ATRANES

XXXV.* CONFORMATIONAL ANALYSIS OF THE 1-METHYLSILATRANE MOLECULE

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The conformational energy of the 1-methylsilatrane molecule for sp^3 and sp^3d hybridization of the silicon atom was calculated. The known data on the structure of the atrane portion of the molecule are in good agreement with the results of the calculation for sp^3d hybridization and differ radically from the results of the calculation for sp^3 hybridization of the silicon atom. The conformational factors constitute a considerable contribution (11.4 kcal/mole) to the forced change in the hybridization of the silicon atom. An analysis of the dependence of the energy of the 1-methylsilatrane molecule on the distance between the Si and N atoms shows that a stable exo form, isolated to any extent by a considerable conformational barrier from the real structure with an $Si \leftarrow N$ transannular interaction, does not exist.

The presence of a transannular bond in molecules of cyclic inorganic ethers and alkoxides of triethanolamine (atranes) $X_{n-3}M^{(n)}(OCH_2CH_2)_3N$ has been confirmed by a number of physicochemical methods [1-7]. It has been established for the most investigated representatives of this interesting class of heteroorganic compounds – silatranes (M = Si) – that the electronic effects of substituent X and of substituents in the atrane half rings affect the strength of the intramolecular $Si \leftarrow N$ coordinate bond. An intimate relationship between the intramolecular coordination of the silicon and nitrogen atoms and the conformational factors has also been observed. To begin with, this is the absence of a transannular interaction of the Si and N atoms in $(CH_3)_2Si(OCH_2CH_2)_2NR$ molecules and the considerably lower strength of the intramolecular $Si \leftarrow N$ coordinate bond in 1-ethoxy-2-carbasilatrane as compared with 1-methylsilatrane and 1-ethoxysilatrane. A bipyramidal structure in which the deviation of the X–Si–O angle from the equilibrium value characteristic for sp^3d hybridization is also explained by interaction of substituent X with the oxygen atoms of the atrane half rings [1-5, 7] has been proposed for the silicon atom in silatrane molecules.

The indications of the importance of conformational factors for an understanding of the properties of atranes have up until now been purely qualitative [3-6]. The present paper is devoted to the elucidation of two problems: the extent to which the real structure of the atrane portion of the molecule corresponds to the minimum of the conformational energy and the energy expenditures required for one or another deformation of the molecule. The formulation of the latter problem is related to the problem of the stability of the exo-atrane structure.†

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*See [1] for communication XXXIV.

†We consider the exo form to be the structure in which the unshared pair of the nitrogen atom is directed away from the heteroring [6].

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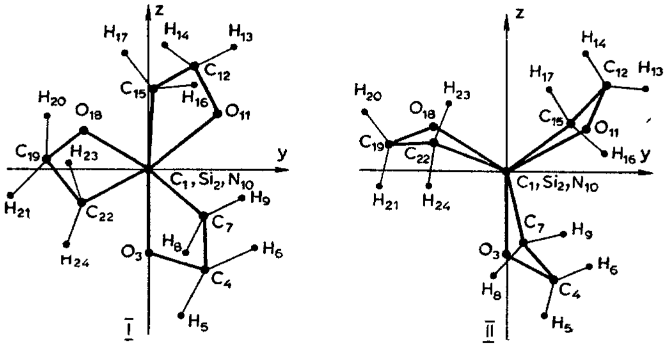
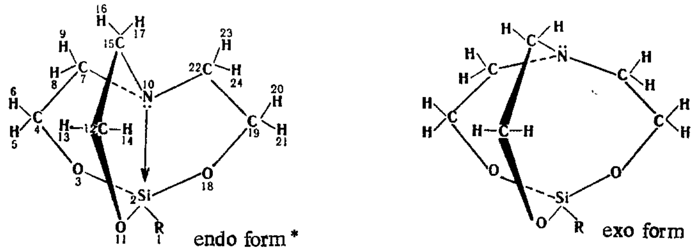


Fig. 1. Spiral (I) and zigzag (II) structures of the 1-methylsilatrane molecule with a silicon atom in sp^3 hybridization.*

TABLE 1. Dependence of the Conformational Energy (E) of the 1-Methylsilatrane Molecule on the Torsion Angle of the $O-C_{(4)}$ Bond

φ°	E, kcal/mole	
	sp^3	sp^3d
150	10,9	—
160	11,9	2,5
170	14,0	0,2
180	17,1	−0,5

A geometrical analysis of the 1-methylsilatrane molecule with a tetrahedral arrangement of the valences of the silicon atoms shows that only a narrow range of distances between the Si and N atoms – 2.35–2.45 and 2.9–3.0 Å, respectively – is possible for the endo and exo structures of this molecule without deformation of the valence angles and bond lengths. In this case, the $C_{(4)}$ atom deviates by a distance of 0.9–1.1 Å from the plane of the SiON triangle.



Two conformations of the half ring, which correspond to torsion angles of the $C_{(4)}-C_{(7)}$ bond of 45–50 and 90–95°, are possible for each of the structures. The projections of the atrane portion of the molecule on the plane perpendicular to the Si–N axis are presented in Fig. 1. Projection I corresponds to a torsion angle of 45–50°, while projection II corresponds to a torsion angle of 90–95°. As seen from Fig. 1, close location of the atoms of adjacent half rings (H_9C_{12}, H_9C_{15}), which correspond to their repulsion under the influence of van-der-Waals forces, is characteristic for both forms.

The conformational energy of 1-methylsilatrane was calculated for a fixed Si–N distance of 2.19 Å. This value was taken from x-ray diffraction data for 1-phenylsilatrane [7], inasmuch as it is known that the Si–N distance depends only slightly on the nature of the substituent attached to the silicon atom. Under the assumption of sp^3 hybridization of the silicon atom, the minimum conformational energies for the I and II forms are 13.0 and 10.9 kcal/mole. The substantially nonplanar structure of the atrane half ring is optimum for both forms. The deviation of the $C_{(4)}$ atom from the SiON plane is 0.6–0.8 Å. The dependence of the conformational energy on the torsion angle of the $O-C_{(4)}$ bond which is presented in Table 1, was obtained for the energically more advantageous II form.

As seen from Table 1, transition from the optimum geometry to arrangement of the $SiOC_{(4)}N$ atoms in one plane ($\varphi = 180°$) requires the expenditure of 6.2 kcal/mole. The minimum conformational energy for sp^3d hybridization of the silicon atom (a bipyramidal arrangement of the substituents) occurs for a planar arrangement of the $SiOC_{(4)}N$ atoms. The deviation of the $C_{(4)}$ atom from the SiON plane requires considerable energy expenditure (Table 1).

A comparison of the results obtained with the experimental data shows that the observed structure of the atrane portion of the molecule corresponds to the minimum of the conformational energy only for sp^3d

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*The numbering of the atoms in the 1-methylsilatrane molecule in the scheme and Figure 1 is chosen for optimal calculation and is not in accord with ordinary chemical usage.

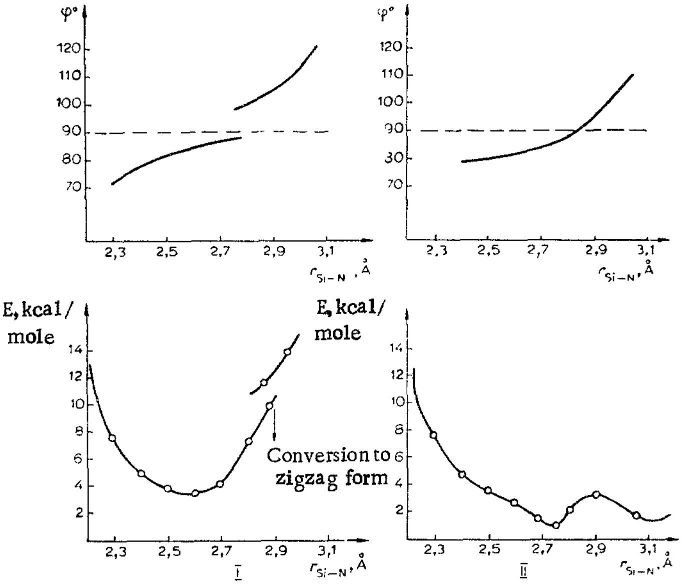

Fig. 2. Dependence of the Si–N–$C_{(7)}$ angle (φ) and the energy (E) on the Si–N distance for the spiral (I) and zigzag (II) forms of the 1-methylsilatrane molecule.

hybridization of the silicon atom. It must be noted that the optimum configuration calculated for sp^3d hybridization of the silicon atom is in agreement with the known structure of silatranes not only with respect to the planar arrangement of the $SiOC_{(4)}N$ atoms; close values of the $C_{(1)}SiO$ angle (94°, experimental value 98°) and of the distance of the $C_{(7)}$ atom from the $SiOC_{(4)}N$ plane (0.45 Å x-ray diffraction value 0.5 Å) were also obtained. Calculation for this hybridization also showed that the low barrier to transition of the $C_{(7)}$ atom through the $SiOC_{(4)}N$ plane (< 0.3 kcal/mole) coincides with the results of PMR spectroscopy, which indicate equivalence of the $H_{(8)}$ and $H_{(9)}$ protons [3-5].

The data in Table 1 make it possible to conclude that a change in the hybridization of the silicon atom from sp^3 to sp^3d is accompanied by a gain in the conformational energy of 11.4 kcal/mole. Conformational factors thus play a large role in the 1-methylsilatrane molecule, promoting a change in the valence state of the silicon atom.

Inasmuch as an unstrained configuration with an Si–N distance of 2.9-3.0 Å may correspond to a tetrahedral direction of the valence bonds of the Si atom, it is extremely interesting to calculate the conformational energy of the optimum structures as a function of the distance between the Si and N atoms. This dependence for structural forms I and II is presented in Fig. 2. The calculated values of the Si–N–$C_{(7)}$ angle are also presented in Fig. 2. As seen from Fig. 2, exo form I of the 1-methylsilatrane molecule is absolutely unstable: it is spontaneously converted to the endo structure at Si–N distances from 2.7 to 2.8 Å. An increase in the Si–N distance for endo form I to 2.85 Å leads to a barrierless conversion to endo form II. In contrast to form I, exo form II has a minimum on the conformational energy curve that corresponds to a stable configuration with an Si–N distance of 3.1 Å and an Si–N–$C_{(7)}$ angle of 95°. A barrier that does not exceed 1.5 kcal/mole separates this stable state from endo form II. This barrier is apparently insufficient for isolation of the exo structure during synthesis. A comparison of the minimum energies of the exo and endo structures with the coordinately bonded nitrogen and silicon atoms shows that the formation of a transannular bond is accompanied by a decrease in the conformational energy of 1.5 kcal/mole. Consequently, shortening of the Si–N distance in the 1-methylsilatrane molecule below 3.1 Å should be associated with a still smaller barrier as compared with the value calculated for sp^3 hybridization of the silicon atom.

The relationship between the conformational energies of the real structure and the hypothetical exo form of 1-methylsilatrane obtained in this study satisfactorily explains the difficulty involved in implicating the nitrogen atom of atranes in intermolecular complexing: the expenditure of energy not only in disruption of the transannular Si ← N bond but also in overcoming the forces of interaction of the nonvalence-bonded atoms is required for this.

EXPERIMENTAL

The conformational energy of 1-methylsilatrane was calculated by means of a special program that permits one to fix any internal coordinates of the molecule. Optimization was accomplished by the method of fastest descent with variation of the torsion and valence angles. The interaction of the nonvalence-bonded atoms was extrapolated by means of the exp-6 potential. The van-der-Waals interaction potential of the methyl group was assumed to be equal to that for the carbon atom. The electrostatic interactions were disregarded. The parameters for the calculation were taken from [8-13]. The equilibrium values of the Si—O—C angle were assumed to be identical for both sp^3 and sp^3d hybridization of the silicon atom. Inasmuch as the magnitude of this angle depends on the nature of the substituents attached to the silicon atom [12], the calculation was made for 113 and 123°, and practically identical values of the conformational energies were obtained. The barrier to the inversion of nitrogen was assumed to be 9.14 kcal/mole on the basis of data on the force constant of the deformation vibrations of methylamine [13].

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