethoxysilyl)ethyl]imidazoles, respectively.

Introduction of an electron-donating aliphatic substituent into imidazole ring somewhat enhances electronic shielding of nuclei in the ring, and their signals are displaced slightly upfield; for example, $\delta_{10\text{-}H}$ 6.98 (**VIII**), 6.85 (**IX**, **X**), 6.68 ppm (**XII**). Increase of electron-donor power of the imidazole ring in turn provides additional shielding of protons in the exocyclic N-ethyl bridge. By contrast, benzene ring fusion weakens electron-donor effect of the imidazole ring, leading to deshielding of protons therein and in the bridging ethyl group, so that their signals are displaced downfield. It should be noted that inductive effect of the imidazole ring almost is not extended to protons in the silatrane fragment, and their chemical shifts are similar for all compounds under study.

Intramolecular transannular N→Si interaction in silatranes also induces a small downfield shift of signals from α- and β-methylene carbon atoms in the exocyclic N-ethyl bridge in *N*-(2-silatranylethyl)imidazoles compared to *N*-[2-(trimethoxysilyl)ethyl]imidazoles: δ_C(α-CH_2) 17.8–19.5 and 11.5–11.8 ppm, δ_C(β-CH_2) 42.6–45.0 and 38.8–40.7 ppm, respectively. Positive inductive effect of substituent in the imidazole leads to a small shielding, and negative, to deshielding of imidazole carbon nuclei: $\delta_C(C^9)$ 136.4 (**VIII**), 135.9 (**XI**, **XII**), 143.3 ppm (**XIII**). The chemical shifts of carbon nuclei in the silatrane fragments of compounds **VIII**–**XIII** are similar.

Variations of ^{13}C chemical shifts of the N-ethyl bridge are not so characteristic as variations of the ^1H chemical shifts. Presumably, this is related to opposite directions of the inductive and polarization effects of the imidazole and silatrane fragments.

To conclude, we have synthesized a series of new *N*-(2-silatranylethyl)imidazoles and studied their structure. These compounds display effective transannular interaction between the nitrogen and silicon atoms in the silatrane fragment, which indices excess electron density delocalized over the SiO_3 fragment. Inductive effects of the imidazole and silatrane fragments almost do not influence their geometric and spectral parameters, but are reflected in the parameters of the bridging ethyl group. Unlike inductive effects, polarization effects appreciably determine the steric structure of the examined compounds. Effective intermolecular electrostatic interaction with participation of the imidazole nitrogen atom and OCH_2 group in the silatrane fragment of neighboring molecules changes orientation of the imidazole ring with respect to the silatranylethyl fragment. Effective electrostatic interaction between silatrane fragments of neighboring molecules leads to distortion of the silicon polyhedron. Intramolecular inductive and intermolecular polarization effects of imidazole and silatrane fragments induce upfield shifts of signals from protons in the exocyclic N-ethyl bridge and silicon atom in the NMR spectra.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded at room temperature on a Bruker AM-360 spectrometer at 360.13 (^1H), 90.55 (^{13}C), and 71.58 MHz (^{29}Si) using $CDCl_3$ as solvent. Single crystals of compounds **VIII**–**X** and **XIII** for X-ray analysis were obtained by crystallization from ethanol. The X-ray diffraction data were acquired on a Bruker SMART 1000 CCD diffractometer (MoK_α irradiation, graphite monochromator, ω-scanning). Hydrogen atoms were localized by difference synthesis and were included in the refinement procedure with fixed thermal and positional parameters.

1-(2-Silatranylethyl)-1*H*-imidazole (VIII). Mixing of 16.2 g (0.075 mol) of 1-[2-(trimethoxysilyl) ethyl]-1*H*-imidazole with 11.1 g (0.075 mol) of 2,2′,2″-nitrilotriethanol gave a crystalline product which was recrystallized from ethanol. Yield 17.9 g (89%), mp 218°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.98 m (2H, $SiCH_2$), 2.83 t (6H, N**C**$\mathbf{H}_2$$CH_2O$, ^3J = 5.9), 3.77 t (6H, OCH_2, ^3J = 5.9), 4.01 m (2H, N**C**$\mathbf{H}_2$$CH_2Si$), 6.93 d.d (1H, 5-H, ^4J = 1.2, ^3J = 1.0), 6.98 d.d (1H, 4-H, ^3J = ^4J = 1.0), 7.48 d.d (1H, 2-H, ^4J = 1.2, 1.0). ^{13}C NMR spectrum, δ_C, ppm: 19.5 ($SiCH_2$), 45.0 (N**C**H_2CH_2Si), 50.7 (3C, N**C**H_2CH_2O), 57.1 (3C, OCH_2), 118.4 (C^5), 128.3 (C^4), 136.4 (C^2). ^{29}Si NMR spectrum: δ_{Si} –72.8 ppm.

Silatranes **IX**–**XIII** were synthesized in a similar way.

2-Methyl-1-(2-silatranylethyl)-1*H*-imidazole (IX). Yield 86%, mp 214°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.88 m (2H, $SiCH_2$), 2.35 s (3H, CH_3), 2.83 t (6H, N**C**$\mathbf{H}_2$$CH_2O$, ^3J = 5.9), 3.77 t (6H, OCH_2, ^3J = 5.9), 3.88 m (2H, N**C**$\mathbf{H}_2$$CH_2Si$), 6.82 d (1H, 5-H, ^3J = 1.1), 6.85 d (1H, 4-H, ^3J = 1.1). ^{13}C NMR spectrum, δ_C, ppm: 12.8 (CH_3), 19.1 ($SiCH_2$), 43.8 (N**C**H_2CH_2Si), 50.7 (3C, N**C**H_2CH_2O), 57.1 (3C, OCH_2), 118.2 (C^5), 125.9 (C^4), 143.8 (C^2). ^{29}Si NMR spectrum: δ_{Si} –72.1 ppm.

2-Ethyl-1-(2-silatranylethyl)-1*H*-imidazole (X). Yield 85%, mp 138°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.87 m (2H, $SiCH_2$), 1.30 t (3H, $CH_2C\mathbf{H}_3$, ^3J = 7.5), 2.67 q (2H, $C\mathbf{H}_2CH_3$, ^3J = 7.5), 2.82 t (6H, N**C**$\mathbf{H}_2$$CH_2O$, ^3J = 5.9), 3.76 t (6H, OCH_2, ^3J = 5.9), 3.88 m (2H, N**C**$\mathbf{H}_2$$CH_2Si$), 6.85 s (2H, 4-H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 11.9 (**C**H_3CH_2), 19.3 (**C**H_2CH_3), 19.9 ($SiCH_2$), 43.5 (N**C**H_2CH_2Si), 50.8 (3C, N**C**H_2CH_2O), 57.2 (3C, OCH_2), 118.2 (C^5), 125.9 (C^4), 148.6 (C^2). ^{29}Si NMR spectrum: δ_{Si} –71.7 ppm.

4-Methyl-1-(2-silatranylethyl)-1*H*-imidazole (XI). Yield 60%, mp 202°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.88 m (2H, $SiCH_2$), 2.16 d (3H, CH_3, ^4J = 1.0), 2.81 t (6H, N**C**$\mathbf{H}_2$$CH_2O$, ^3J = 5.9), 3.75 t (6H, CH_2O, ^3J = 5.9), 3.87 m (2H, N**C**$\mathbf{H}_2$$CH_2Si$), 6.66 d.q (1H, 5-H, ^4J = 1.2, 1.0), 7.41 d (1H, 2-H, ^4J = 1.2). ^{13}C NMR spectrum, δ_C, ppm: 9.0 (CH_3), 19.0 ($SiCH_2$),

42.6 (N**C**H_2CH_2Si), 50.8 (3C, N**C**H_2CH_2O), 57.2 (3C, OCH_2), 125.8 (C^4), 126.9 (C^5), 135.9 (C^4). ^{29}Si NMR spectrum: δ_{Si} –71.8 ppm.

5-Methyl-1-(2-silatranylethyl)-1*H*-imidazole (XII). Yield 30%, mp 202°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 m (2H, $SiCH_2$), 2.16 d (3H, CH_3, ^4J = 0.9), 2.81 t (6H, NC**H**$_2CH_2O$, ^3J = 5.9), 3.75 t (6H, CH_2O, ^3J = 5.9), 3.91 m (2H, NC**H**$_2CH_2Si$), 6.61 d.q (1H, 4-H, ^4J = 1.5, 0.9), 7.33 d (1H, 2-H, ^4J = 1.5). ^{13}C NMR spectrum, δ_C, ppm: 9.0 (CH_3), 19.0 ($SiCH_2$), 42.6 (N**C**H_2CH_2Si), 50.8 (3C, N**C**H_2CH_2O), 57.2 (3C, OCH_2), 125.8 (C^4), 126.9 (C^5), 135.9 (C^4). ^{29}Si NMR spectrum: δ_{Si} –71.8 ppm.

1-(2-Silatranylethyl)-1*H*-benzimidazole (XIII). Yield 93%, mp 210°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 m (2H, $SiCH_2$), 2.80 t (6H, NC**H**$_2CH_2O$, ^3J = 5.9), 3.75 t (6H, OCH_2, ^3J = 5.9), 4.25 m (2H, NC**H**$_2CH_2Si$), 7.20 (1H, 7-H, $^3J_{AC}$ = 8.2, $^3J_{AB}$ = 7.2, $^4J_{AD}$ = 1.1), 7.22 (1H, 6-H, $^3J_{BD}$ = 8.1, $^3J_{AB}$ = 7.2, $^4J_{BC}$ = 1.0), 7.47 (1H, 8-H, $^3J_{AC}$ = 8.2, $^4J_{BC}$ = 1.0, $^5J_{CD}$ = –0.7), 7.74 (1H, 5-H, $^3J_{BD}$ = 8.1, $^4J_{AD}$ = 1.1, $^5J_{CD}$ = –0.7), 7.94 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 17.8 ($SiCH_2$), 42.6 (N**C**H_2CH_2Si), 50.1 (3C, N**C**H_2CH_2O), 56.6 (3C, OCH_2), 109.7 (C^8), 119.0 (C^5), 120.6 (C^7), 121.3 (C^6), 133.4 (C^9), 142.0 (C^4), 143.3 (C^2). ^{29}Si NMR spectrum: δ_{Si} –73.0 ppm.

ACKNOWLEDGMENTS

The authors thank A.V. Kisin and M.G. Kuznetsova for recording the NMR spectra.

REFERENCES

1. Sheludyakov, V.D., Kuz'mina, N.E., Abramkin, A.M., Cheshkov, D.A., and Storozhenko, P.A., *Zh. Obshch. Khim*., 2011, vol. 81, no. 12, p. 2010.
2. Egorochkin, A.N., Voronkov, M.G., and Kuznetsova, O.V., *Polyarizatsionnyi effekt v organicheskoi, elemento-organicheskoi i koordinatsionnoi khimii* (Polarization Effect in Organic, Organometallic, and Coordination Chemistry), Nizhnii Novgorod: Nizhegorod. Univ., 2008.
3. Voronkov, M.G., Brodskaya, E.I., Belyaeva, V.V., and Lazareva, N.F., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2001, no. 3, p. 725.
4. Puri, K.J., Singh, R., and Chahal, V.K., *Chem. Soc. Rev*., 2011, vol. 40, p. 1791.
5. Voronkov, M.G. and D'yakov, V.M., *Silatrany* (Silatranes), Novosibirsk: Nauka, 1978.
6. Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.G., and Taylor, R., *J. Chem. Soc., Perkin Trans. 2*, 1987, no. 12, p. S1.
7. Pauling, L., *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, Ithaca: Cornel Univ., 1960, 3rd ed.
8. Emsley, J., *Chem. Soc. Rev*., 1980, vol. 9, no. 1, p. 91.
9. Steed, J.W. and Atwood, J.L., *Supramolecular Chemistry*, Chichester: Wiley, 2000. Translated under the title *Supramolekulyarnaya khimiya*, Moscow: Akademkniga, 2007, vol. 1, p. 52.