STABILITY OF THE endo FORM OF THE 1-METHYLSILATRANE MOLECULE

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UDC 547.895'245 : 541.63

We have compared [1] the calculated conformational energies of the exo and endo forms of the 1-methylsilatrane molecule (I). The calculations for the latter were made with allowance for both sp^3 and sp^3d hybridization of the silicon atom. However, the absence at that time of necessary data made it impossible for us to correctly take into account the strain due to the formation of a transannular $Si \leftarrow N$ bond.

A recent calculation of the force field of the 1-hydrosilatrane molecule [2] enabled us to evaluate the contributions to the energy of the strain of the endo form of I assocated with deformations of the $O-Si-N$ valence angles and the $Si \leftarrow N$ bond, during which the $Si \leftarrow N$ bond length for optimization of the geometry of the endo form of I turned out to be 0.03 Å shorter than the equilibrium value (2.19 Å).

In the case of optimization of this sort the conformational energy of the endo form of I increases from −0.5 kcal/mole [1] to 2.4 kcal/mole, which exceeds the minimum energy of the exo form of I by 1.4 kcal/mole. Thus the previous conclusion [1] that the formation of a transannular bond between the nitrogen and silicon atoms in I is accompanied by a decrease in the conformational energy of the endo form as compared with the exo form proved to be erroneous.

The experimentally observed increased stability of the endo structure of silatranes can be explained only under the assumption of a considerable contribution of the energy of formation of the transannular $Si \leftarrow N$ bond to the total energy of the molecule. One is easily convinced of this on comparison of the atomization energies of the endo and exo structures of I evaluated within the approximation $-H_{at} = \Sigma E_{bond} - E_{conf}$. When $E^{endo}_{conf} > E^{exo}_{conf}$, higher stability of the endo form is realized only when the condition $\sum E^{endo}_{bond} > \sum E^{exo}_{bond}$ is satisfied.

Moreover, the conclusion [1] that there is a significant gain (~8.5 kcal/mole) in the conformational energy when the hybridization of the silicon atom in the endo form of I changes from sp^3 to sp^3d remains valid.

For a more profound understanding of the peculiarities of the structures of silatranes we are currently performing quantum-chemical calculations, the results of which will be published in the future.

LITERATURE CITED

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 715-716, May, 1975. Original article submitted November 27, 1974.