# ATRANES

## XLIX.* CONFORMATIONAL ANALYSIS OF THE 1-METHYL-2-CARBASILATRANE MOLECULE

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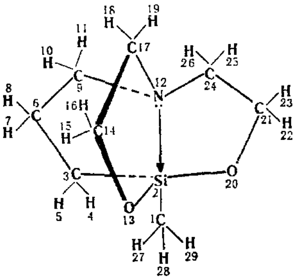
The dependence of the strain energy on the distance between the nitrogen and silicon atoms was studied for the 1-methyl-2-carbasilatrane molecule within the framework of the Westheimer method. For models with the postulated silicon coordination numbers of 5 and 4, respectively, Si...N distances of 2.31 Å (19.4 kcal/mole) and 2.41 Å (32.4 kcal/mole) correspond to the minimum of the conformational energy of the endo form. The exo form is the most stable when the distance between the Si and N atoms is 3.10 Å, and it is also the least strained system (1.8 kcal/mole). Since 1-methyl-2-carbasilitrane exists only in the endo form, the stability of the latter can be justified only under the condition that the energy of the transannular Si←N interaction exceeds 17.6 kcal/mole.

The establishment of the factors that promote the formation and chemical stability of silatranes that have a "cage" structure is an important theoretical and practical problem. Its solution requires the development of certain model representations, in particular, representations of the energetics of the conversion of the silatrane molecules to their hypothetical reactive exo form.

Previously (for example, see [2]) in the case of 1-methylsilatrane (II) we demonstrated the fruitfulness of conformational analysis within the framework of the Westheimer method for the solution of the structural problems of the chemistry of silatranes. In the present study we selected the 1-methyl-2-carbasilatrane (I) molecule as the subject of a similar study.



From a chemical point of view, this compound is less stable than silatrane II. Its synthesis is more difficult and gives the product in low yield. The distance between the nitrogen and silicon atoms in 2-carbasilatranes is ~0.2 Å greater than in the corresponding silatranes [3]. The R−Si−O angle, the magnitude of which to a certain degree reflects the valence state of the silicon atom, is ~98° in 2-carbasilatranes, i.e., it is intermediate between the values peculiar to compounds of tetra- and pentacoordinated silicon [3]. We therefore used two sets of starting data in the conformational analysis of carbasilatrane I. The first set (A) corresponds to a trigonally bipyramidal equilibrium orientation of the valence bonds of the silicon atom, and the second set (B) corresponds to a tetrahedral orientation.

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* See [1] for communication XLVIII.

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TABLE 1. Calculated and Experimental Valence Angles (in degrees) in the 1-Methyl-2-carbasilatrane Molecule

| Angle | Calculated value | Experimental value |
|---|---|---|
| $C_1SiC_3$ | 102.8 | 103.0 |
| $SiC_3C_6$ | 115.3 | 115.7 |
| $C_1SiO_{13}$ | 97 | 98 |
| $SiO_{13}C_{14}$ | 122.0 | 123 |
| $C_3C_6C_9$ | 109.3 | 110.0 |
| $C_6C_9N$ | 106.5 | 107.4 |
| $C_{14}C_{17}N$ | 111.6 | 107.5 |

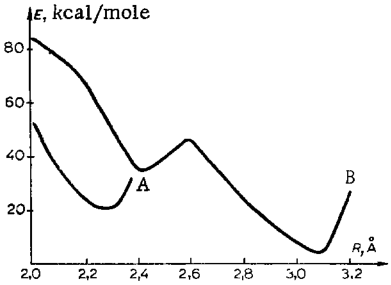


Fig. 1. Potential functions of models A and B of the 1-methyl-2-carbasilatrane molecule.

We studied the dependence of the conformational energy of carbasilatrane molecule I on the length of the Si←N bond for variant A and on the distance between the silicon nitrogen atoms for variant B. The results are presented in Fig. 1. The relatively small interval of the change in $l_{Si \leftarrow N}$ is due to the fact that the dependence of the force constant of this bond on its length has not been established. An $l_{Si \leftarrow N}$ value of 2.31 Å corresponds to the absolute minimum of the energy for model A (19.4 kcal/mole). However, in the case of B the minimum energy of the endo form is 32.4 kcal/mole at a distance (R) of 2.41 Å between the silicon and nitrogen atoms. These energies and distances are appreciably larger than the values we found [2] for the optimum conformation of the II molecule. Thus conformational analysis explains in a natural way the observed change in the internuclear distances and the stability of 2-carbasilatranes as compared with silatranes.

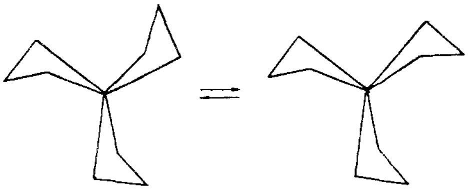
An analysis of the difference in the strain energies (~13 kcal/mole) between optimized structures A and B showed that its origin is associated to a large extent with the energy of the van der Waals repulsion of Si and N (~4.5 kcal/mole) in B, which substantially exceeds the strain energy of the Si←N bond in A (~0.5 kcal/mole). However, the deformations of most of the valence angles for both models are, on the average, of identical magnitude, with the exception of the six NCH angles, which are strained to a greater degree in model B (~6 kcal/mole) than in model A (~3 kcal/mole).

The valence angles calculated for optimum conformation A are in good agreement with the experimental values [3] (Table 1).

It must be noted that, in agreement with the experimental data [3], the calculations showed an "angular" structure of the $C_1Si...N$ fragment, in which the calculated angle is 177.9° as compared with the experimental value of 176.8°.

The calculated configuration of the five-membered atrane ring has the envelope form typical for silatranes. In agreement with the experimental data [3], the β-carbon atoms ($C_6$, $C_{14}$, and $C_{21}$) deviate from the plane, and the average deviation is ~0.55 Å. The calculated φ angle between the corner of the envelope and its base, which determines the noncoplanarity of the ring, is in good agreement with the experimental value. Thus, for example, the calculated φ angle for the $Si-C_3-C_6-C_9-N$ ring is 139.5° as compared with the experimental value of 140.4°.

The high conformational mobility of the 2-carbasilatrane molecule, which is responsible for the equivalence of the protons within each of its methylene groups in the PMR spectra [4], is satisfactorily conveyed by the results of the calculation. The barriers to synchronous conversion for five-membered rings in carbasilatrane I are less than 1 kcal/mole, and the conversion is realized through a nonplanar transition state. In addition, we considered the asynchronous conversion of the $\beta$-carbon atoms to be theoretically possible:



The calculated potential function of this sort of conversion provides evidence for its energic disadvantageousness, since the barrier to conversion is more than 13 kcal/mole, and the energy of the asymmetrical configuration exceeds the energy of the symmetrical configuration by ~10 kcal/mole. The barriers to rotation of the methyl group relative to the Si—C bond are less than 1.5 kcal/mole.

The potential function for model B when $R_{Si...N} = 3.1$ Å has a minimum that corresponds to the exo form of carbasilatrane I. A comparison, with respect to the energy, of the optimum conformations A and B with the exo form (E ~ 1.8 kcal/mole) shows that it is not possible to explain the experimentally observed stability of the endo form within the framework of the Westheimer method. Those possible interactions that stabilize the endo form that were disregarded in the calculation must be taken into account for agreement between the theoretical results and the experimental data; they should exceed 17.6 kcal/mole for model A and 30.6 kcal/mole for model B.

In a previous paper [2] we have already invoked the approximate equation [5]

$$-\Delta H_{at} = \Sigma H_b - E_{conf}$$

where $\Delta H_{at}$ is the atomization enthalpy and $\Sigma H_{bond}$ is the sum of the enthalpies of the chemical bonds for the endo or exo form, for an understanding of the problem of the stability of silatranes. On the basis of this equation, it is difficult to find interactions that stabilize the endo form for model B, though they might be electrostatic interactions of the type involving the unshared pair of nitrogen and a polar bond (C—O, Si—O, etc). However, our estimates showed that allowance for these interactions insures the necessary energy gain of the endo form of B as compared with the exo form only in the case of unrealistically high dipole moments of the C—O and Si—O bonds. As an example, the dipole moment of the C—O bond should be ~4 D instead of the actual value of ~0.8 D [6].

However, to substantiate the stability of the endo form of model A it is sufficient in the expression for $\Delta H_{at}$ to assume that the enthalpy of the Si←N bond exceeds 17.6 kcal/mole.

Thus from energy considerations one should prefer a model with a pentacoordinated silicon atom. A more profound examination of this problem requires quantum chemical methods. The results of studies that we have begun in this direction will be published soon.

## EXPERIMENTAL

The conformational energy of 1-methyl-2-carbasilatrane was calculated from a special program that allows fixing of any internal coordinates of the molecule. Optimization was realized by the fastest-descent method with variation of the torsion and valence angles. Variation of the Si←N bond length was permitted in model A. The interaction of the valence-nonbonded atoms was extrapolated by the exp-6 potential. The electrostatic interactions were disregarded. The force constants of the corresponding valence and torsion angles were assumed to be identical for both variants, but the A set, in contrast to the B set, contained the force constant for the transannular Si←N bond and for the OSiN, $C_1SiN$, and $C_3SiN$ angles. The parameters used in the calculation were taken from [7-13].

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# ASSOCIATION CONSTANTS OF SUBSTITUTED 2-ACETYLTHIOPHENES WITH PHENOL

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The association constants ($K_{ass}$) of a number of substituted 2-acetylthiophenes and 3-acetylthiophene with phenol in tetrachloroethylene solutions at 25, 50, and 80° were determined by IR spectroscopy. It is shown that acetylthiophenes are stronger proton acceptors than the corresponding acetophenones. The thermodynamic characteristics (ΔH and ΔS) of the association were calculated, and the presence of a compensation effect was established. It is shown on the basis of correlation of the $K_{ass}$ values by means of the Brown, Yukawa–Tsuno, and Swain–Lupton equations that the thiophene ring is a better transmitter of the effect of substituents than the benzene ring because of the increased conductivity of the conjugation effect.

In order to characterize the effect of the thiophene ring on the proton-acceptor capacity of the carbonyl group and the efficiency of transmission of the electronic effects of substituents in this heteroaromatic system as compared with the benzene ring [1, 2], we measured the association constants ($K_{ass}$) of a number of substituted acetylthiophenes with phenol in tetrachloroethylene solutions at 25, 50, and 80°C and determined the thermodynamic characteristics (ΔH and ΔS) of the investigated process (Table 1).

At all of the investigated temperatures the $K_{ass}$ values obtained for 2- and 3-acetylthiophenes (I and II) exceed the values obtained for acetophenone (X). At the same time, the previously determined $\Delta\nu_{OH}$ values for 2-acetylthiophene ($196 \pm 1$ cm$^{-1}$) and acetophenone ($197 \pm 1$ cm$^{-1}$) [2] do not differ. These facts are a consequence of the effect of the proton-acceptor capacity of the carbonyl group of, on the one hand, the electronic effects of the hetaryl ring bonded to it and, on the other, the steric hindrance to the formation of H bonds created by the heteroatom, which, as is well known [3, 4], is in the s-cis position relative to the oxygen atom.* When the phenyl group in acetophenone is replaced by the electron-donor 2-thienyl group [6], the effect of the abovementioned oppositely acting factors on the $\Delta\nu_{OH}$ value is compensated and as a result does not change. However the increase in $K_{ass}$ on passing from X to I indicates that the $K_{ass}$ values are considerably less sensitive to steric effects, and the polarity of the carbonyl group has a greater effect on them; this is in agreement with the results obtained during a study of the proton-acceptor capacity of substituted acetophenones, 2-acetylselenophenes [2], and other carbonyl bases [7].

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*See [5] for the existence of steric hindrance between the carbonyl group and an adjacent thiophene ring.

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