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Hypercoordinated Carbon in 2,8,9-Sila- and Thia-Substituted Carbatranes

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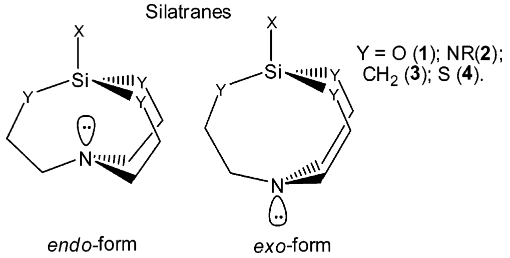
The structures of carbatranes $XC(SiH_2CH_2CH_2)_3N$ (**8**) and $XC(SCH_2CH_2)_3N$ (**9**), where X = H, F, and their *in* and *out* protonated forms were studied at the MP2 level of theory using the 6-31G*, 6-311G**, and 6-311++G** basis sets. Compounds **8** and **9** are the first representatives of the derivatives of 5-aza-1-carbabicyclo[3.3.3]undecanes, whose endo-isomer contains a nitrogen lone electron pair directed inside the cage. The geometrical, AIM, and NBO peculiarities of sila- (**8**) and thiacarbatranes (**9**) are indicative of the existence of a weak coordination $XC \leftarrow N$ interaction in these compounds, which is enhanced with the increasing of electronegativity of the axial substituent X. The MP2 and MP4/SDQ(T) (single-point calculations) methods demonstrate that the *in* protonated forms of compounds **8** are significantly (>6 kcal/mol) more favorable than their *out* forms. The quantum-topological AIM approach suggests that the main reason for this is the formation of a medium-strength (4−15 kcal/mol) hydrogen $C^1 \cdots H^+N$ bond unknown previously in the *in* silacarbanyl cations. That bond provides a high pentacoordination degree (>60%) of the bridged carbon atom C^1 in the compounds.

Introduction

Regardless of the nature of the substituent X, the molecules of 2,8,9-substituted 5-aza-1-silabicyclo[3.3.3]undecanes, $XSi(YCH_2CH_2)_3N$ (at Y = O (**1**), NR (**2**), CH_2 (**3**), S (**4**)), possess geometries with an *endo*-orientation of the nitrogen lone electron pair (LEP). This orientation is in principle favorable for its donor−acceptor interaction with the orbitals of the $XSiY_3$ fragment.[1−8] The possibility of this interaction is excluded for the probable *exo*-isomers of these molecules. At the same time, according to ab initio calculations, the *exo*-isomers do not correspond to minima on the corresponding potential energy surfaces (PES).[9−11]

According to the Verkade definition,[6] atranes $XSi(YCH_2CH_2)_3N$ with Y = O, NR, CH_2, and S are the oxa-, aza-, carba-, and thiasilatranes, respectively. Various oxasilatrane derivatives **1** are often referred to as silatranes. Throughout this paper we use the designation “silatranes” for $XSi(YCH_2CH_2)_3N$ with any Y. An increase in the coordination number of the Si atom in silatranes to five is observed with milder electronegativity demands on the axial substituent X (for example, X may be H, Alk) as compared with other hypervalent silicon compounds.[12−15] This can be attributed to the following. In compounds **1**−**4** the connection of three equatorial Y atoms with the N-donor center ensures a linear structure of the axial XSiN fragment, and the three five-membered SiYCCN heterocycles formed with Si⋯N interaction are almost unstrained.[16,17]

Chart 1



A steric promotion to the trigonal-bipyramidal (TBP) structure of the coordination center $XSiY_3N$, being characteristic of the

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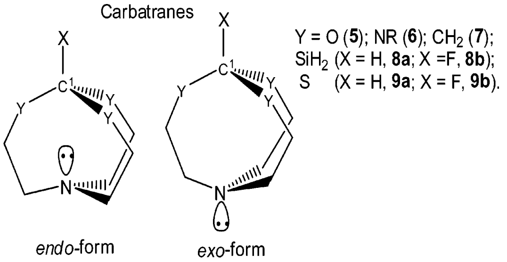
Chart 2



5-aza-1-silabicyclo[3.3.3]undecane derivatives, is a promising reason to obtain their carbon analogues, carbatranes $XC(YCH_2CH_2)_3N$.[18] However, numerous efforts to synthesize the oxa- (Y = O (**5**)) and azacarbatranes (Y = NR (**6**)) have failed.[2,6] More recently, it has become clear from ab initio and DFT calculations that carbatrane molecules **5**, **6**, and **7** (Y = CH_2), regardless of the X nature, exist exclusively in the *exo*-form; this is their essential distinction from silatranes **1**−**3**.[19−21] Minima corresponding to *endo*-forms have not been found on the PES of **5**−**7**. A possible reason for the dramatic change of the N atom configuration upon substitution of the silicon atom in **1**−**3** by the carbon is a drastic increase in the strain that occurs when these heterocycles try to retain the atrane structural arrangement. It is interesting to consider whether this reason is an insurmountable obstacle for carbatranes to achieve a geometry with a nitrogen LEP directed inside the cage. Can carbatrane isomers have a pentacoordinate carbon atom C^1? To explore this question, we have considered the structures of the molecules of 5-aza-1-carbabicyclo[3.3.3]undecanes $XC(YCH_2CH_2)_3N$ possessing relatively long equatorial bonds to the bridged C^1 atom with the third-row atoms Si (**8**) and S (**9**).

Computational Methods

General Methods. The basic computations on the molecules of sila- and thiacarbatranes **8** and **9** and their protonated forms were performed with full optimization of geometry at the MP2 level of theory using the basis sets 6-31G*, 6-311G**, and 6-311++G**. The correspondence of the optimized structures to the minima on the PES was confirmed by the positive eigenvalues of the MP2/6-31G* Hessian.

The relative stability of the protonated forms (ΔE) was estimated as a difference in their total electronic energy (E) corrected for the zero-point vibrational energies (ZPVE). A proton affinity of the nitrogen atom was calculated employing eq 1:

$$\mathrm{PA} = \Delta E_{\mathrm{el}} - \Delta \mathrm{ZPVE} \qquad (1)$$

where $\Delta E_{\mathrm{el}} = [E(\mathrm{B}) - E(\mathrm{BH}^+)]$ and $\Delta\mathrm{ZPVE} = [\mathrm{ZPVE(B)} - \mathrm{ZPVE(BH^+)}]$ are the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. Here, B denotes the molecule in question and BH^+ designates its protonated form. The ΔE and PA values were estimated using the MP2 method with the geometry and ZPVE obtained at the MP2/6-31G* level of theory and were refined with the single-point MP4(SDQ(T))/6-311G** calculations.

The integral equation formalism version of the polarized continuum model (IEF-PCM)[22] was employed for the estimation of polar solution (DMSO) effects on the MP2/6-31G* geometry of **8**.

The calculations were performed using the GAUSSIAN[23] program package. The GAMESS[24] electronic structure code was employed for performing the resource consuming harmonic frequency calculations with the same exponents as have been used for geometry optimizations.

We used the geometrical criterion shown in eq 2 to estimate the trigonal bipyramidal (TBP) pentacoordination character of the bridged carbon atom, η_e, in carbatranes, where θ_n are the equatorial Y−C^1−Y angles. The η_e parameter was suggested by Tamao et al.[25] for determination of the "ideal" TBP structure contribution to the geometry of actual hypervalent silicon compounds. The η_e value is equal to 0% at the "ideal" tetrahedral configuration of bonds at C^1 ($\theta = 109.5°$) and $\eta_e = 100\%$ ($\theta = 120.0°$) at a TBP configuration.

$$\eta_e = [1 - [(120 - 1/3\sum_{n=1}^{3}\theta_n)/(120 - 109.5)]] \times 100\% \qquad (2)$$

Analysis of the electron density in terms of the atoms in molecules (AIM) theory[26] was performed using the MORPHY1.0[27] program. The NBO[28] analysis was carried out on the MP2/6-31G* geometries and the HF/6-31G* wave functions.

Results and Discussion

1. Structure of Carbatranes 8 and 9. The introduction of third-row atoms S and Si into the equatorial Y_3 plane of $XC(YCH_2CH_2)_3N$ changes the structure of these molecules dramatically. According to the MP2 calculations, there is one

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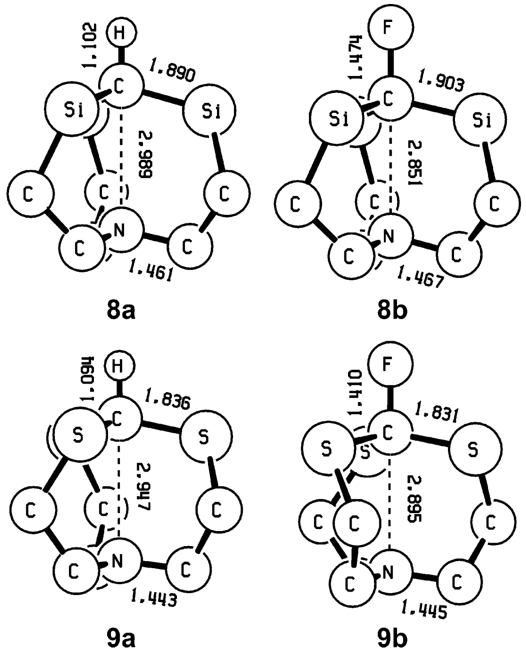

8a **8b**

9a **9b**

Figure 1. MP2/6-31G*-optimized geometries (in Å) of carbatranes $XC(YCH_2CH_2)_3N$, where X = H, F and Y = SiH_2, S. Nonaxial hydrogens are omitted for clarity.

minimum on the PES of **8** and **9**, which corresponds not to the *exo*-isomer (as for Y = O, NR, CH_2), but to an *endo* one (see Figure 1). Judging by the values of the displacement of the N atom out of the plane of the three neighboring C atoms, Δ_N (see Table 1), the degree of nitrogen pyramidalization in silacarbatranes is close to that for most of the oxasilatranes **1** (Δ_N = 0.3−0.4 Å),$^{5-7}$ whereas in the thia derivatives **9** it is considerably less.

Compounds **8** and **9** are the first examples of 1−5-bridged C,N-cage amines with the orientation of the nitrogen LEP inside the cage. A similar configuration of the N atom is known for large nitrogen-containing cycles (beginning from 6-aza[4.4.4]-tetradecanes).^{29,30}

The CYCCN fragments of **8** and **9** adopt an envelope conformation characteristic for the silatranes **1**−**3**: the C_β atoms (with respect to N) lying in the vertex of their corners deviate from the $CYC_\alpha N$ planes by ~0.7 Å.^{5,7,8} The calculated values of their frame bond lengths C−Si, C−S, C−C, and C−N are close to the standard values 1.87, 1.82, 1.54, and 1.47 Å, respectively. In contrast, the axial C−F bonds in **8b** and **9b** are noticeably longer than "normal" (1.37 Å).

Using compound **8b** as an example, we found that extension of the basis set from 6-31G* to 6-311++G** has an insignificant effect on the MP2 values of the structural characteristics of the carbatranes studied (see Table 1).

The values of the $X-C^1-Y$ angles in 2,8,9-trisila- and trithia-substituted carbatranes are 3−8° smaller, and the $Y-C^1-Y$ values are 3−7° greater, than the "ideal" value (109.5°) for a saturated tetracoordinated carbon atom. Such deformation of the bond angles at the bridged C^1 atom is in the direction toward a TBP arrangement of its bonds with $X-C^1-Y = 90°$ and $Y-C^1-Y = 120°$. The possible reason is a 1−5 attractive C···N interaction. Indeed, the internuclear distances d_{C1-N} in **8** and **9** are ~0.5 Å shorter than the sum of the van der Waals (vdW) radii of ~3.35 Å for C and N. Note that in silatranes **1**, possessing a relatively strong coordination Si←N bond (according to various estimates,^{2,8} its energy is higher than 10 kcal/mol), the length of d_{Si-N} is less than the sum of the vdW radii of Si and N by ~1 Å, as shown by electron diffraction (ED) data,$^{31-33}$ X-ray experiments,^{3,5,8} and ab initio calculations.$^{9-11,20,34-38}$

An increase of the electronegativity of substituent X (replacement of H by F) results in the shortening of the C^1-N distance both in **8** and in **9**. Considering the transition from **8a** to **8b**, one can notice a rather essential decrease in d_{C1-N} (>0.1 Å), together with the flattening of the bonding configuration around the C^1 atom and the increase in the degree of nitrogen pyramidalization (see Table 1). An analogous correlation in the change of geometrical parameters d_{Si-N}, Σ_1^3 (O−Si−O), and Δ_N upon the variation of σ-acceptor properties of a substituent X at the silicon atom is also characteristic of silatranes **1**.^{2,5,8}

The AIM analysis data (see Table 2) are suggestive of the covalent nature of the axial $H-C^1$ and $F-C^1$ bonds in **8** and **9** and the equatorial C^1-S bond in **9**, for which the Laplacian of the electron density ($\nabla^2\rho(\boldsymbol{r}_c)$) is negative at their bond critical points (BCPs).

In contrast, at the BCP of the equatorial C^1-Si bond of **8** $\nabla^2\rho(\boldsymbol{r}_c) > 0$, but the electron density ($\rho(\boldsymbol{r}_c)$) is greater than 0.2 e/Å^3, the electron energy density ($E(\boldsymbol{r}_c)$) is negative, and $|E(\boldsymbol{r}_c)| > 0.04$ hartree/Å^3. According to the criteria of Cremer and Kraka,$^{39-42}$ the C^1-Si bond may be classified as covalent and highly polar.

The assumption of the existence of $C^1\cdots N$ coordination in the 5-aza-1-carbabicycloundecanes **8** and **9** (based on the foregoing geometrical factors) is supported by the results of the AIM analysis of their electron density distribution. Indeed, a (3,−1) bond critical point in the internuclear $C^1\cdots N$ region and three (3,+1) ring critical points, RCP, were found for these compounds (see Figure 2, examples of **8a** and **8b**).

Judging by the small value of $\rho(\boldsymbol{r}_c)$, the positive sign of $\nabla^2\rho(\boldsymbol{r}_c)$, and the positive and close to zero value of $E(\boldsymbol{r}_c)$ in BCP-($C^1\cdots N$), the C^1N interactions in **8** and **9** are weak and may be assigned to ionic-type bonding (see Table 2).$^{26,39-41}$ Its attractive character in the fluoro derivatives of sila- and thiacarbatranes is attested to by the presence of the "bulge" of the electron density concentration region in the nitrogen atom valence shell (assigned to the nitrogen LEP) and the "hollow" of its depletion in the basin of the bridged C^1 atom on the C^1N bond path (see

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Table 1. Selected Structural Parameters for Carbatranes 8 and 9 Calculated at the MP2/6-31G*, MP2/6-311G (in parentheses), and MP2/6-311++G** (in square brackets) Levels of Theory.**

	bond lengths (Å)			bond angles (deg)				
	d_{X-C1}	d_{C1-Y}	d_{C1-N}	X−C^1−Y	Y−C^1−Y	C−N−C	Σ_1^3(Y−C^1−Y)[a] (deg)	Δ_N[b] (Å)
8a	1.102	1.890	2.989	106.0	112.7	114.7	338.1	0.340
	(1.103)	(1.888)	(2.974)	(105.5)	(113.1)	(114.7)	(339.3)	(0.340)
8b	1.474	1.903	2.851	103.6	114.7	113.5	344.1	0.381
	(1.463)	(1.905)	(2.863)	(104.1)	(114.2)	(113.4)	(342.6)	(0.383)
	[1.467]	[1.909]	[2.874]	[104.2]	[114.2]	[113.6]	[342.6]	[0.378]
9a	1.094	1.836	2.947	101.7	116.0	118.5	348.0	0.177
9b	1.410	1.831	2.895	101.4	116.2	118.0	348.6	0.204

[a] Σ_1^3(Y−C^1−Y) = 328.5 (°) corresponds to the "ideal" tetrahedron C^1 atom, and 360 (°) corresponds to the planar C^1 atom in the "ideal" trigonal-bipyramid. [b] Δ_N is the value of displacement toward the C^1 atom of the N atom out of the plane of three neighboring C atoms.

Table 2. Electron Density ($\rho(r_c)$), Laplacian ($\nabla^2\rho(r_c)$), and Electron Energy Density ($E(r_c)$) at Some (3,−1) Bond Critical Points in Sila- and Thiacarbatranes 8 and 9 Calculated at the MP2/6-31G* (1) and MP2/6-311G (2) Levels of Theory[a]**

		8a	**8a**	**8b**	**9a**	**9b**
		1	2	1	1	1
BCP(X−C^1)	$\rho(\mathbf{r}_c)$ (e/Å^3)	1.710	1.719	1.798	1.882	1.588
	$\nabla^2 r(\mathbf{r}_c)$ (e/Å^5)	−18.675	−18.351	−2.769	−24.183	−7.253
	$E(\mathbf{r}_c)$ (hartree/Å^3)	−1.663	−1.679	−1.566	−1.969	−2.203
BCP(C^1−Y)	$\rho(\mathbf{r}_c)$ (e/Å^3)	0.740	0.755	0.752	1.162	1.202
	$\nabla^2 r(\mathbf{r}_c)$ (e/Å^5)	6.731	5.633	6.598	−6.254	−6.941
	$E(\mathbf{r}_c)$ (hartree/Å^3)	−0.404	−0.458	−0.419	−0.797	−0.857
BCP(C^1···N)	$\rho(\mathbf{r}_c)$ (e/Å^3)	0.106	0.111	0.118	0.102	0.109
	$\nabla^2 r(\mathbf{r}_c)$ (e/Å^5)	1.213	1.187	1.381	1.079	1.105
	$E(\mathbf{r}_c)$ (hartree/Å^3)	0.005	0.003	0.004	0.002	0.001

[a] 1 au of ρ = 1 e/a$_0^3$ = 6.748 e/Å^3, 1 au of $\nabla^2\rho$ = 1 e/a$_0^5$ = 24.099 e/Å^5, 1 au of $E(\mathbf{r}_c)$ = 1 e^2/a$_0^4$ = 6.748 hartree/Å^3.

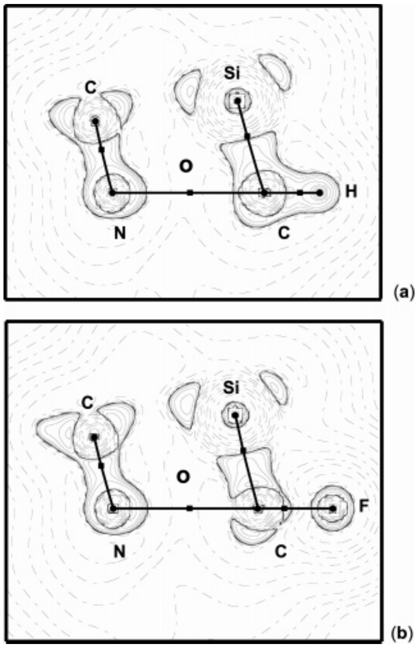

Figure 2. MP2/6-31G* contour maps of $\nabla^2\rho(\mathbf{r})$ for compounds **8a** (a) and **8b** (b). Each map is for a plane of N, C, and Si nuclei. The diagrams are overlaid with selected bond paths. Critical points (3,−1) are denoted by solid squares, and (3,+1) is designated by a large open cycle. Dashed lines correspond to $\nabla^2\rho(\mathbf{r}) > 0$ (regions of charge depletion) and solid lines to $\nabla^2\rho(\mathbf{r}) < 0$ (regions of charge concentration). The contour values in e/a$_0^5$ are ±0.002, ±0.004, and ±0.008 increasing in powers of 10 to ±8.0.

Figure 2b). The replacement of F by a less electronegative H atom results in the disappearance of the "hollow" in the C^1 region on the $\nabla^2\rho(\mathbf{r})$ contour map of **8a** and **9a** (see Figure 2a, for **8a**). According to the NBO analysis data at the HF/6-31G*//MP2/6-31G* level of theory, the interaction of the nitrogen LEP, n_N, with the antibonding orbital σ^*_{CX} of the CX bond is small (~1 kcal/mol) in molecule **8a** and rather stronger (~4 kcal/mol) in **8b**. Note that in silatranes **1** (X = H, F) the interval of the n_N,σ^*_{SiX} interaction was estimated as 3−8 kcal/mol at the B3LYP/6-311G** level of theory.[20]

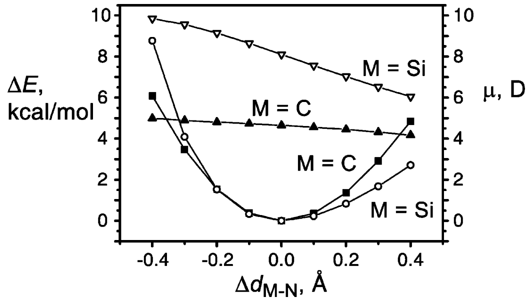

Figure 3. Dependence of relative energies (ΔE) and dipole moments (μ) of the molecules FC(SiCH$_2$CH$_2$)$_3$N **8b** (M = C) and FSi(OCH$_2$CH$_2$)$_3$N **1b** (M = Si) upon the deformation of the internuclear M−N distance Δd_{MN}. The solid squares and triangles correspond to ΔE and μ of **8b** and open cycles and triangles to ΔE and μ of **1b**, respectively. Energies and internuclear distances d_{M-N} in corresponding minima were taken to be equal to zero values.

The soft character of the dependence of the total energy on d_{Si-N} established for **1**−**3**[9−11,43] is manifested in a significant medium effect on their geometry and spectral properties.[8,10,31−33,43] For example, for silatranes **1** (X = H, CH$_3$, F) upon going from the gas phase to the solid state a dramatic shortening (by ~0.3 Å) of the coordination Si···N contact is observed.[31−33] Therefore, on the basis of the form of the potential function of silacarbatrane **8b** (see Figure 3), one would expect a substantial decrease in the C^1···N distance upon the influence of external factors in polar compounds **8** and **9** as well.

However, MP2/6-31G*-PCM calculations have demonstrated the insignificant ~0.012 Å decrease in the d_{C1-N} value for **8b** in polar solution (DMSO) as compared with that characteristic

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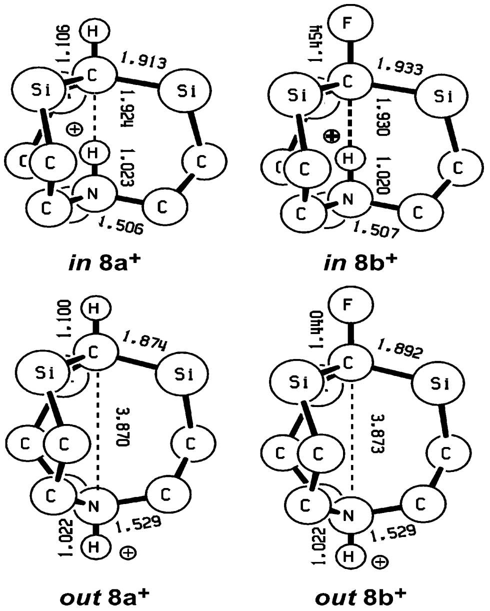
(43) Sidorkin, V. F.; Balakhchi, G. K.; Voronkov, M. G.; Pestunovich, V. A. *Dokl. Akad. Nauk USSR* **1987**, *296*, 113; *Dokl. Phys. Chem. (Engl. Transl.)* **1987**, *296*, 400.

of the isolated molecule. This may be a consequence of the considerably smaller value of the gradient ($\Delta\mu/\Delta d$) of the dipole moment (μ) of carbatranes when compared to that for silatranes (see Figure 3). Note that in the framework of the reaction field model the degree of deformation of a certain bond (Δd) induced by a polar medium depends linearly, among other factors, on the $\Delta\mu/\Delta d$ value.[14,43]

It seems to be impossible to obtain a structure possessing a strong attractive $C^1\cdots N$ interaction through varying the X, Y substituents at the bridged C^1 atom in a series of 2,8,9-substituted 5-aza-1-carbabicyclo[3.3.3]undecanes. By introducing the S and Si atoms in the equatorial plane of the molecules of carbatranes $XC(YCH_2CH_2)_3N$ we were able to solve the problem of their existence in the form of an *endo*-isomer. However, the electronic factor is not very favorable for the formation of the strong coordination C^1N bond because the electronegativity of Y is less than that of C.

2. Structure of the Protonated Forms of Carbatranes 8 and 9. Among the established peculiarities of the electron-spatial structure of compounds **8** and **9** are the pseudobasic (in the absence of LEP at C^1) properties of the XC^1Si_3[44a] and XC^1S_3 fragments, i.e., the concentration of considerable electron density in the atomic basin of C^1 [45] and the nitrogen LEP orientation inside the cavity (see Figure 2). These reasons open up new possibilities for increasing the coordination number of their bridged C^1 atom to 5 by the formation of the intramolecular hydrogen bond $X-C^1\cdots H^+-N$.

Indeed, our calculations show a significant energy advantage of the internally protonated forms of silacarbatranes ***in* 8H**$^+$ over the externally protonated structures ***out* 8H**$^+$. MP2/6-311G** geometries of the protonated forms of carbatranes **8a**,**b** are presented in Figure 4.



in **8a**$^+$ *in* **8b**$^+$

out **8a**$^+$ *out* **8b**$^+$

Figure 4. MP2/6-311G**-optimized geometries (in Å) of the protonated forms of carbatranes $XC(SiH_2CH_2CH_2)_3N$, where X = H, F. Nonaxial hydrogens are omitted for clarity.

In contrast, upon protonation of the thiacarbatranes, the formation of the exocyclic NH^+ bond is energetically more favorable than the "confinement" of a proton inside the cavity of these compounds (at the MP2/6-31G* level of theory E(***in* 9aH**$^+$) − E(***out* 9aH**$^+$) = 2.8 kcal/mol, and E(***in* 9bH**$^+$) − E(***out* 9bH**$^+$) = 3.3 kcal/mol). Selected structural and energetic characteristics of the *in* and *out* protonated forms of silacarbatranes **8a** and **8b** are presented in Table 3 and Figure 4.

The existence of the hydrogen bond $C^1\cdots H^+-N$ in the internally protonated forms of **8** is evidenced by the both geometrical and quantum-topological factors:

(a) The distance from the bridged C^1 atom to the proton, d_{C1-H^+}, is ~1 Å smaller than the sum of the vdW radii of ~2.9 Å for carbon and hydrogen (see Table 3).[46] The bonding $C^1\cdots H^+$ interaction is revealed also from the high value (64% for X = H and F) of the pentacoordination character of the central C^1 atom, η_e.

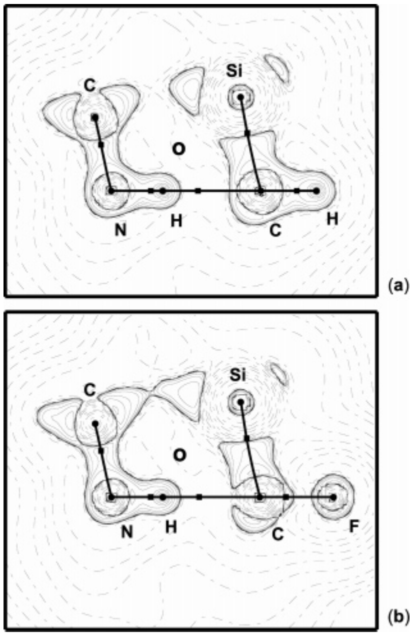


Figure 5. MP2/6-31G* contour maps of $\nabla^2\rho(\mathbf{r})$ for compounds ***in* 8aH**$^+$ (a) and ***in* 8bH**$^+$ (b). Each map is for a plane of N, C, and Si nuclei. The diagrams are overlaid with selected bond paths. Critical points (3,−1) are denoted by solid squares, and (3,+1) is designated by a large open cycle. Dashed lines correspond to $\nabla^2\rho(\mathbf{r}) > 0$ (regions of charge depletion) and solid lines to $\nabla^2\rho(\mathbf{r}) < 0$ (regions of charge concentration). The contour values in e/a$_0^5$ are ±0.002, ±0.004, and ±0.008 increasing in powers of 10 to ±8.0.

(b) In the internuclear region of $C^1\cdots H^+$ the AIM analysis detected bond critical points BCP(3,−1) (see Figure 5).

The MP2/6-31G* values of the electron density and the Laplacian of the electron density at the BCP($C^1\cdots H^+$) of **8aH**$^+$ ($\rho(\mathbf{r}_c) = 0.033$ au, $\nabla^2\rho(\mathbf{r}_c) = 0.096$ au) and **8bH**$^+$ ($\rho(\mathbf{r}_c) = 0.030$ au, $\nabla^2\rho(\mathbf{r}_c) = 0.097$ au) fall in the range of $\rho(\mathbf{r}_c)$ and $\nabla^2\rho(\mathbf{r}_c)$ ($\rho(\mathbf{r}_c) = 0.002-0.040$ au, $\nabla^2\rho(\mathbf{r}_c) = 0.024-0.130$ au), being

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[44] The pseudobasic properties of the C atom of the CSi_3 group are well-known in the chemistry being used in the formation of a carbon−metal bond; see: (a) Faborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89. (b) Eaborn, C.; Smith, J. D. *Coord. Chem. Rev.* **1996**, *154*, 125.

[45] To a large extent the concentration of the electron density on the bridged C^1 atoms is inherent in the molecule of silacarbatrane **8a**, in which the negative charge on C^1 exceeds even that on N. **8a**: $q_{C1}^m = -1.017$, $q_N^m = -0.635$ e; **8b**: $q_{C1}^m = -0.368$, $q_N^m = -0.644$ e; **9a**: $q_{C1}^m = -0.614$, $q_N^m = -0.625$ e; **9b**: $q_{C1}^m = -0.034$, $q_N^m = -0.635$ e, where q^m is a HF/6-31G*//MP2/6-31G* Mulliken atomic charge.

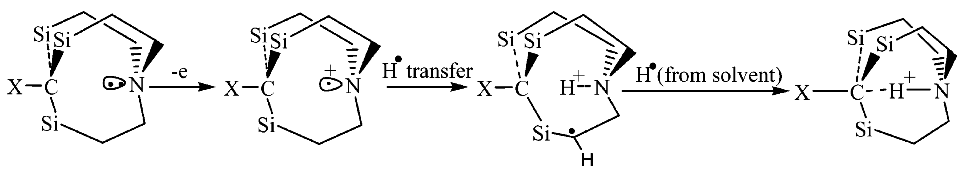
[46] In the framework of the AIM approach the following relationships are usually used as geometrical criteria for the formation of the hydrogen H···B bond: $\Delta r_H + \Delta r_B > 0$ and $\Delta r_H > \Delta r_B$, where $\Delta r_{H(B)} = r_{H(B)}^0 - r_{H(B)}$; $r_{H(B)}^0$ and $r_{H(B)}$ are the nonbonding and bonding radii of the atoms H and B. For the intramolecular H-bonds the use of these inequalities (notably the second one) is difficult because of the problems associated with the estimations of $r_{H(B)}^0$ see: (a) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *39*, 9747. (b) Mallinson, P. R.; Smith, G. T.; Wilson, C. C.; Grech, E.; Wozniak, K. *J. Am. Chem. Soc.* **2003**, *125*, 4259. (c) Grabovski, S. J. *J. Phys. Org. Chem.* **2004**, *17*, 18.

Table 3. Selected Structural Parameters, Relative Stability (Δ*E*) of *in* and *out* Protonated Molecules of Silacarbatranes 8a,b, and the Proton Affinity of Their Nitrogen Atom (PA) Calculated at the MP2/6-31G*, MP2/6-311G (in parentheses) and MP4(SDQ(T)/6-311G** (in square brackets) Levels of Theory**

	bond distances (Å)			bond angles (deg)				
	d_{C1-H^+}	d_{N-H^+}	d_{C1-N}	X−C−Y	Y−C−Y	$\sum_1^3$(Y−C^1−Y) (deg)	Δ^b (kcal/mol)	PA (kcal/mol)
***in* 8aH$^+$**	1.958	1.023	2.981	102.2	115.7	347.1	0.0	223.0
	(1.924)	(1.023)	(2.947)	(101.4)	(116.2)	(348.6)	(0.0)	(224.8)
							[0.0]	[225.4]
***out* 8aH$^+$**		1.026	3.876	107.5	111.4	334.2	6.9	216.1
		(1.022)	(3.870)	(107.2)	(111.7)	(335.1)	(6.8)	(217.6)
							[6.2]	[219.2]
***in* 8bH$^+$**	1.939	1.019	2.958	101.3	116.2	348.6	0.0	215.0
	(1.930)	(1.020)	(2.950)	(101.5)	(116.1)	(348.3)	(0.0)	
***out* 8bH$^+$**		1.026	3.843	106.3	112.5	337.5	6.8	208.2
		(1.022)	(3.873)	(106.9)	(111.9)	(335.7)	(6.1)	

[a] $\sum_1^3$(Y−C^1−Y) = 328.5 (°) corresponds to the "ideal" tetrahedron C^1 atom, and 360 (°) corresponds to the planar C^1 atom in the "ideal" trigonal-bipyramid. [b]The energies of the internally protonated forms were taken to be equal to zero.

Chart 3. Scheme of Introduction of a Proton into the Cavity of a Silacarbatrane



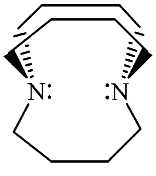
typical of the H-bonds.[46a−c] The density characteristics of these BCPs, i.e., the value of $\rho(\mathbf{r}_c)$, the $\nabla^2\rho(\mathbf{r}_c)$ magnitude and its positive sign, and the small negative value of $E(\mathbf{r}_c)$ (**8aH$^+$**: $E(\mathbf{r}_c) = -0.003$ au, **8bH$^+$**: $E(\mathbf{r}_c) = -0.002$ au) suggest[46c,47] that compounds ***in* 8aH$^+$** possessing medium-strength (4−15 kcal/mol) hydrogen bonds C^1•••H$^+$N have ionic character.

The difference between the total energies of *out* and *in* cations of **8**, Δ*E*, depends only slightly on the basis set size as well as the level of electron correlation (MP2 or MP4) (see Table 3). Undoubtedly, this difference includes the contribution from the attractive C^1•••H$^+$ interaction and falls in the range of the energies of medium hydrogen bonds (4−15 kcal/mol) as well. Judging by the MP2/6-311G** calculations (see Table 3), it is possible to noticeably increase the stability of the *in*-protonated forms of **8** with respect to the *out* ones by decreasing the electronegativity of X (as shown with substitution of F by H).

The proton affinity (PA) value calculated for the nitrogen of the externally protonated 2,8,9-sila-5-aza-1-carbabicyclo[3.3.3]-undecane **8a** (see Table 3) coincides remarkably with the experimental value of 217.0 kcal/mol presented for 6-azabicyclo-[4.4.4]tetradecane.[48a] This is obviously due to the similarity of the degree of nitrogen pyramidalization in the compounds compared. MP2/6-31G* calculations reproduce closely the experimental values of PA known for the molecule of manxine **7** (PA^{calc} = 233.2 kcal/mol, PA^{exp} = 233.4 kcal/mol[48a]) and the X-ray data for the salt [**7H**$^+$]Cl$^-$ ($d_{CN}^{calc} = 3.370$ Å, $\Delta_N^{calc} = 0.342$ Å, $d_{CN}^{exp} = 3.328$ Å,[48b] $\Delta_N^{exp} = 0.326$ Å[48b]).

How might a proton be introduced into the cavity of a silacarbatrane? The probable mechanism seems to be a redox one[29] rather than a classical mechanism of exchange. It involves a stage of oxidation of the nitrogen atom followed by intramolecular transfer of the hydrogen atom to this nitrogen. The redox mechanism has been employed to explain the experimentally observed internal protonation of the molecule diazabicyclo[4.4.4]-tetradecane[29] (**10**), which is topologically similar to silacarbatrane **8a** in its electron density distribution in the region between the bridged nitrogen atoms and in the cage size (d_{N-N} ≈ 2.8 Å).[49] The promising problem is a synthesis of cations ***in* 8H$^+$** along with the neutral silacarbatranes by the reaction of polyfunctional tris(silyl)methanes RC(SiMe$_2$X)$_3$ and protonated amines H$^+$N(CH$_2$CH$_2$Y)$_3$.

Chart 4



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Conclusions

The introduction of the third-row atoms Si and S in the equatorial Y$_3$ plane of 5-aza-1-carbabicyclo[3.3.3]undecanes XC(YCH$_2$CH$_2$)$_3$N (X = H, F) makes it possible for these molecules to attain an *endo*-geometry with the nitrogen lone pair inside the cavity. The geometrical, AIM, and NBO analyses are suggestive of a weak coordination XC←N interaction in sila- (**8**) and thiacarbatranes (**9**). Its magnitude is enhanced by increasing the electronegativity of the axial substituent X. For polar molecule **8** the soft character of the dependence of the total energy on d_{C1N} is established. However, the MP2/6-31G*-PCM calculations exhibit an insignificant ~0.012 Å decrease in the d_{C1N} value of **8** (X = F) in a polar solvent (DMSO) as compared with that of the isolated molecule. This may be a consequence of the small value of the dipole moment gradient ($\Delta\mu/\Delta d$) for silacarbatranes. The MP2 and MP4 calculations show a significant energy advantage (>6 kcal/mol) of the *in*-protonated forms of compounds **8** over the *out* forms. The main reason for this is the formation, according to the AIM analysis, of an earlier unknown and medium-strength (4−15 kcal/mol) hydrogen bond C^1•••H$^+$−N in the *in* cations of silacarbatranes.

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(47) Rozal, I.; Alkorta, I.; Elgnero, J. *J. Am. Chem. Soc.* **2000**, *122*, 11154.

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It provides a high degree (>60%) of pentacoordination, η_e, of the bridged C^1 atom in these molecules.

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Supporting Information Available: Detailed list of the contents, Cartesian coordinates of all investigated structures, the absolute and relative values of the total energies, enthalpies, and Gibbs free energies ($T = 298.15$ K, 1 atm) of the structures **8** and **9** and their protonated forms calculated at the different theoretical levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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