The synthesis and stereoelectronic structure of 1- and 2-(trimethoxysilylmethyl)- and 1- and 2-(silatranylmethyl)benzotriazole

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Dedicated to Professor B. Trofimov on his Jubilee

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Abstract
Only 2-benzotriazolyl sodium is formed in the reaction of benzotriazole (BtH) with sodium methoxide. Its reaction with trimethyl- or trimethoxy-(chloromethyl)-silane affords a mixture of 1- and 2-(trimethylsilylmethyl)- **1** and **2**, and 1- and 2-(trimethoxysilylmethyl)benzotriazoles, **3** and **4**, which were separated into the individual isomers. trans-Etherification of the latter with tris-(2-hydroxyethyl)amine leads to 1- and 2-(silatranylmethyl)benzotriazoles **5** and **6**. The electronic structures of the compounds prepared were investigated using IR, UV, multinuclear NMR spectroscopy, mass spectrometry, and X-ray diffraction. The organosilicon benzotriazole derivatives **1**, **3** and **5** show a benzenoid structure, whereas **2**, **4** and **6** have ortho-quinonoid structures.

Keywords: 1- and 2-(Trimethoxysilylmethyl)benzotriazole, 1- and 2-silatranylmethylbenzotriazole, electronic and molecular structure

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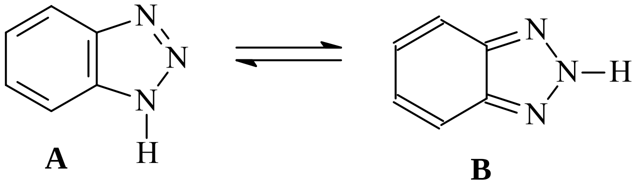
Introduction

The tautomerism of 1H- (benzenoid form **A**) and 2H- (quinonoid form **B**) benzotriazole (BtH) and their tautomeric ratio, as well as the electronic structure of 1- and 2-substituted benzotriazoles have attracted the attention of many chemists.[1–15]



Unfortunately, the available experimental and theoretical results are often contradictory. Thus, for example, it has been reported that according to UV spectra the 2H-tautomer in the gas phase is approximately 4 kcal/mol more stable than the 1H-tautomer.[1] However, this does not agree with the previously published results of experimental and theoretical studies.[2–4] IR Spectra show that BtH in the gas phase at 140°C is mainly represented by the 1H-tautomer.[5–8] The microwave spectrum at 90°C has established only 1H-BtH.[7] All the peculiarities of the fluorescence excitation spectrum of BtH at 70°C are explained by the presence of the 2H-tautomer.[1,6] The complete optimization of the geometry at the MP2-6-31G** level leads to a $\Delta E_{1H\rightarrow 2H}$ (-2.5 kcal mol^{-1}) closer to the experimental results (≈ -4 kcal mol^{-1}).[1] The 1H-tautomer was found to be predominant in the solid state and solution.[9–12]

According to the UV spectra of BtH, and 1-Me- and 2-Me-BtH at 90°C, there is a mixture of both BtH tautomers in an approximately 80/20 ratio.[1] The probable reason why ≈20% of the 2H-tautomer has not been detected is easy to understand, considering the corresponding dipole moments (4.2 and 0.4 D, respectively). Since the microwave signals are proportional to the square of the dipole moments, the signals of the 1H-tautomer should be almost 500 times more intense than those of the 2H-tautomer.

The proportion of the 2H-tautomers is about 45, 35 and 25% at 30, 50 and 80^{0}C, respectively, and shows[2] that, contrary to all available calculations, the 2H-tautomer is enthalpically more stable than the 1H-tautomer by about 3.8 kcal mol^{-1}.

The intrinsically most stable tautomer of benzotriazole is the 2H-, and the origin of the difference in stability with regard to the 1H- tautomer results in a balance between the lone-pair repulsion (6.5 kcal mol^{-1}) [16–18] which favors the 2H tautomer and the aromaticity which favors the 1H tautomer.[1]

The goal of our research is to synthesize the individual organosilicon BtH derivatives containing at the nitrogen atoms organosilicon substituents such as $-CH_2SiMe_3$ (**1** and **2**), $-CH_2Si(OMe)_3$ (**3** and **4**), and $-CH_2Si(OCH_2CH_2)_3N$ (**5** and **6**)[19] in position 1 or 2, and to study their electronic structure using IR, UV, multinuclear NMR spectroscopy, mass spectrometry and X-ray diffraction. The interest in the BtH derivatives containing at the nitrogen atoms such bulky substituents is explained by the stability of their 1- and 2-isomers to interconversion, as well as the possibility of establishing the influence of electron-donor inductive effect of $-CH_2SiMe_3$, $-CH_2Si(OMe)_3$ and $-CH_2Si(OCH_2CH_2)_3N$ groups ($\sigma_I = -0.04$, $\sigma^* = -0.25$ for **1** and **2;** $\sigma_I = -0.10$, $\sigma^* = -0.62$ for **3** and **4** and $\sigma_I = -0.36$, $\sigma^* = -2.24$ for **5** and **6**) on the electron structure of molecules **1**–**6**.[20–22] The clearly defined crystalline structure of N-silatranylmethyl derivative **6** is favorable for structural investigation using X-ray diffraction.

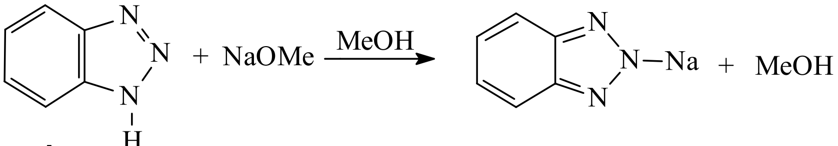
Results and Discussion

Synthesis

The 1- and 2-benzotriazole organosilicon derivatives, Bt-CH_2SiX_3 (Bt- = 1- or 2-benzotriazolyl) with

X = Me (**1** and **2**), OMe (**3** and **4**), 1/3 $(OCH_2CH_2)_3N$ (**5** and **6**) have been synthesized. Compounds **2–6** were not known previously. A liquid mixture of 1- and 2-(trimethylsilylmethyl)-benzotriazoles **1** and **2** (isomer ratio 4:1) was prepared earlier by Katritzky and Lam, from which a crystalline 1-isomer was isolated.[23] Physical data for these compounds are given in Table 1.

We have established that the reaction of 1-BtH with sodium methoxide in methanol in the temperature range from -5 to 60°C gives only (2-benzotriazolyl)sodium **7** in all cases.

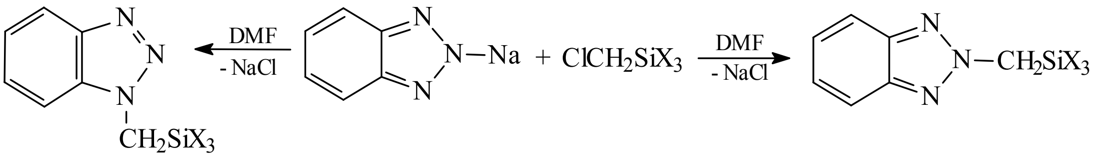


(1)

A **7**

The formation of (2-benzotriazolyl)sodium (but not the 1-isomer) has been proved by UV spectroscopy (see below, Table 2).[19]

The reaction of (2-benzotriazolyl)sodium **7** with trimethyl- or trimethoxy-(chloromethyl)silane in DMF in the presence of 18-crown-6 leads to mixtures of the 1- and 2-isomers **1** and **2**, **3** and **4**, in a ratio of ~ 4:1.



(2)

1, 3 **7** **2, 4**

X = Me (**1, 2**); OMe (**3, 4**)

The BtH organosilicon derivatives **2–4** are yellowish liquids, whereas **1** is a colorless crystalline substance. The Bt-trimethoxysilylmethyl derivatives **3** and **4** are hydrolytically unstable. The physico-chemical characteristics and elemental analysis data of compounds **1**–**4** are presented in Table 1.

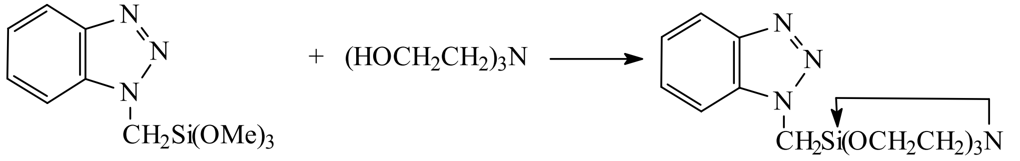
The trans-etherification of 1- and 2-(trimethoxysilylmethyl)benzotriazoles, **3** and **4**, by tris-(2-hydroxyethyl)amine in the absence of catalysts afforded the corresponding 1- and 2-(silatranylmethyl)-benzotriazoles **5** and **6** in nearly quantitative yield.

Compounds **5** and **6** are colorless crystals, soluble in DMF and DMSO. Their physico-chemical characteristics and elemental analysis data are also presented in Table 1. Upon keeping, even in a sealed ampoule, the crystals of **5** become turbid and this did not permit structural determination by X-ray diffraction. **See Table 1 on page 234.**

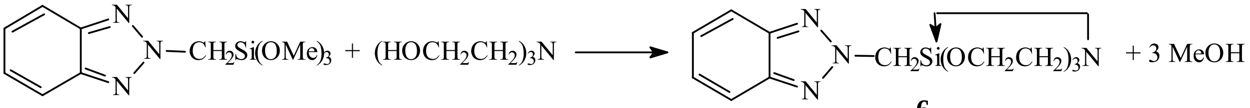
Spectroscopic studies

UV and IR spectroscopy

The UV spectrum of (2-benzotriazolyl)sodium **7** in polar solvents (MeOH, DMF) shows only one intense maximum at 283 nm (Table 2) similar to the spectra of 2-Me-Bt[1,2] which has an *ortho*-quinonoid structure. Its IR spectrum also indicates the sodium atom to be in the benzotriazole ring position 2 (Table 3).



3 **5** (3)



4 **6** (4)

See Table 2 on page 235.

The UV spectra of the organosilicon derivatives **1**, **3**, **5**, and **2**, **4**, **6**, respectively, which show benzenoid and *ortho*-quinonoid structures, differ in both the number and intensity of electronic transitions. Thus, in the spectra of solutions of the 1-substituted BtH **1**, **3** and **5** there are two absorption maxima in the 270–290 and 250–270 nm regions, which are analogous to those of 1H- and 1Me-Bt.[1,2,5] The UV spectra of the 2-isomers **2**, **4** and **6** display only one maximum in the 270–285 nm region, as in the spectra of 2Me- and 2Na-Bt (Figure 1, Table 2).

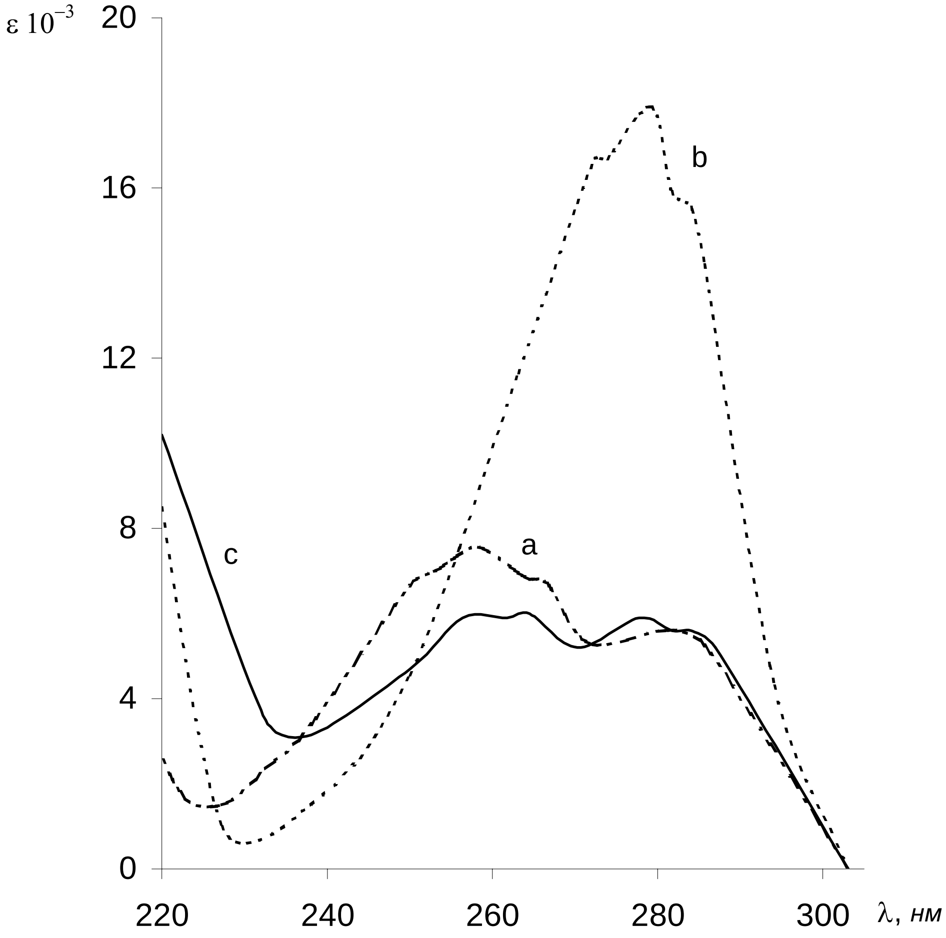


Figure 1. UV absorption spectra of the compounds **3** (a) and **4** (b) in MeCN; reaction mixture from **3** and **4** in DMF, dissolved in MeCN (c).

From what is said above, it follows that UV spectroscopy provides an adequate instrument for establishing of the N-substituent position in the benzotriazole ring (1- or 2-). A slight hypsochromic shift of bands in the UV spectra of the (trimethoxylsilylmethyl)benzotriazoles **3** and **4** compared to the spectra of the corresponding trimethylsilylmethyl- (**1** and **2**) and silatranylmethyl- (**5** and **6**) BtH derivatives is likely to be brought about by the effect of n,σ*-hyperconjugation in the N-CH$_2$Si fragment,[24,25] absent in molecules **1**, **2**, **5** and **6**. The benzenoid **1**, **3** and **5**, and *ortho*-quinonoid structures **2**, **4**, **6** and **7**, are clearly expressed in their IR spectra as well (Table 3).[19] **See Table 3 on page 236.**

In the spectra of the 1-substituted benzotriazoles **1, 3** and **5** there are frequencies observed at 665–670, 1565–1590, 1614–1616 cm^{-1}, whereas in the spectra of the 2-substituted benzotriazoles **2, 4, 6** and **7** they occur at 620–630, 1567–1569 cm^{-1}. The IR absorption spectra of the CH$_2$SiX$_3$ group in compounds **1–6** do not depend much on the position of substituent (1- or 2-). With X =

Me **1** and **2**, the IR spectra show bands at 743 and 746, 843 and 846, 1248 and 1251 cm^{-1}, respectively, with X = OMe **3** and **4** the bands are observed at 838 and 844, 1090 and 1090, 2845 and 2845 cm^{-1}, respectively, and with X = 1/3 $(OCH_2CH_2)_3N$, in **5** and **6**, one can see the bands at 583 and 578, 641 and 651, 784 and 789, 812 and 819, 915 and 913, 938 and 938, 1085 and 1087, 1126 and 1123 cm^{-1}, respectively.

Nuclear magnetic resonance

The ^{1}H-, ^{13}C NMR chemical shifts of the BtH fragment of 1- and 2-isomers of compounds **3–6** and the corresponding N-methylbenzotriazoles[26] (Table 4) are practically identical. The same is also true for the proton chemical shifts in the spectra of compounds **1**, **3**–**6**, with an identical position of the N-substituent in the exocyclic fragment -N-CH_2Si. The ^{13}C- chemical shifts of the 1-substituted BtH, **3** and **5**, in the -N-CH_2Si fragment are displaced upfield by ~ 10 ppm compared to those of the 2-substituted BtH. The ^{29}Si- resonance in the spectra of the isomeric silatrane derivatives **5** and **6** is displaced by 25-ppm upfield compared to that of the corresponding trimethoxysilylmethyl derivatives **3** and **4**. This is due to the fact that in compounds **5** and **6** the silicon atom is pentacoordinate, whereas in **3** and **4** it is in the tetracoordinate state. At the same time, the difference of the organosilicon substituent's position (1- or 2-) in compounds **3–6** does not influence much the ^{29}Si chemical shift. In this case, the ^{13}C- signals of the N-CH_2Si fragment in the spectra of the tetracoordinate silicon derivatives **3** and **4** are displaced upfield by more than 7 ppm compared to the ^{13}C- signals in the spectra of the corresponding silatranyl BtH derivatives, **5** and **6**.

The ^{15}N- NMR chemical shifts in the spectra of 1- and 2-(trimethoxysilylmethyl)- **3** and **4**, and the 1- and 2-(silatranylmethyl)benzotriazoles, **5** and **6**, are strongly dependent on the organosilicon substituent's position in the triazole ring (1- or 2-) (Table 4). Differences in the chemical shifts of the 1- and 2-isomers are over 100 ppm.

In the spectra of the 1- and 2-(trimethoxysilylmethyl)benzotriazoles, **3** and **4,** and the 1- and 2-methylbenzotriazoles,[27] the ^{15}N- chemical shifts differ insignificantly (1–5 ppm). Compared to 1-(trimethoxysilylmethyl)benzotriazole **3,** in the spectrum of 1-(silatranylmethyl)benzotriazole **5** the ^{15}N chemical shift of the N-1 atom is displaced downfield by 12 ppm, whereas the atom N-3 shows a 5-ppm displacement upfield. The chemical shifts of the N-2 atom in the spectra of **3** and **5** are nearly identical, and displaced slightly upfield (Table 4). The ^{15}N- resonance signal of the nitrogen atom in the silatrane skeleton of 1- and 2-(silatranylmethyl)benzotriazoles, **5** and **6**, is practically the same.

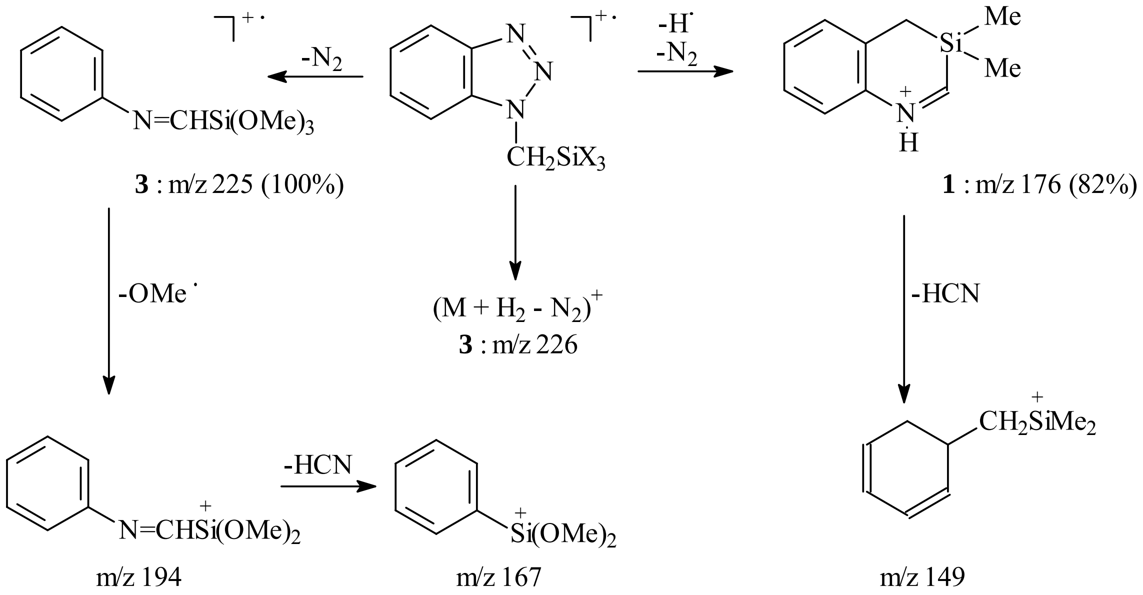
Thus, the ^{15}N NMR spectra of BtH organosilicon derivatives **3–6** provide evidence that the nature of the CH_2SiX_3 substituent does not much influence the electron density of all the nitrogen atoms, but is sufficiently dependent on the nitrogen position (1- or 2-).

See Table 4 on page 237.

Mass spectrometry

Electron-impact induced disintegration of 1- and 2-(trimethylsilylmethyl)- **1** and **2**, and 1- and 2-(trimethoxysilylmethyl)benzotriazoles, **3** and **4**, depends on the position of the CH_2SiX_3 substituted in the benzotriazole ring. None of the spectra of the 1-isomers, **1** and **3**, contains molecular ions; the heaviest are generated by the elimination of molecular N_2. The initial elimination of N_2 is a process typical of 1-BtH and its 1-methyl-, 1-vinyl-, and 1-methoxy derivatives.[28]

The disintegration of compound **1** involves elimination of the hydrogen atom from the CH_2 group in fragment NCH_2Si atoms, and formation of an ion m/z 176 (82%) (Scheme 1).



Scheme 1

The significant intensity of this ion, and subsequent disintegration by elimination of the HCN molecule to form an ion with m/z 149 (82%), suggests its possible bicyclic structure.

The 1-(trimethoxysilylmethyl)benzotriazole **3** generates odd-electron ions $(M\text{-}N_2)^{+\bullet}$ with m/z 225 (100%), and ions $(M\text{+}H\text{-}N_2)^+$ with m/z 226 (47%). Further disintegration of the ions formed is caused by an elimination of an $^\bullet OCH_3$ radical (ion m/z 194 (2%)) and HCN molecule (ion m/z 167 (16%)).

The mass spectra of 1-(trimethylsilylmethyl)- and 1- (trimethoxysilylmethyl)-benzotriazoles, **1** and **3**, demonstrate high intensity peaks for $[SiX_3]^+$ ions with m/z 73 (100%) and 121 (50%), respectively.

The fragmentation of 2-(trimethylsilylmethyl)- and 2-(trimethoxysilylmethyl)-benzotriazoles, **2** and **4**, is distinguished by the presence of an intense peak from the molecular ion, with m/z 205 (91%) and m/z 253 (95%), ion $[M\text{-}H]^+$ with m/z 204 (31 %), and $(M\text{+}H)^+$ m/z 254 (45%), respectively, and by the absence of peaks of $(M\text{-}N_2)^{+\bullet}$ ions. Peaks of ions $[SiX_3]^+$ with m/z 73 (100%) and m/z 121 (100%), respectively, in the mass spectra of **2** and **4** are also observed.

Despite the above-mentioned similarity of the mass spectra of 1- and 2-(trimethylsilylmethyl)- and 1- and 2-(trimethoxysilylmethyl)-benzotriazoles, **3** and **4**, they are sufficiently different. In the spectra of compounds **3** and **4** there is no peak for a $[M\text{-}X]^+$ ion with m/z 190 (6 and 28 %, respectively), characteristic of compounds **1** and **2**, but there are ion peaks arising as a result of benzotriazole cycle fragmentation, with m/z 105 (6 and 0 %), m/z 91 (70 and 77 %), m/z 77 (15 and 4 %, respectively). The high intensity of the ion with m/z 91 seems to be due to overlapping of the isobaric $[Si(OMe)_3\text{-}OCH_2]^+$ ion with m/z 91.

Thus, the fragmentation of 1- and 2-(trimethylsilylmethyl)- and 1- and 2-(trimethoxysilylmethyl)- benzotriazoles, **1–4**, analogous to that of N-arylbenzotriazoles,[29] allows an unambiguous verification of the N-substituent position.

The mass spectra of 1-and 2-(silantranylmethyl)benzotriazoles, **5** and **6**, are rather meager. They contain a maximum peak of the silatrane skeleton ion with m/z 174 (100%), and low-intensity peaks of ions brought about exclusively by its disintegration (ions m/z 144 (7%), 130 (1%)). Minor disintegration of these ions is conditioned by C-Si bond breakage in the molecular ion with the positive charge localization on the silatrane skeleton $Si(OCH_2CH_2)_3N^+$. The intensity of molecular ion peak of silatrane derivatives **5** and **6** is about 2%.

Crystal and molecular structure

The molecular structure of 2-(1-silatranylmethyl)benzotriazole **6** was established using X-ray diffraction (Fig. 2).[30] In the heterocyclic fragment **6** the length of the exocyclic N_2–C_7 bond (1.460 Å) is close to the standard length of a single bond (1.47 Å). Nearly the same length for the N–C_7 bond is observed in the molecules of (1-silatranylmethyl)-1,2,4-triazole (1.464 Å), [31] -pyrrole (1.470 Å), [32] -indole (1.470 and 1.490 Å, for α- and β-, respectively)[33] and -carbazole (1.467 Å) .[34]

The lengths of the endocyclic bonds C_9–N_3 (1.360 Å) and C_8–N_1 (1.364 Å) are similar, whereas those of the N_1–N_2 (1.317Å) and N_2–N_3 bonds (1.337 Å) are 0.02 Å different.

The length of the C_8–C_9 bond binding the benzene and triazole cycles is 1.402 Å. The lengths of C_{10}–C_{11} and C_{12}–C_{13} bonds in the benzene ring of molecule **6** are much shorter (1.361 and 1.365 Å) than those of the C_8–C_{13} and C_9–C_{10} bonds (1.416 and 1.399 Å).

See Table 5 on page 238.

All these interatomic distances strongly confirm that the molecule of 2-(silatranyl-methyl)-benzotriazole **6** is of *ortho*-quinonoid structure (more exactly, of *ortho*-quinone-diimine-type) presented in equation (4).

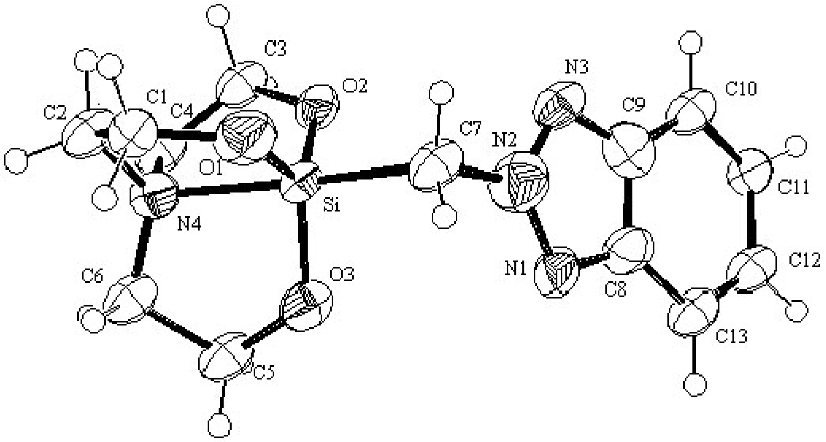


Figure 2. 2-(1-Silatranylmethyl)benzotriazole **6**.

The SiC_7N_2 angle of 117.8° in the molecule **6** is also analogous to that in the molecule of (1-silatranylmethyl)-1,2,4-triazole (117.9°), -pyrrole (116.9°), -indole (118.5 and 117.6°, for α- and β-, respectively) and -carbazole (117.5°). The bond lengths and valence angles in the silatranylmethyl fragment (Table 5) are close to those in (1-silatranylmethyl)-1,2,4-triazole,[31] -pyrrole,[32] -indole,[33] and -carbazole.[34] The coordination polyhedron of the silicon atom in the molecule **6** shows a trigonal-bipyramidal configuration, typical of silatranes, with the N_4 nitrogen and C_7 carbon atoms in the axial positions. The equatorial apexes of this polyhedron are occupied with O_1, O_2, O_3 oxygen atoms (Fig. 2).

Starting from the known correlations between the $N_4\rightarrow Si$ bond length and the inductive constant of substitute at the silicon atom[35] the inductive constants of 2-benzotriazolyl and 2-benzotriazolylmethyl groups were calculated as $\sigma_I = 0.56$, $\sigma^* = 3.09$ and $\sigma_I = 0.29$, $\sigma^* = 1.62$, respectively. The Si-CH_2 bond length (1.908 Å) is 0.066 Å longer than in the model molecule of (methyltrimethoxy)silane (1.842 Å),[36] which is conditioned by coordination of the silicon atom involved in the hypervalent $N\rightarrow Si\text{-}CH_2$ system. The $N_4\cdots Si$ interatomic distance is 2.089 Å. It is noteworthy that the N···Si interatomic distance in molecule **6** is almost coincident with the corresponding value in the molecule of (1-silatranylmethyl)-1,2,4-triazole (2.095 Å), [31] -pyrrole (2.089 Å), [32] -indole (2.11 Å) [33] and –carbazole (2.097 Å). [34] This testifies to the fact that the electron-accepting inductive effect is practically equal for all the above heterocyclic substituents. The lengths of equatorial Si–O_1, Si–O_2, Si–O_3 bonds (1.665, 1.653, 1.655 Å, respectively) are almost the same as those in molecules of (1-silatranylmethyl)-1,2,4-triazole (1.660, 1.660, 1.662 Å, respectively), -pyrrole (1.664, 1.664, 1.668 Å, respectively), -indole (1.67, 1.64, 1.66 Å for α, and 1.66, 1.65, 1.67 Å for β, respectively) and -carbazole (1.667, 1.665, 1.661 Å, respectively). All these values are considerably greater that the Si–O bond length in the $MeSi(OMe)_3$,[36] that is typical when the silicon atom transfers from the tetracoordinate to the pentacoordinate state.[37] The displacement of the silicon atom from the bipyramidal equatorial plane towards the C_7 carbon atom is 0.14 Å. This value is characteristic of silatranes whose silicon polyhedron is close to the ideal trigonal bipyramid.[37] The $N_4\rightarrow SiC_7$ angle (176.2°) is close to an ideal value of 180°.

The bond lengths and valence angles in five-membered SiOCCN cycles of the silatranyl group in the molecule **6** are close (within the limits of error) to analogous parameters of molecules of (1-silatranylmethyl)-1,2,4-triazole, -pyrrole, -indole and -carbazole. Their conformation is a poorly defined envelope with the C_α atoms displaced from its plane.

Experimental Section

General Procedures. UV absorption spectra of solutions of compounds **1**–**7** were registered on a SPECORD UV–Vis spectrophotometer. IR absorption spectra were recorded on a SPECORD 75 IR spectrometer (thin films or KBr pellets). ^{1}H-, ^{13}C-, ^{15}N-, and ^{29}Si NMR spectra were run on a Bruker DPX-400 spectrometer (frequency 400.13 MHz, 100.61 MHz, 40.56 MHz, 79.49 MHz). Those of compounds **1**–**7** were recorded as solutions in $CDCl_3$ (TMS internal standard). ^{29}Si NMR spectra were obtained by using the INEPT pulse sequence. ^{15}N- NMR chemical shifts were measured from inverse two-dimensional ^{1}H–^{15}N spectra using the HMBCGP technique. The precision of measurements of the ^{1}H- and ^{13}C- chemical shifts was 0.01 and 0.02 ppm, respectively, and 0.1 ppm for ^{15}N- and ^{29}Si- nuclei. Mass Spectra were recorded on an LKB-2091 mass spectrometer, ionizing voltage 60 eV, using direct introduction of the sample into the ion source (T_{source} 250^{o}C). The intensities of 3608 independent reflections were measured on a Syntex P21 automatic diffractometer (MoKa-radiation, graphite monochromator, w-scanning). Cell parameters of compound **6**: a = 11.351(3), b = 11.529(3), c = 11.596(3) Å, b = 103.14(2)°, Vcell = 1478(1) Å3, d(calc.) = 1.377(1) g/cm^3, Z = 4, sp. gr. P21/n.

2-Benzotriazolyl sodium (7). A solution of freshly prepared MeONa (0.1 g of sodium in 10 ml of dry methanol) was added dropwise to a solution of 0.5 g of 1H-Bt in 5 ml of dry methanol. The reaction mixture was stirred for about 20 min. Methanol was distilled off, using a rotary evaporator. The product **1** thus obtained was used in further reactions.

1- and 2-(Trimethylsilylmethyl)benzotriazoles, (1) and (2). Keeping of the reaction mixture at room temperature leads to the precipitation of colorless crystals **1**, which are filtered off and recrystallized from hexane (yield 8.33 g, 70%), m.p. 53–55^{o}C. On distilling the filtrate in vacuum, 2.34 g (19%) of compound 2, b.p. 112^{o}C (5 mm Hg) was isolated.

1- and 2-(Trimethoxysilylmethyl)benzotriazoles, (3) and (4). To a solution of 4.52 (32 mmol) of 2-benzotriazolyl sodium, **7**, and 0.063 g of 18-crown-6 in 50 ml of freshly distilled DMF, 5.46 g (32 mmol) of trimethoxy(chloromethyl)silane was added. The reaction mixture was stirred at 25–30^{o}C for 2 h, then precipitated NaCl filtered off. Upon distillation in vacuum, 1.46 g (18 %) of compound **4,** b.p. 118–120^{o}C (3 mm Hg) and 5.03 g (60%) of compound **3,** b.p. 152–153^{o}C (3 mm Hg) were isolated.

1-(Silatranylmethyl)benzotriazole (5). A mixture of 4.31 g (17 mmol) **3** and 2.54 g (17 mmol) of tris-(2-hydroxyethyl)amine was stirred at 25^{o}C for 10 min. The white precipitate formed was recrystallized from chloroform/hexane (1:1), giving 5.01 g (96%) of silatrane **5**.

2-(Silatranylmethyl)benzotriazole **(6)** was prepared in an analogous manner.

Acknowledgments

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