Molecular and crystal structures of 2-phenyl-2-hydro-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane

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HIGHLIGHTS

- X-ray structure is determined.
- Structures of various molecular conformations are optimized at B3LYP and MP2 levels of theory.
- Molecular structure in crystalline state is compared with the structure of conformers proposed for liquid state.

GRAPHICAL ABSTRACT
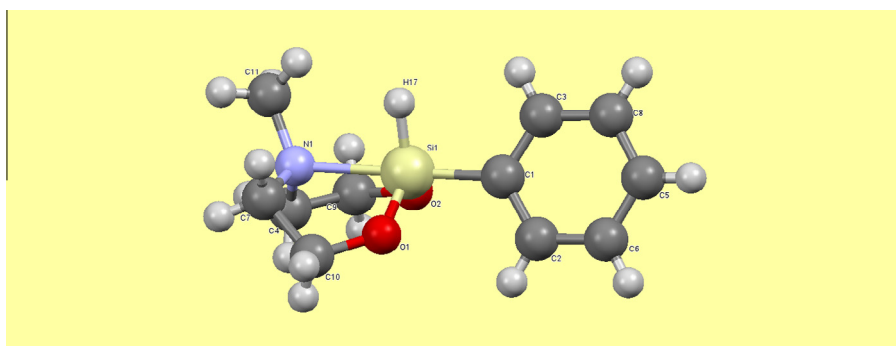
ARTICLE INFO

ABSTRACT

The crystal structure of 2-phenyl-2-hydro-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane [HPhSi(OCH$_2$CH$_2$)$_2$NMe – phenylhydrosilocane (I)] is determined by single-crystal X-ray diffraction at 100 K. The unit cell consists of four molecules connected only by Van-der-Waals interactions. Each molecule has an eight-membered heterocycle with a phenyl group in the axial position. The Si$\cdots$N transannular bond has a short (2.206 Å) interatomic distance which exceeds only this distance in ocanes with highly electronegative fluorine substituents at Si. Since there exist experimental data on the occurrence of different conformers of I in the liquid phase, the PES of the molecule was analyzed by DFT B3LYP and MP2 methods with the aug-cc-pVDZ basis set. The energy minimum belongs to the boat–chair conformation with the axial position of the phenyl group. Rotation of the phenyl ring around the SiC bond has a barrier ca. 1 kcal/mol. The conformer with the equatorial position of this group lies 6 kcal/mol higher. Interconversion of this conformers which was observed in experiment proceeds through the chair–chair configuration in which the Si$\cdots$N transannular bond is absent and coordination at silicon is tetrahedral, rather than trigonal bipyramidal one observed in other conformers.

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Introduction

Silocanes XYSi(OCH$_2$CH$_2$)$_2$NR (aka quasisilatranes) are analogues of better known silatranes XSi(OCH$_2$CH$_2$)$_3$N. In contrast to the latter they contain only two SiOCH$_2$CH$_2$N heterocycles. As well as tricyclic silatranes, bicyclic silocanes are highly promising biologically active products [1]. Several molecular structures already have been determined by X-ray diffraction: X = Y = Ph, R = H (II) [2], X = Y = Ph, R = Me (III), X = Y = Ph, R = CMe$_3$ (IV), X = Y = Me, R = Ph (V), X = Y = Ph, R = Ph (VI) [3], X = Y = F, R = H (VII) [4], X = F, Y = Ph, R = Me (VIII) [5], X = F, Y = Me, R = H (IX) [6]. The

major part of the determined silocane structures [**II,III,VIII,IX**] have a boat–boat (BB) configuration of eight-membered heterocycles Si–(OCC)$_2$–N while structures **IV** and **VII** have boat–chair configurations of the skeleton. In all these structures the short Si$\cdots$N contact (with the exception of **IV**) is observed which vary within the 1.98–2.30 Å range thus indicating a N → Si donor–acceptor bond.

Two structures are known (**V** and **VI**) which possess chair–chair conformations [3] and in which Si–N interatomic distances are substantially longer (3.08–3.19 Å).

The NMR study of Ar$_2$Si(OCH$_2$CH$_2$)$_2$NR compounds [7] revealed the occurrence in solution of an equilibrium between boat–boat (with Si–N transannular bond) and chair–chair (without transannular bond) conformations. In ocanes with different substituents at Si (X ≠ Y) there exists a possibility of isomers differing by their position in the trigonal bipyramidal configuration at silicon. In the NMR study [8] of HPhSi(OCH$_2$CH$_2$)$_2$NCH$_3$ (I) it was shown that there exist two isomers and they correspond to the axial and equatorial arrangement of the phenyl group.

However, the presence of only one SiH stretching band in the IR spectrum of HPhSi(OCH$_2$CH$_2$)$_2$NCH$_3$ [9,10] both in liquid and solids phases allows authors to propose that the boat–chair conformation is predominant in solution and that the content of the structures with axial position of the H atom is low [9]. There are no doubts that the phenyl group in crystalline phenylhydrosilocane (I) occupies the axial position, since in the known structures of ocanes with different substituents at Si, that are FPhSi(OCH$_2$CH$_2$)$_2$NCH$_3$ (**VIII**) and FMeSi(OCH$_2$CH$_2$)$_2$NH (**IX**), more electronegative substituent occupies the axial position. However, no X-ray data on **I** exist. Our interest in this compound is also explained by the fact that we intend to use this compound as a source of nucleogenic [11] cations PhSi$^+$(OCH$_2$CH$_2$)$_2$NMe. In the second part of our study we used quantum chemical methods to bring light on plausible isomers of I and the mechanisms of their interconversion.

Experimental and computational details

The title compound was prepared by the reaction of phenylsilane with methyldiethanolamine [12]. It crystallizes as colorless crystals from hexane solution. The synthesized product was identified by ^{1}H and ^{13}C NMR spectra. Five groups of signals were observed, those are a singlet at 2.43 ppm, double triplets with the average shift of 2.81 ppm, a group of lines at 3.94 ppm, singlet at 5.15 ppm and two group of lines in the 7.2–7.6 ppm range. In the ^{13}C NMR spectrum signals corresponding to phenyl ring carbons (143.3, 133.7, 128.8, 128.9 ppm) to methylene groups (68.2, 55.1 ppm) and to the methyl group (41.9 ppm) were observed These spectra coincide with the NMR spectra earlier reported for 2-phenyl-2-hydro-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane by Kupce et al. [8]

An isometric specimen of C$_{11}$H$_{17}$NO$_2$Si, approximate dimensions 0.16 mm × 0.19 mm × 0.23 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Saxi-CrysAlisPro CCD system equipped with a graphite monochromator and a Mo Kα sealed tube (λ = 0.71073 Å). Data collection temperature was 100 K.

The frames were integrated with the Agilent Technologies CrysAlisPro software package [13]. The integration of the data using a monoclinic unit cell yielded a total of 5723 independent reflections to a maximum θ angle of 37.28°, (completeness = 99.9%, Rint = 7.74%) and 3281 were greater than 3σ(F). The final cell dimensions a = 9.9205(7) Å,   b = 9.5937(5) Å,   c = 12.2489(8) Å, β = 108.860(7)°, V = 1103.19(12) Å^3, with 2.17° < 2θ < 37.28°. Data were corrected for absorption effects using the multi-scan method and using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.931 and 1.0. The

structure was solved and refined using the SIR2011 Software Package [14], using the space group P21/c, with Z = 4 for the formula unit C$_{11}$H$_{17}$NO$_2$Si. The final anisotropic full-matrix least-squares refinement on F with 81 variables converged at R1 = 0.042, for the observed data and wR2 = 0.049 for all data. The goodness-of-fit was 0.988. The carbon and nitrogen-bound H atoms were placed in calculated positions and were included in the refinement in the rigid body approximation, with U$_{iso}$(H) set to 1.2U$_{eq}$(C) and C–H 0.97 Å. Positions of atom H$_{17}$ were localized from difference Fourier maps and refined without any restrictions, with individual isotropic temperature parameters. The largest peak in the final difference electron density synthesis was 0.24 ē/Å^3 and the largest hole was −0.23 ē/Å^3 with an RMS deviation of 0.145 ē/Å^3. On the basis of the final model, the calculated density was 1.345 g/cm^3 and F(000) = 480 ē. (CCDC number is 000100021398).

Geometries of stationary points have been fully optimized and characterized by harmonic vibrational frequency calculations using the B3LYP [15,16] density functional method and the second-order Moller–Plesset perturbation theory (MP2) with the frozen core approximation [17]. The Dunning correlation-consistent sets aug-cc-pVDZ [18] was employed. All the methods and basis sets were used as implemented in the Gaussian09 program [19].

Results and discussion

The structure of 2-phenyl-2-hydro-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane obtained in the X-ray study is depicted in Fig. 1. Coordinates of atoms of 2-phenyl-2-hydro-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane obtained in the X-ray study together with isotropic displacement parameters, bond lengths, and angles are listed in Tables S1-S3 in supplementary materials.

Similar to structures of other silocanes refined earlier [2–6] the coordination geometry of silicon is close to trigonal bipyramidal with a phenyl group in the axial position. The average C1–Si–O angle in this trigonal bipyramid is 97.9(2)°, while the C1–Si–H17 angle is 95(2)°. Note, that in other ocane containing one phenyl group, that is FPhSi(OCH$_2$CH$_2$)$_2$NCH$_3$ (**VIII**), phenyl group is in equatorial position. Obviously, more electronegative substituent occupies an axial position.

Silicon lies practically on the plane formed by the equatorial atoms O1, O2, and H17 (the deviation from this plane towards the phenyl ring is only 0.189 Å). The phenyl ring plane is slightly twisted from the N1–Si1–H17 plane [the dihedral angle H17–Si1–C1–C3 is −21.5(2)°].

The intramolecular SiN bond divides the Si(OCH$_2$CH$_2$)N eight-membered heterocycle to two five-membered heterocycles SiOCCN. As in silatranes these heterocycles are nonplanar.

In both five-membered heterocycles carbon atoms located in the α-position to nitrogen are deflected from the SiOC$_β$N plane. Bond lengths in the Si–(OCC)$_2$–N heterocycle do not differ substantially from corresponding distances in other silatranes and silocanes (Table S2 in Supplementary materials).

The substitution of electronegative oxygen atom in 1-phenylsilatrane for more positive hydrogen leads to the shortening of the Si$\cdots$N transannular bond from 2.312 Å in silatrane [20] to 2.206 Å in the studied ocane. However, the substitution of H by another phenyl group in II leads to a substantial increase of the Si$\cdots$N distance (2.260 Å) [3]. Note, that the Si$\cdots$N distance depends not only on substituents at Si but also at N. Thus, this distance in Ph$_2$Si(OCH$_2$CH$_2$)$_2$NR compounds grows from 2.30 Å for R = H to 3.16 Å for R = CMe$_3$. Nevertheless, the shortest transannular bond (1.981 Å) is in silocane with two fluorine substituents [5]. However in FPhSi(OCH$_2$CH$_2$)$_2$NCH$_3$ (VII) it is 2.175 Å that is only slightly shorter than in HPhSi(OCH$_2$CH$_2$)$_2$NCH$_3$ (2.206 Å).

No intermolecular hydrogen bonds were observed in the structure of I. Molecular packing in the crystalline structure is realized