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# Synthesis and Structure of *N*-(2-Silatranylethyl)pyrazoles

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**Abstract**—Organosilicon pyrazole derivatives containing a 2-siltranylethyl fragment on the nitrogen atom were synthesized, and their structural and stereoelectronic parameters were determined by X-ray analysis and $^{1}$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. The nature of interaction between the pyrazole and silatrane fragments was studied.

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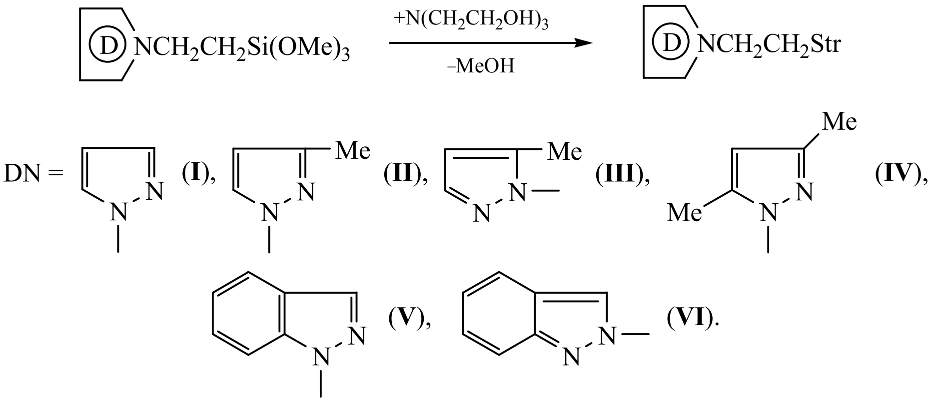
The present work continues our studies in the field of synthesis and structure of new five-coordinate silicon compounds (silatranes) containing a diazole fragment [1]. Transannular N→Si interaction in silatranes gives rise to specific chemical [2, 3] and biological properties [4]. Diazoles and their numerous derivatives in turn attract interest from the viewpoints of medicine and agrochemistry due to their diverse biological activity, including antioxidant, bactericidal, bacteriostatic, insecticidal, fungicidal, sedative, antitumor, psychopharmacological, and other kinds of activity.

The electronic and steric structures of silatranes have long been studied. A substituent X on the silicon atom was found to affect the efficiency of intramolecular transannular donor–acceptor interaction, hybriddization of valence orbitals of the silicon atom, and structures of the silicon polyhedron and silatrane skeleton as a whole. The nature of this effect is fairly complex (conjugation, inductive and polarization effects [5–7]) and is related to electronic properties of the X substituent and its orientation with respect to the silatrane fragment. On the other hand, silatrane fragment exerts a superelectron-donor inductive effect [5–7] on the electronic and geometric parameters of the substituent. In this connection, mutual effects of the diazole and silatrane fragments in silatranyl derivatives of diazoles attract strong interest.

Mutual effect of such dissimilar functionalities depends on the length of aliphatic tether $(CH_2)_n$ connecting them. Obviously, inductive effect weakens as $n$ increases; on the other hand, the molecule becomes conformationally more labile, and the possibility for polarization effect increases. We previously studied the effect of the silatrane fragment on the heteroaromatic ring structure linked to the former through a methylene bridge [8]. It was interesting to examine mutual effects of the silatrane (Str) and diazole (DN) fragments in β-carbofunctional organosilicon compounds with the general formula $DN(CH_2)_2Str$ which, unlike their α- ($n = 1$) and γ-analogs ($n = 3$), were poorly studied because of difficulties in their preparation.

This problem was solved after the discovery of the addition of diazoles DNH to vinyltrialkoxysilanes on heating an equimolar mixture of the reactants in the presence of finely dispersed lithium or its source.

In the present study, the set of *N*-(2-silatranylethyl)-diazoles as model structures was limited to pyrazole and indazole derivatives which were synthesized by classical reaction leading to silatranes, transetherification of *N*-[2-(trimethoxysilyl)ethyl]pyrazoles and -indazole with 2,2′,2″-nitrilotriethanol. The reaction required no catalyst, and silatranes **I**–**VI** were formed in high yield. Compounds **I**–**VI** were isolated as



crystalline substances which were stable on exposure to air; this is quite important for performing X-ray analysis.

The structure of the newly synthesized pyrazole-containing silatranes was proved by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. The molecular and crystalline structures of compounds **I** and **IV** were determined by X-ray analysis. The principal crystallographic and structure refinement parameters are collected in Table 1, and the bond lengths and bond angles in molecules **I** and **IV** are given in Tables 2 and 3. Both compounds were represented by two crystallographically independent molecules in the asymmetric part of a unit cell (**I** and **IA**, **IV** and **IVA**; see figure) with similar geometric parameters (Tables 2, 3).

The silicon atom in the silatrane fragment of molecules **I** and **IV** has a trigonal bipyramid configuration. The oxygen atoms are located in the equatorial plane, and the $N^1$ and $C^7$ atoms occupy the axial apices. Almost linear axial fragment [the $N^1Si^1C^7$ angle is 177.7 (**I**), 177.9 (**IA**), 179.8 (**IV**), or 178.6° (**IVA**)] is almost orthogonal to the equatorial plane: the dihedral angle between the equatorial plane and the plane defined by the $C^7$, $Si^1$, and $N^1$ atoms is 90.2, 89.7, 90.3, and 89.9° for molecules **I**, **IA**, **IV**, and **IVA**, respectively.

It should be noted that the silicon atom in symmetrically nonequivalent molecules of both compounds is displaced from the equatorial plane toward $C^7$. The displacement ($\Delta$) is equal to 0.192 (**I**), 0.183 (**IA**), 0.166 (**IV**), and 0.173 Å (**IVA**). A correlation is observed between $\Delta$ and $Si^1$–$N^1$ bond length [2.157 (**I**), 2.133 (**IA**), 2.102 (**IV**), 2.112 Å (**IVA**)]: the larger the $\Delta$ value, the longer the $Si^1$–$N^1$ distance [9]. Comparison with published data shows that the inductive effect of the pyrazole fragment in structure **I** is analogous to that found for 1-phenylsilatrane (interatomic distance 2.123 Å [10]). The inductive effect of the substituent in molecule **IV** is stronger: the Si–N distance in **IV** differs from the corresponding distance in *N*-(silatranylmethyl)imidazole (2.088 Å [11]) by only 0.02 Å.

The $Si^1$–O, O–C, C–C, and C–$N^1$ bond lengths in the silatrane fragment of molecules **I**, **IA**, **IV**, and **IVA** vary within the ranges 1.660–1.678, 1.409–1.427, 1.501–1.535, and 1.461–1.484 Å, respectively. The average $Si^1$–O bond length in **I** and **IA** (1.673 and 1.674 Å) are slightly larger than the corresponding values for molecules **IV** and **IVA** (1.663 and 1.667 Å). By contrast, the average O–C distance in **I** is shorter than in **IV** [1.417 (**I**), 1.417 (**IA**), 1.425 (**IV**), 1.424 Å (**IVA**)]. The average C–C distance in the silatrane fragment of molecules **I**, **IA**, and **IVA** is 1.519 Å and is almost equal to the C–C distance in the exocyclic N-ethyl bridge (1.522 Å). The endocyclic C–C bond in the silatrane fragment of **IV** is longer than the exocyclic C–C bond (1.523 and 1.508 Å, respectively). The $C^8$–$N^2$ bonds [1.481 (**I**), 1.461 (**IA**), 1.471 (**IV**), 1.459 Å (**IVA**)] deviate in opposite directions from the standard $C_{sp^3}$–$N_{sp^3}$ bond length (1.469 Å [12]).

The pyrazole rings in the examined molecules tend to leveling of the endocyclic bonds (Table 4) as compared to the corresponding standard bonds: $N^2$–$N^3$ (1.366 Å), $N^3$–$C^9$ (1.329 Å), $C^9$–$C^{10}$ (1.410 Å), $C^{10}$–$C^{11}$ (1.369 Å), $C^{11}$–$N^2$ (1.357 Å) [12]. Therefore, it may be presumed that introduction of a silatranylethyl group makes the pyrazole ring more aromatic.

A specific feature of the steric structure of the compounds under study is coplanar orientation of the exocyclic N-ethyl bridge and vertical axis of the silicon trigonal bipyramid: the $N^1$, $Si^1$, $C^7$, $C^8$, and $N^2$ atoms deviate from the plane by 0.061 (**I**), 0.060 (**IA**),

**Table 1.** Crystallographic and structure refinement parameters of compounds **I** and **IV**

| Parameter | **I** | **II** |
|---|---|---|
| Formula | $C_{11}H_{19}N_3O_3Si$ | $C_{13}H_{23}N_3O_3Si$ |
| Molecular weight | 269.38 | 297.43 |
| Temperature, K | 120 | 120 |
| Crystal system | Monoclinic | Rhombic |
| Space group | $P2_1$ | *Pbca* |
| *Z* | 4 | 16 |
| *a*, Å | 6.6399(6) | 16.5436(19) |
| *b*, Å | 13.8445(13) | 11.9898(14) |
| *c*, Å | 13.7492(13) | 30.300(4) |
| α, deg | 90.00 | 90.00 |
| β, deg | 94.765(2) | 90.00 |
| γ, deg | 90.00 | 90.00 |
| $V$, Å$^3$ | 1259.5(2) | 6010.2(12) |
| $d_{calc}$, g/cm$^3$ | 1.421 | 1.315 |
| μ, cm$^{-1}$ | 1.92 | 1.68 |
| *F*(000) | 576 | 2560 |
| $2\theta_{max}$, deg | 60.14 | 60.18 |
| Total number of reflections | 14902 | 87594 |
| Number of independent reflections ($R_{int}$) | 7266 (0.0242) | 8777 (0.0822) |
| Number of reflections with $I > 2\sigma(I)$ | 6232 | 5014 |
| Number of refined parameters | 325 | 375 |
| $R_1$ | 0.0415 | 0.0629 |
| $wR_2$ | 0.0847 | 0.1293 |
| *GOOF* | 1.002 | 1.064 |
| Residual electron density, $e$ Å$^{-3}$ ($d_{min}/d_{max}$) | 0.345/–0.283 | 0.544/–0.312 |

0.004 (**IV**), and 0.051 Å (**IVA**). This plane is almost orthogonal to the pyrazole ring plane: the corresponding dihedral angle is 83.7 (**I**), 80.5 (**IA**), 85.0 (**IV**), and 100.3° (**IVA**). Analogous pattern was observed for N-(2-silatranylethyl)imidazoles [1].

Thus the X-ray diffraction data suggest that the pyrazole and silatrane fragments affect the structure of each other. Electron-donor silatranyl group enhances aromaticity of the heteroring. The latter in turn affects transannular interaction between the silicon and nitrogen atoms and hence the steric structure of the siltrane skeleton. The effect of 3,5-dimethylpyrazole fragment is comparable with that of alkyl-substituted imidazole ring in *N*-(2-silatranylethyl)imidazoles [1]. Unsubstituted pyrazole ring as substituent induces a stronger distortion of the silatrane fragment than that caused by unsubstituted imidazole ring [Δ 0.188, $Si^1–N^1$ 2.145 Å for *N*-(2-silatranylethyl)pyrazole and Δ 0.171, $Si^1–N^1$ 2.110 Å for *N*-(2-silatranylethyl)imidazole]. Two crystallographically independent molecules of compounds **I** and **IV** are characterized by different geometric parameters of the silatrane fragment, which may be due to effect of crystal packing. As shown previously [13], this effect is responsible for shortening of the Si–N distance in going from isolated molecule to crystal or solution.

The effect of crystal packing was studied by analysis of shortened contacts between atoms that are not linked by a covalent bond in the crystalline structure of compounds **I** and **IV**. Shortened interatomic contacts (i.e., shorter than the sum of van der Waals radii of the corresponding atoms) indicate the existence of intermolecular interactions that are considerably stronger than common van der Waals interactions. In the present work we used Pauling's scale of van der Waals radii ($r_{vdW}$ = 1.2, 1.4, 1.5, and 1.7 Å for H, O, N, and C, respectively [14]). It should be noted that the positions of hydrogen atoms were calculated on the basis of apparent hybridization of carbon atoms and geometry considerations and that the C–H bond lengths were fixed at 0.96–0.99 Å in the refinement procedure, which complicated analysis of shortened contacts. With a view to reduce possible errors in the determination of coordinates of hydrogen atoms, the C–H bond lengths were normalized by a value of 1.08 Å, in keeping with the neutron diffraction data [12].

Analysis of interatomic distances in the crystalline structures of compounds **I** and **IV** showed the absence of shortened intramolecular contacts. The main intermolecular interactions occurring in crystals of **I** and **IV** are H···H, C–H···N, and C–H···O (Table 4).

According to [15], the main structure-forming interactions in organic molecules are weak C–H···O hydrogen bonds whose energy is 1–2 kcal/mol. Such interactions in structures **I** and **IV** were revealed by analysis of geometric parameters of C–H···O fragments. Weak C–H···O hydrogen bonds were identified

**Table 2.** Bond lengths (*d*, Å) and bond angles (ω, deg) in crystallographically independent molecules of 1-(2-silatranylethyl)-1*H*-pyrazole (**I**)

| **I** | | **IA** | | **I** | | **IA** | |
|---|---|---|---|---|---|---|---|
| Bond | *d* | Bond | *d* | Bond | *d* | Bond | *d* |
| $\mathrm{Si^{1}{-}O^{1}}$ | 1.6631 (15) | $\mathrm{Si^{1A}{-}O^{3A}}$ | 1.6688 (15) | $\mathrm{N^{2}{-}N^{3}}$ | 1.353 (2) | $\mathrm{N^{2A}{-}C^{11A}}$ | 1.347 (3) |
| $\mathrm{Si^{1}{-}O^{3}}$ | 1.6738 (15) | $\mathrm{Si^{1A}{-}O^{1A}}$ | 1.6743 (15) | $\mathrm{N^{2}{-}C^{11}}$ | 1.348 (3) | $\mathrm{N^{2A}{-}N^{3A}}$ | 1.354 (2) |
| $\mathrm{Si^{1}{-}O^{2}}$ | 1.6764 (15) | $\mathrm{Si^{1A}{-}O^{2A}}$ | 1.6774 (15) | $\mathrm{N^{2}{-}C^{8}}$ | 1.473 (2) | $\mathrm{N^{2A}{-}C^{8A}}$ | 1.464 (3) |
| $\mathrm{Si^{1}{-}C^{7}}$ | 1.8815 (19) | $\mathrm{Si^{1A}{-}C^{7A}}$ | 1.887 (2) | $\mathrm{N^{3}{-}C^{9}}$ | 1.335 (3) | $\mathrm{N^{3A}{-}C^{9A}}$ | 1.343 (3) |
| $\mathrm{Si^{1}{-}N^{1}}$ | 2.1537 (18) | $\mathrm{Si^{1A}{-}N^{1A}}$ | 2.1313 (18) | $\mathrm{C^{1}{-}C^{4}}$ | 1.527 (3) | $\mathrm{C^{1A}{-}C^{4A}}$ | 1.518 (3) |
| $\mathrm{O^{1}{-}C^{1}}$ | 1.415 (2) | $\mathrm{O^{1A}{-}C^{1A}}$ | 1.417 (3) | $\mathrm{C^{2}{-}C^{5}}$ | 1.518 (3) | $\mathrm{C^{2A}{-}C^{5A}}$ | 1.517 (3) |
| $\mathrm{O^{2}{-}C^{2}}$ | 1.422 (2) | $\mathrm{O^{2A}{-}C^{2A}}$ | 1.426 (3) | $\mathrm{C^{3}{-}C^{6}}$ | 1.519 (3) | $\mathrm{C^{3A}{-}C^{6A}}$ | 1.517 (3) |
| $\mathrm{O^{3}{-}C^{3}}$ | 1.414 (2) | $\mathrm{O^{3A}{-}C^{3A}}$ | 1.424 (2) | $\mathrm{C^{7}{-}C^{8}}$ | 1.519 (3) | $\mathrm{C^{7A}{-}C^{8A}}$ | 1.524 (3) |
| $\mathrm{N^{1}{-}C^{5}}$ | 1.477 (2) | $\mathrm{N^{1A}{-}C^{6A}}$ | 1.473 (3) | $\mathrm{C^{9}{-}C^{10}}$ | 1.396 (3) | $\mathrm{C^{9A}{-}C^{10A}}$ | 1.387 (3) |
| $\mathrm{N^{1}{-}C^{6}}$ | 1.475 (3) | $\mathrm{N^{1A}{-}C^{4A}}$ | 1.474 (3) | $\mathrm{C^{10}{-}C^{11}}$ | 1.365 (3) | $\mathrm{C^{10A}{-}C^{11A}}$ | 1.378 (3) |
| $\mathrm{N^{1}{-}C^{4}}$ | 1.480 (2) | $\mathrm{N^{1A}{-}C^{5A}}$ | 1.479 (2) | | | | |
| Angle | ω | Angle | ω | Angle | ω | Angle | ω |
| $\mathrm{O^{1}Si^{1}O^{3}}$ | 120.35 (8) | $\mathrm{O^{3A}Si^{1A}O^{1A}}$ | 118.27 (8) | $\mathrm{C^{6}N^{1}Si^{1}}$ | 105.12 (12) | $\mathrm{C^{4A}N^{1A}Si^{1A}}$ | 105.14 (12) |
| $\mathrm{O^{1}Si^{1}O^{2}}$ | 117.47 (8) | $\mathrm{O^{3A}Si^{1A}O^{2A}}$ | 120.26 (8) | $\mathrm{C^{4}N^{1}Si^{1}}$ | 104.66 (12) | $\mathrm{C^{5A}N^{1A}Si^{1A}}$ | 105.15 (12) |
| $\mathrm{O^{3}Si^{1}O^{2}}$ | 118.28 (8) | $\mathrm{O^{1A}Si^{1A}O^{2A}}$ | 117.92 (8) | $\mathrm{N^{3}N^{2}C^{11}}$ | 111.84 (17) | $\mathrm{C^{11A}N^{2A}N^{3A}}$ | 112.03 (18) |
| $\mathrm{O^{1}Si^{1}C^{7}}$ | 98.64 (9) | $\mathrm{O^{3A}Si^{1A}C^{7A}}$ | 96.47 (8) | $\mathrm{N^{3}N^{2}C^{8}}$ | 120.36 (16) | $\mathrm{C^{11A}N^{2A}C^{8A}}$ | 126.43 (18) |
| $\mathrm{O^{3}Si^{1}C^{7}}$ | 95.65 (8) | $\mathrm{O^{1A}Si^{1A}C^{7A}}$ | 97.81 (8) | $\mathrm{C^{11}N^{2}C^{8}}$ | 126.77 (17) | $\mathrm{N^{3A}N^{2A}C^{8A}}$ | 120.47 (17) |
| $\mathrm{O^{2}Si^{1}C^{7}}$ | 95.47 (8) | $\mathrm{O^{2A}Si^{1A}C^{7A}}$ | 94.61 (9) | $\mathrm{C^{9}N^{3}N^{2}}$ | 104.33 (18) | $\mathrm{C^{9A}N^{3A}N^{2A}}$ | 104.18 (18) |
| $\mathrm{O^{1}Si^{1}N^{1}}$ | 83.90 (7) | $\mathrm{O^{3A}Si^{1A}N^{1A}}$ | 83.28 (7) | $\mathrm{O^{1}C^{1}C^{4}}$ | 108.79 (16) | $\mathrm{O^{1A}C^{1A}C^{4A}}$ | 109.30 (17) |
| $\mathrm{O^{3}Si^{1}N^{1}}$ | 82.90 (7) | $\mathrm{O^{1A}Si^{1A}N^{1A}}$ | 84.18 (7) | $\mathrm{O^{2}C^{2}C^{5}}$ | 108.70 (16) | $\mathrm{O^{2A}C^{2A}C^{5A}}$ | 108.20 (16) |
| $\mathrm{O^{2}Si^{1}N^{1}}$ | 83.42 (7) | $\mathrm{O^{2A}Si^{1A}N^{1A}}$ | 83.69 (7) | $\mathrm{O^{3}C^{3}C^{6}}$ | 108.80 (17) | $\mathrm{O^{3A}C^{3A}C^{6A}}$ | 108.46 (17) |
| $\mathrm{C^{7}Si^{1}N^{1}}$ | 177.46 (8) | $\mathrm{C^{7A}Si^{1A}N^{1A}}$ | 177.84 (9) | $\mathrm{N^{1}C^{4}C^{1}}$ | 105.78 (16) | $\mathrm{N^{1A}C^{4A}C^{1A}}$ | 105.33 (16) |
| $\mathrm{C^{1}O^{1}Si^{1}}$ | 122.04 (13) | $\mathrm{C^{1A}O^{1A}Si^{1A}}$ | 120.80 (13) | $\mathrm{N^{1}C^{5}C^{2}}$ | 106.33 (16) | $\mathrm{N^{1A}C^{5A}C^{2A}}$ | 106.52 (16) |
| $\mathrm{C^{2}O^{2}Si^{1}}$ | 122.48 (12) | $\mathrm{C^{2A}O^{2A}Si^{1A}}$ | 122.49 (13) | $\mathrm{N^{1}C^{6}C^{3}}$ | 106.14 (16) | $\mathrm{N^{1A}C^{6A}C^{3A}}$ | 105.02 (16) |
| $\mathrm{C^{3}O^{3}Si^{1}}$ | 123.35 (13) | $\mathrm{C^{3A}O^{3A}Si^{1A}}$ | 121.71 (13) | $\mathrm{C^{8}C^{7}Si^{1}}$ | 116.93 (13) | $\mathrm{C^{8A}C^{7A}Si^{1A}}$ | 116.99 (14) |
| $\mathrm{C^{5}N^{1}C^{6}}$ | 113.94 (16) | $\mathrm{C^{6A}N^{1A}C^{4A}}$ | 113.68 (16) | $\mathrm{N^{2}C^{8}C^{7}}$ | 111.71 (16) | $\mathrm{N^{2A}C^{8A}C^{7A}}$ | 112.20 (17) |
| $\mathrm{C^{5}N^{1}C^{4}}$ | 113.86 (16) | $\mathrm{C^{6A}N^{1A}C^{5A}}$ | 112.62 (16) | $\mathrm{N^{3}C^{9}C^{10}}$ | 111.71 (19) | $\mathrm{N^{3A}C^{9A}C^{10A}}$ | 111.9 (2) |
| $\mathrm{C^{6}N^{1}C^{4}}$ | 113.17 (16) | $\mathrm{C^{4A}N^{1A}C^{5A}}$ | 113.17 (16) | $\mathrm{C^{11}C^{10}C^{9}}$ | 104.66 (18) | $\mathrm{C^{11A}C^{10A}C^{9A}}$ | 104.67 (19) |
| $\mathrm{C^{5}N^{1}Si^{1}}$ | 104.82 (12) | $\mathrm{C^{6A}N^{1A}Si^{1A}}$ | 106.12 (12) | $\mathrm{N^{2}C^{11}C^{10}}$ | 107.43 (19) | $\mathrm{N^{2A}C^{11A}C^{10A}}$ | 107.16 (18) |

by a C···O distance approaching the sum of the corresponding van der Waals radii and a CHO angle close to straight (150–180°) [16]. Analogous criteria are also applicable to C–H···N interactions. We revealed a number of C–H···O and C–H···N interactions which contributed most to the cohesion energy of crystalline compounds **I** and **IV**. Other intermolecular interactions were revealed only on the basis of the shortest C···H and H···H distances, taking into account that they are characterized by lower energy and are non-directional [17].

The numbers of C–H···O and C–H···N interactions with participation of the silatrane fragment in

**Table 3.** Bond lengths (*d*, Å) and bond angles (ω, deg) in crystallographically independent molecules of 3,5-dimethyl-1-(2-silatranylethyl)-1*H*-pyrazole (**IV**)

| **IV** | | **IVA** | | **IV** | | **IVA** | |
|---|---|---|---|---|---|---|---|
| Bond | *d* | Bond | *d* | Bond | *d* | Bond | *d* |
| $Si^1$–$O^3$ | 1.6637 (17) | $Si^{1A}$–$O^{1A}$ | 1.6687 (18) | $N^2$–$C^8$ | 1.465 (3) | $N^{1A}$–$C^{5A}$ | 1.476 (3) |
| $Si^1$–$O^1$ | 1.6646 (17) | $Si^{1A}$–$O^{3A}$ | 1.6676 (17) | $N^3$–$C^9$ | 1.331 (3) | $N^{2A}$–$C^{11A}$ | 1.354 (3) |
| $Si^{1-}O^2$ | 1.6691 (17) | $Si^{1A}$–$O^{2A}$ | 1.6679 (18) | $C^1$–$C^{4'}$ | 1.524 (6) | $N^{2A}$–$N^{3A}$ | 1.360 (3) |
| $Si^1$–$C^7$ | 1.883 (2) | $Si^{1A}$–$C^{7A}$ | 1.884 (2) | $C^1$–$C^4$ | 1.527 (4) | $N^{2A}$–$C^{8A}$ | 1.459 (3) |
| $Si^1$–$N^1$ | 2.102 (2) | $Si^{1A}$–$N^{1A}$ | 2.113 (2) | $C^2$–$C^5$ | 1.509 (4) | $N^{3A}$–$C^{9A}$ | 1.334 (3) |
| $O^1$–$C^1$ | 1.422 (3) | $O^{1A}$–$C^{1A}$ | 1.428 (3) | $C^2$–$C^{5'}$ | 1.517 (6) | $C^{1A}$–$C^{4A}$ | 1.494 (4) |
| $O^2$–$C^2$ | 1.417 (3) | $O^{2A}$–$C^{2A}$ | 1.422 (3) | $C^3$–$C^6$ | 1.530 (4) | $C^{2A}$–$C^{5A}$ | 1.518 (4) |
| $O^3$–$C^3$ | 1.425 (3) | $O^{3A}$–$C^{3A}$ | 1.417 (3) | $C^3$–$C^{6'}$ | 1.537 (6) | $C^{3A}$–$C^{6A}$ | 1.524 (3) |
| $N^1$–$C^4$ | 1.456 (3) | $N^{1A}$–$C^{6A}$ | 1.465 (3) | $C^7$–$C^8$ | 1.512 (3) | $C^{7A}$–$C^{8A}$ | 1.523 (3) |
| $N^1$–$C^{4'}$ | 1.462 (6) | $N^{1A}$–$C^{4A}$ | 1.471 (3) | $C^9$–$C^{10}$ | 1.394 (3) | $C^{9A}$–$C^{10A}$ | 1.396 (3) |
| $N^1$–$C^6$ | 1.471 (3) | $N^1$–$C^5$ | 1.478 (3) | $C^9$–$C^{12}$ | 1.501 (3) | $C^{9A}$–$C^{12A}$ | 1.504 (3) |
| $N^1$–$C^{6'}$ | 1.476 (6) | $N^2$–$C^{11}$ | 1.354 (3) | $C^{10}$–$C^{11}$ | 1.387 (3) | $C^{10A}$–$C^{11A}$ | 1.377 (3) |
| $N^1$–$C^{5'}$ | 1.473 (6) | $N^2$–$N^3$ | 1.364 (3) | $C^{11}$–$C^{13}$ | 1.482 (3) | $C^{11A}$–$C^{13A}$ | 1.495 (3) |
| Angle | ω | Angle | ω | Angle | ω | Angle | ω |
| $O^3Si^1O^1$ | 119.37 (10) | $O^{1A}Si^{1A}C^{7A}$ | 97.35 (10) | $C^6N^1C^5$ | 112.3 (2) | $N^1C^{4'}C^1$ | 105.4 (4) |
| $O^3Si^1O^2$ | 118.70 (10) | $O^{3A}Si^{1A}C^{7A}$ | 94.89 (9) | $C^{6'}N^1C^5$ | 147.6 (6) | $N^1C^{5'}C^2$ | 106.2 (4) |
| $O^1Si^1O^2$ | 118.90 (9) | $O^{2A}Si^{1A}C^{7A}$ | 95.76 (10) | $C^4N^1Si^1$ | 105.50 (15) | $N^1C^{6'}C^3$ | 105.3 (4) |
| $O^3Si^1C^7$ | 95.54 (9) | $O^{1A}Si^{1A}N^{1A}$ | 84.02 (8) | $C^{4'}N^1Si^1$ | 106.1 (4) | $C^8C^7Si^1$ | 115.12 (16) |
| $O^1Si^1C^7$ | 96.17 (9) | $O^{3A}Si^{1A}N^{1A}$ | 83.94 (8) | $C^6N^1Si^1$ | 104.49 (16) | $N^2C^8C^7$ | 113.93 (19) |
| $O^2Si^1C^7$ | 95.70 (9) | $O^{2A}Si^{1A}N^{1A}$ | 84.04 (8) | $C^{6'}N^1Si^1$ | 103.5 (5) | $N^3C^9C^{10}$ | 111.8 (2) |
| $O^3Si^1N^1$ | 84.55 (8) | $C^{7A}Si^{1A}N^{1A}$ | 178.52 (10) | $C^{5'}N^1Si^1$ | 105.2 (5) | $N^3C^9C^{12}$ | 120.4 (2) |
| $O^1Si^1N^1$ | 84.11 (8) | $C^{1A}O^{1A}Si^{1A}$ | 121.87 (15) | $C^5N^1Si^1$ | 105.30 (16) | $C^{10}C^9C^{12}$ | 127.8 (2) |
| $O^2Si^1N^1$ | 83.93 (8) | $C^{2A}O^{2A}Si^{1A}$ | 122.60 (15) | $C^{11}N^2N^3$ | 112.48 (19) | $C^{11}C^{10}C^9$ | 105.4 (2) |
| $C^7Si^1N^1$ | 179.61 (10) | $C^{3A}O^{3A}Si^{1A}$ | 122.45 (15) | $C^{11}N^2C^8$ | 127.5 (2) | $N^2C^{11}C^{10}$ | 105.9 (2) |
| $C^1O^1Si^1$ | 121.91 (14) | $C^{6A}N^{1A}C^{4A}$ | 113.5 (2) | $N^3N^2C^8$ | 119.7 (2) | $N^2C^{11}C^{13}$ | 123.0 (2) |
| $C^2O^2Si^1$ | 122.84 (16) | $C^{6A}N^{1A}C^{5A}$ | 114.0 (2) | $C^9N^3N^2$ | 104.40 (19) | $C^{10}C^{11}C^{13}$ | 131.1 (2) |
| $C^3O^3Si^1$ | 122.21 (15) | $C^{4A}N^{1A}C^{5A}$ | 113.0 (2) | $O^1C^1C^{4'}$ | 111.1 (4) | $C^{5A}N^{1A}Si^{1A}$ | 105.23 (15) |
| $C^4N^1C^6$ | 115.1 (2) | $C^{6A}N^{1A}Si^{1A}$ | 105.30 (15) | $O^1C^1C^4$ | 108.2 (2) | $C^{11A}N^{2A}N^{3A}$ | 111.90 (19) |
| $C^{4'}N^1C^6$ | 145.9 (7) | $C^{4A}N^{1A}Si^{1A}$ | 104.61 (15) | $O^2C^2C^5$ | 109.2 (2) | $C^{11A}N^{2A}C^{8A}$ | 127.6 (2) |
| $C^4N^1C^{6'}$ | 72.5 (5) | $C^4N^1C^{5'}$ | 144.1 (7) | $O^2C^2C^{5'}$ | 109.4 (5) | $N^{3A}N^{2A}C^{8A}$ | 120.05 (19) |
| $C^{4'}N^1C^{6'}$ | 112.1 (8) | $C^{4'}N^1C^{5'}$ | 111.5 (8) | $O^3C^3C^6$ | 107.9 (2) | $C^{9A}N^{3A}N^{2A}$ | 104.75 (19) |
| $C^6N^1C^{6'}$ | 45.0 (5) | $C^6N^1C^{5'}$ | 74.0 (5) | $O^3C^3C^{6'}$ | 108.2 (5) | $O^{1A}C^{1A}C^{4A}$ | 109.1 (2) |
| $O^{1A}Si^{1A}O^{3A}$ | 119.23 (10) | $C^{6'}N^1C^{5'}$ | 117.2 (8) | $N^1C^4C^1$ | 105.5 (2) | $O^{2A}C^{2A}C^{5A}$ | 109.3 (2) |
| $O^{1A}Si^{1A}O^{2A}$ | 118.28 (10) | $C^4N^1C^5$ | 113.0 (2) | $N^1C^5C^2$ | 106.3 (2) | $O^{3A}C^{3A}C^{6A}$ | 108.87 (19) |
| $O^{3A}Si^{1A}O^{2A}$ | 119.25 (10) | $C^{4'}N^1C^5$ | 73.5 (5) | $N^1C^6C^3$ | 105.9 (2) | $N^{1A}C^{4A}C^{1A}$ | 106.5 (2) |

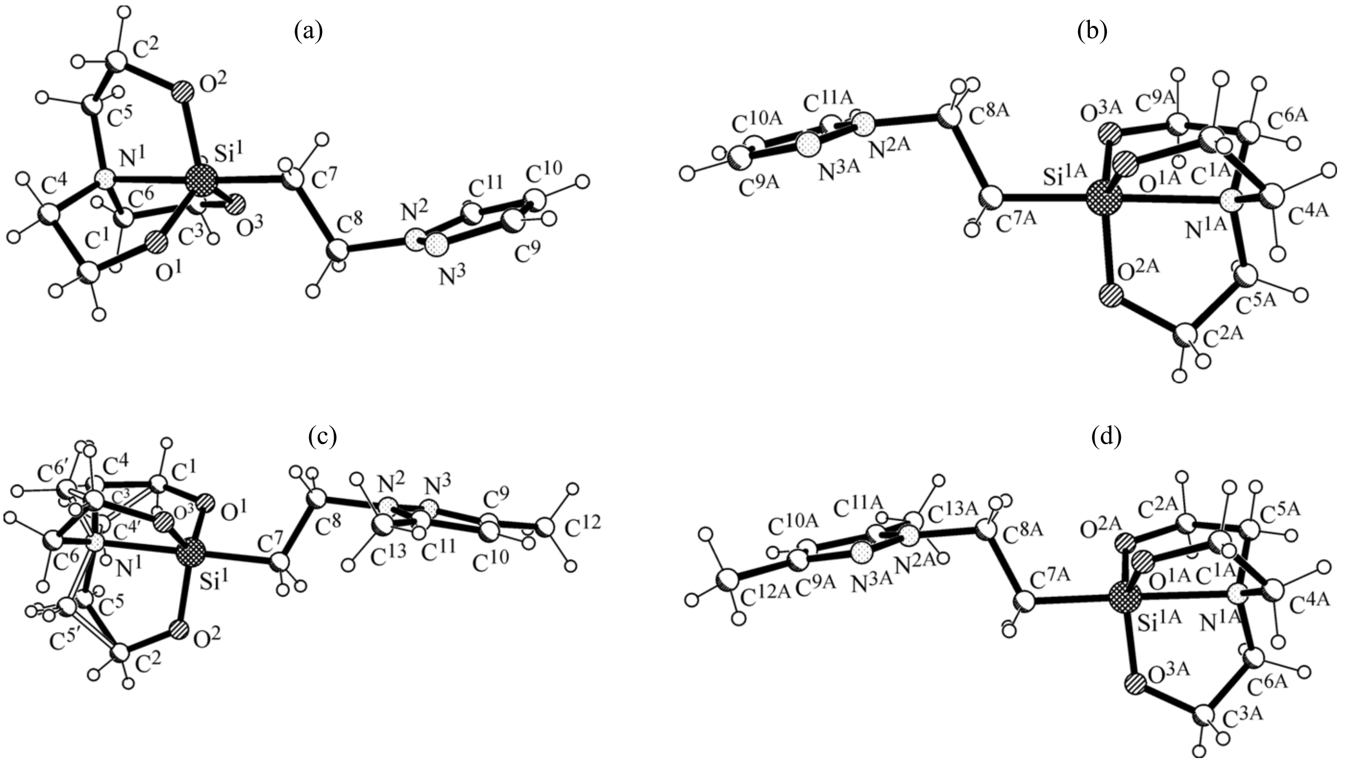
**Table 3.** (Contd.)

| **IV** | | **IVA** | | **IV** | | **IVA** | |
|---|---|---|---|---|---|---|---|
| Angle | ω | Angle | ω | Angle | ω | Angle | ω |
| $N^{1A}C^{5A}C^{2A}$ | 106.1 (2) | $N^{2A}C^{8A}C^{7A}$ | 113.45 (19) | $C^{10A}C^{9A}C^{12A}$ | 129.7 (2) | $N^{2A}C^{11A}C^{13A}$ | 122.2 (2) |
| $N^{1A}C^{6A}C^{3A}$ | 105.8 (2) | $N^{3A}C^{9A}C^{10A}$ | 111.4 (2) | $C^{11A}C^{10A}C^{9A}$ | 105.4 (2) | $C^{10A}C^{11A}C^{13A}$ | 131.3 (2) |
| $C^{8A}C^{7A}Si^{1A}$ | 115.31 (16) | $N^{3A}C^{9A}C^{12A}$ | 118.9 (2) | $N^{2A}C^{11A}C^{10A}$ | 106.6 (2) | | |

molecules **IV** and **IVA** are different. Molecule **IVA** is involved in three weak hydrogen bonds C–H···O, and the $Si^1$–$N^1$ distance therein is slightly longer than in **IV** which is involved in only one C–H···N bond. The different structures of molecules **I** and **IA** may be related to different natures of contacts in which they participate. The numbers of weak hydrogen bonds involving the atrane fragments in **I** and **IA** are similar (two C–H···O bonds and one C–H···N bond). In addition, molecule **I** is involved only in H···H contacts with atrane fragments of neighboring molecules. The atrane fragment in **IA** in turn forms H···C contacts with π-electron system of the pyrazole ring.

The observed differences in the structure of two independent molecules are consistent with the nature of the intramolecular N–Si bond. Quantum-chemical calculations performed for a series of 1-methyl- and 1-fluorosilatranes [18, 19] showed that the potential energy curve for the N–Si bond is very flat, and even small variation of electronegativity or dielectric permittivity of the medium leads to appreciable change of the interatomic distance N···Si.

To conclude, we synthesized six new *N*-(2-silatranylethyl)pyrazoles, and the molecular and crystalline structures of two compounds **I** and **IV** were determined by X-ray analysis. Analysis of the experimental data showed that the effect of the pyrazole ring on the silatrane fragment is comparable to the effect of weak electron-withdrawing substituents. The different bond lengths in two crystallographically independent



Structures of crystallographically independent molecules of 1-(2-silatranylethyl)-1*H*-pyrazole (**I**) and 3,5-dimethyl-1-(2-silatranylethyl)-1*H*-pyrazole (**IV**) according to the X-ray diffraction data.

**Table 4.** Shortened intermolecular contacts in the crystalline structures of compound **I** and **IV**

| X–H · · · Y | Symmetry transformation | X · · · Y, Å | H · · · Y, Å (XHY, deg) |
|---|---|---|---|
| **I** | | | |
| $C^{4}{-}H^{4B}\cdots O^{3}$ | $-1 + x, y, z$ | 3.527(2) | 2.50 (158) |
| $C^{9}{-}H^{9A}\cdots O^{3}$ | $1 - x, 1/2 + y, -z$ | 3.626(3) | 2.55 (173) |
| $C^{11}{-}H^{11A}\cdots O^{2}$ | $1 + x, y, z$ | 3.423(2) | 2.35 (171) |
| $H^{4B}\cdots H^{8B}$ | $-1 + x, y, z$ | | 2.29 |
| $H^{1A}\cdots H^{1AB}$ | – | | 2.22 |
| $H^{7A}\cdots H^{5AB}$ | $-x, -1/2 + y, -z$ | | 2.22 |
| $H^{8B}\cdots H^{4B}$ | $1 + x, y, z$ | | 2.29 |
| $H^{4A}\cdots H^{8AA}$ | $-x, -1/2 + y, 1 - z$ | | 2.16 |
| **IA** | | | |
| $C^{3A}{-}H^{3AA}\cdots N^{3}$ | – | 3.450(3) | 2.53 (143) |
| $C^{4A}{-}H^{4AB}\cdots O^{3A}$ | $-1 + x, y, z$ | 3.544(2) | 2.51 (159) |
| $C^{11A}{-}H^{11B}\cdots O^{2A}$ | $1 + x, y, z$ | 3.455(2) | 2.40 (165) |
| $H^{7AA}\cdots H^{3B}$ | $x, 1 + y, z$ | | 2.30 |
| $H^{6AA}C^{10}$ | $-1 + x, y, z$ | | 2.88 |
| $H^{1B}\cdots C^{10A}$ | $1 - x, -1/2 + y, 1 - z$ | | 2.85 |
| $H^{1B}\cdots C^{11A}$ | $1 - x, -1/2 + y, 1 - z$ | | 2.84 |
| $H^{3A}\cdots C^{10A}$ | $x, -1 + y, z$ | | 2.79 |
| $H^{1AA}\cdots C^{9A}$ | $-x, -1/2 + y, 1 - z$ | | 2.79 |
| **IV** | | | |
| $C^{4}{-}H^{4B}\cdots N^{3A}$ | $1/2 + x, 1/2 - y, 2 - z$ | 3.322(4) | 2.60 (123) |
| $H^{7B}\cdots H^{6AB}$ | – | | 2.07 |
| $*H^{2C}\cdots H^{13D}$ | $1/2 + x, -1/2 - y, 2 - z$ | | 2.05 |
| $*H^{4'B}\cdots H^{8AA}$ | $1/2 + x, 1/2 - y, 2 - z$ | | 2.18 |
| $*H^{1D}\cdots H^{13A}$ | $1 - x, 1/2 + y, 3/2 - z$ | | 2.14 |
| $*H^{5'B}\cdots H^{7AB}$ | $1 - x, -y, 2 - z$ | | 2.25 |
| $H^{7B}\cdots H^{4AA}$ | $1/2 - x, -1/2 + y, z$ | | 2.14 |
| $H^{13A}\cdots *H^{1D}$ | $1 - x, -1/2 + y, 3/2 - z$ | | 2.14 |
| $*H^{1C}\cdots H^{2AA}$ | $1/2 - x, 1/2 + y, z$ | | 2.30 |
| **IVA** | | | |
| $C^{1A}{-}H^{1AA}\cdots O^{3A}$ | $1/2 - x, 1/2 + y, z$ | 3.589(3) | 2.60 (152) |
| $C^{3A}{-}H^{3AA}\cdots O^{2}$ | – | 3.517(3) | 2.46 (167) |

**Table 4.** (Contd.)

| X–H · · · Y | Symmetry transformation | X · · · Y, Å | H · · · Y, Å (XHY, deg) |
|---|---|---|---|
| | **IVA** | | |
| $C^{13A}–H^{13D}\cdots O^{2}$ | $-1/2 + x, -1/2 - y, 2 - z$ | 3.547(3) | 2.48 (169) |
| $H^{5AA}\cdots C^{10}$ | $1/2 - x, 1/2 + y, z$ | | 2.85 |
| $H^{5AA}\cdots C^{11}$ | $1/2 - x, 1/2 + y, z$ | | 2.80 |
| $H^{3C*}\cdots C^{9}$ | $1/2 + x, y, 3/2 - z$ | | 2.88 |
| $H^{6B*}\cdots C^{9A}$ | $1 - x, -y, 2 - z$ | | 2.53 |
| $H^{6B*}\cdots C^{10A}$ | $1 - x, -y, 2 - z$ | | 2.74 |
| $H^{6'A*}\cdots C^{9A}$ | $1 - x, -y, 2 - z$ | | 2.71 |
| $H^{6'A*}\cdots C^{10A}$ | $1 - x, -y, 2 - z$ | | 2.84 |

molecules of **I** and **IV** were interpreted in terms of different systems of contacts formed by the silatrane fragment in crystal. Specific role of H···H and C–H···π interactions was revealed. The silatrane fragment in turn affects aromaticity of the pyrazole fragment.

## EXPERIMENTAL

The $^{1}H$, $^{13}C$, and $^{29}Si$ NMR spectra were recorded at room temperature on a Bruker AM-360 spectrometer (operating frequency 360.13, 90.55, and 71.58 MHz, respectively) from solutions in $CDCl_3$.

The X-ray diffraction data were acquired on a Bruker SMART 1000 CCD diffractometer ($MoK_\alpha$ irradiation, graphite monochromator, ω-scanning). The structures of compounds **I** and **IV** were solved by the direct method and were refined by the least-squares procedure in full-matrix anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were localized by difference synthesis and were included in the refinement procedure with fixed thermal and positional parameters. Refinement of structure **IV** revealed statistical disordering of the $C^4$–$C^6$ silatrane fragment by two positions. The positions of $C^4$–$C^6$ and $C^{4'}$–$C^{6'}$ were refined with restrictions imposed on C–C and C–N bond lengths and anisotropic thermal parameters.

**1-(2-Silatranylethyl)-1*H*-pyrazole (I).** A three-necked flask equipped with a stirrer, thermometer, and reflux condenser was charged with 16.2 g (0.075 mol) of 1-[2-(trimethoxysilyl)ethyl]-1*H*-pyrazole and 11.1 g (0.075 mol) of 2,2′,2″-nitrilotriethanol. A crystalline product was formed and was recrystallized from ethanol. Yield 17.3 g (86%), mp 177°C. $^{1}H$ NMR spectrum, δ, ppm: 1.04 m (2H, $SiCH_2$), 2.82 t (6H, $NC\mathbf{H}_2CH_2O$, $^{3}J = 5.9$ Hz), 3.76 t (6H, $OCH_2$, $^{3}J = 5.9$ Hz), 4.24 m (2H, $NC\mathbf{H}_2CH_2Si$), 6.16 t (1H, 4-H, $^{3}J = 2.0$ Hz), 7.42 d (2H, 3-H, 5-H, $^{3}J = 2.0$ Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 18.4 ($SiCH_2$), 49.9 ($N\mathbf{C}H_2CH_2Si$), 50.6 (3C, $N\mathbf{C}H_2CH_2O$), 57.1 (3C, $OCH_2$), 104.1 ($C^4$), 127.0 ($C^3$), 137.6 ($C^5$). $^{29}Si$ NMR spectrum: $\delta_{Si}$ –71.9 ppm.

Single crystals suitable for X-ray analysis were obtained by repeated recrystallization from ethanol.

Silatranes **II**–**VI** were synthesized in a similar way.

**3-Methyl-1-(2-silatranylethyl)-1*H*-pyrazole (II).** Yield 46%, mp 199°C (from ethanol). $^{1}H$ NMR spectrum, δ, ppm: 1.02 m (2H, $SiCH_2$), 2.25 d.d (3H, $CH_3$, $^{4}J = {}^{5}J = 0.5$ Hz), 2.82 t (6H, $NC\mathbf{H}_2CH_2O$, $^{3}J = 5.9$ Hz), 3.76 t (6H, $CH_2O$, $^{3}J = 5.9$ Hz), 4.16 m (2H, $NCH_2$), 5.93 d.q (1H, 4-H, $^{3}J = 2.2$, $^{4}J = 0.5$ Hz), 7.31 d.q (1H, 5-H, $^{3}J = 2.2$, $^{5}J = 0.5$ Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 13.4 ($CH_3$), 18.4 ($SiCH_2$), 49.6 ($N\mathbf{C}H_2CH_2Si$), 50.9 (3C, $N\mathbf{C}H_2CH_2O$), 57.3 (3C, $OCH_2$), 103.7 ($C^4$), 127.9 ($C^5$), 146.8 ($C^3$). $^{29}Si$ NMR spectrum: $\delta_{Si}$ –70.7 ppm.

**5-Methyl-1-(2-silatranylethyl)-1*H*-pyrazole (III).** Yield 46%, mp 199°C (from ethanol). $^{1}H$ NMR spectrum, δ, ppm: 0.94 m (2H, $SiCH_2$), 2.27 d.d (3H, $CH_3$, $^{4}J = 0.7$, $^{5}J = 0.4$ Hz), 2.81 t (6H, $NC\mathbf{H}_2CH_2O$, $^{3}J = 5.9$ Hz), 3.76 t (6H, $CH_2O$, $^{3}J = 5.9$ Hz), 4.15 m (2H, $NCH_2$), 5.92 d.q (1H, 4-H, $^{3}J = 1.9$, $^{4}J = 0.7$ Hz), 7.31 d.q (1H, 3-H, $^{3}J = 1.9$, $^{5}J = 0.4$ Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 10.9 ($CH_3$), 18.6 ($SiCH_2$), 47.0

(N**C**$H_2CH_2$Si), 50.9 (3C, N**C**$H_2CH_2$O), 57.3 (3C, $OCH_2$), 104.3 ($C^4$), 136.9 ($C^3$), 137.3 ($C^5$). $^{29}$Si NMR spectrum: $\delta_{Si}$ –71.1 ppm.

**3,5-Dimethyl-1-(2-silatranylethyl)-1*H*-pyrazole (IV).** Yield 93%, mp 185°C (from ethanol). $^1$H NMR spectrum, δ, ppm: 0.92 m (2H, $SiCH_2$), 2.19 s (3H, 3-$CH_3$), 2.21 s (3H, 5-$CH_3$), 2.80 t (6H, NC**$H_2$**$CH_2$O, $^3J$ = 5.8 Hz), 3.75 t (6H, $OCH_2$, $^3J$ = 5.8 Hz), 4.07 m (2H, NC**$H_2$**$CH_2$Si), 5.70 s (1H, 4-H). $^{13}$C NMR spectrum, $\delta_C$, ppm: 10.8 (3-$CH_3$), 13.3 (5-$CH_3$), 18.8 ($SiCH_2$), 46.7 (N**C**$H_2CH_2$Si), 50.9 (3C, N**C**$H_2CH_2$O), 57.3 (3C, $OCH_2$), 104.0 ($C^4$), 137.5 ($C^3$), 145.8 ($C^5$). $^{29}$Si NMR spectrum: $\delta_{Si}$ –70.6 ppm.

**1-(2-Silatranylethyl)-1*H*-indazole (V).** Yield 66%, mp 178°C (from ethanol). $^1$H NMR spectrum, δ, ppm: 1.08 m (2H, $SiCH_2$), 2.78 t (6H, NC**$H_2$**$CH_2$O, $^3J$ = 5.8 Hz), 3.72 t (6H, $OCH_2$, $^3J$ = 5.8 Hz), 4.52 m (2H, NC**$H_2$**$CH_2$Si), 7.06 d.d.d (1H, 6-H, $^3J$ = 7.7, 6.8, $^4J$ = 0.9 Hz), 7.29 d.d.d (1H, 7-H, $^3J$ = 8.5, 6.8, $^4J$ = 1.1 Hz), 7.51 d.d.d.d (1H, 8-H, $^3J$ = 8.5, $^5J$ = 1.0, 1.0, $^4J$ = 0.9 Hz), 7.67 d.d.d (1H, 5-H, $^3J$ = 7.7, $^4J$ = 1.1, $^5J$ = 1.0 Hz), 7.91 d (1H, 3-H, $^5J$ = 1.0 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 18.2 ($SiCH_2$), 46.7 (N**C**$H_2CH_2$Si), 49.9 (3C, N**C**$H_2CH_2$O), 56.6 (3C, $OCH_2$), 109.2 ($C^8$), 119.2 ($C^6$), 120.1 ($C^5$), 123.3 ($C^4$), 124.6 ($C^7$), 130.8 ($C^3$), 138.1 ($C^9$). $^{29}$Si NMR spectrum: $\delta_{Si}$ –72.5 ppm.

**2-(2-Silatranylethyl)-2*H*-indazole (VI).** Yield 22%, mp 178°C (from ethanol). $^1$H NMR spectrum, δ, ppm: 1.19 m (2H, $SiCH_2$), 2.82 t (6H, NC**$H_2$**$CH_2$O, $^3J$ = 5.9 Hz), 3.77 t (6H, $OCH_2$, $^3J$ = 5.9 Hz), 4.54 m (2H, NC**$H_2$**$CH_2$Si), 7.00 d.d.d (1H, 6-H, $^3J$ = 8.4, 6.7, $^4J$ = 1.0 Hz), 7.21 d.d.d (1H, 7-H, $^3J$ = 8.7, 6.7, $^4J$ = 1.2 Hz), 7.68 d.d.d.d (1H, 8-H, $^3J$ = 8.7, $^5J$ = 1.1, 0.9, $^4J$ = 1.0), 7.61 d.d.d (1H, 5-H, $^3J$ = 8.4, $^4J$ = 1.2, $^5J$ = 1.1 Hz), 7.97 d (1H, 3-H, $^5J$ = 0.9 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 19.1 ($SiCH_2$), 51.6 (N**C**$H_2CH_2$Si), 49.9 (3C, N**C**$H_2CH_2$O), 56.5 (3C, $OCH_2$), 116.5 ($C^8$), 119.6 ($C^5$), 120.1 ($C^6$), 121.1 ($C^4$), 124.3 ($C^7$), 130.8 ($C^3$), 147.6 ($C^9$). $^{29}$Si NMR spectrum: $\delta_{Si}$ –73.7 ppm.

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