

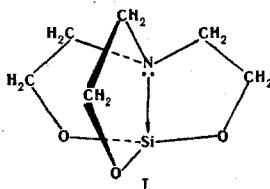
ATRANES
XLIII.* POLARITY OF THE TRANSANNULAR
Si ← N BOND IN SILATRANES

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The dipole moments of the $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ heterocyclic framework were calculated within the framework of an additive scheme by means of data from x-ray diffraction and conformational analysis of silatranes. The direction of the dipole moment of this fragment coincides with the "experimentally" determined value (from nitrogen to silicon), and its magnitude is ~ 3 D. The dipole moment of the Si ← N coordinate bond was estimated to be 2.2 D, which corresponds to charge transfer from the nitrogen atom to the silicon atom (to the extent of 0.2 e). These results refute the existing concepts of the exceptionally high polarity of the transannular Si ← N bond in silatranes.

The hypothesis of the existence of an Si ← N donor-acceptor bond in silatrane molecules (I) enables one to explain the peculiarity of the chemical behavior and physicochemical properties of these compounds [2-4]. Of the proofs for transannular interaction between the nitrogen and silicon atoms in I molecules, the exceptionally large (~ 5 D) surpassing of the experimental values of their dipole moments as compared with the values calculated via an additivity scheme [5] has been considered to be the most persuasive evidence, whereas a number of experimental results (above all those of PMR spectroscopy [6, 7]) do not confirm the conclusion [5] regarding the high polarity of the Si ← N bond in I and provide evidence only for a small amount of transfer of the electron density from the nitrogen atom to the silicon atom. The reason for the contradiction consists, in our opinion, in the use of an idealized geometry of the silatranes in the calculation [5] of the dipole moments.



Later x-ray diffraction studies [8-10] and our calculations of an optimized geometry for I molecules [11] revealed appreciable distortion in the orientation of the substituents attached to the silicon atom from a trigonal-bipyramidal orientation and an increase of 0.3-0.4 Å in the Si-N internuclear distance as compared with the value adopted in [5]. This compelled us to recalculate the dipole moments of I by an additive scheme.

*See [1] for communication XLII.

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TABLE 1. Calculated Dipole Moments (D) of the Silatrane $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ Fragment in I

Set of bond moments	Model		
	1.	2.	3.
1.	3.01	3.08	3.31
2.	2.95	2.95	3.24
3.	2.92	2.89	3.21

In order to ascertain the effect of the fine peculiarities of the three-dimensional structure of the silatrane grouping (and its possible changes on passing from the crystalline state to solutions) on the dipole moment of the I molecule, we made calculations for three models.

The atomic coordinates of the atrane skeleton for the second and third models were taken from x-ray diffraction data for 1-phenyl- and 1-(m-nitrophenyl)silatrane [8, 9], respectively.* These molecules differ not only with respect to the Si-N internuclear distance but also with respect to the fact that different carbon atoms deviate from the plane of the atrane SiOCCN semicycles. The geometry of the first model corresponds to the optimized (by the Westheimer method) structure of the 1-methylsilatrane molecule [11] and, consequently, is free of perturbations introduced by the effects of intermolecular interaction.

Three sets of bond moments were used for the calculation of the dipole moment of the $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ fragment. The dipole moments of the C-H (0.4 D), C-O (0.7 D), and C-N (0.45 D) bonds remained identical in each of them [12]. Only the dipole moment of the Si-O bond was varied. This was due to the fact that the absence of any information at all on the bond moments in silatranes compels one to use the $\mu_{\text{Si-O}}$ values obtained for model compounds - trialkoxysilanes - in the calculations. The $\mu_{\text{Si-O}}$ values presented by various authors [13-15] for the latter range from 1.19 to 1.7 D. In our calculations we therefore used these extreme values of the dipole moments of the Si-O bonds (the first and third sets) and the intermediate value (1.54 D) (the second set), which has already figured in a previous study [5]. It is clear that this sort of indeterminacy in the selection of the bond moments, in addition to the known inadequacies of the additive scheme [12], substantially limits the significance of the results, which should be considered only as approximate.

The calculations were made with a BESM-6 computer with a special program.

An analysis of the results (Table 1) makes it possible to arrive at the following conclusions. In contrast to earlier calculations [5], the direction of the calculated dipole moment of the silatrane $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ skeleton coincides with the "experimental" direction (from nitrogen to silicon), and its magnitude is much greater than the previously published value [5].

Variation of the magnitude of the dipole moment of the Si-O bond leads only to a small change in the dipole moment of the silatrane skeleton (~ 0.3 D when $\mu_{\text{Si-O}}$ changes by 0.5 D).

The changes in the dipole moment of the $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ grouping (without allowance for the dipole moment of the Si-N bond) caused by variation of the three-dimensional structure of I (from the first to the third model) reached ± 0.3 D for any of the sets of bond moments used. The previous conclusion [5] regarding the determining electronic effect of substituent R on the dipole moment of both the entire $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ fragment in I and of the dipole moment of the Si-N bond is therefore invalid. The results of our calculations show that steric factors also have an appreciable effect on the values of the dipole moments of I.

Our calculated dipole moment of the silatrane skeleton of the doubly convex (exo) [2, 11] form of the I molecule† was found to be 1.04 D (in agreement with the results in [5]). This confirms the previous conclusion [5] regarding the absence of appreciable amounts of the exo form of I in solution.

The results make it possible to estimate the dipole moment of the Si-N coordinate bond. The experimental values of the dipole moment of the silatrane $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ skeleton for 1-methyl- and 1-phenylsilatrane are 5.03 and 5.14 D [5], respectively. The average (the second and third sets of bond moments) calculated dipole moment of this grouping without allowance for $\mu_{\text{Si-N}}$ is 2.8 D for the 1-methylsilatrane model and 2.9 D for the 1-phenylsilatrane model. On the basis of this, the dipole moment of the Si-N transannular bond in I can be considered to be 2.2 D.‡

*The coordinates for the hydrogen atoms of the methylene groups were calculated under the assumption of a symmetrical orientation relative to the C-C-X plane (X = O or N).

†The atomic coordinates were taken from a calculation of its optimized structure [11] with $\mu_{\text{Si-O}} = 1.54$ D.

‡Bearing in mind the limitations inherent in the additive scheme of calculation of the dipole moments [12] and the arbitrary character of the selection of the parameters used in the calculations, one should assume that the true $\mu_{\text{Si-N}}$ value may differ from the found value by ± 1 D. In fact, the use of a $\mu_{\text{Si-O}}$ value of 1.2 D in the calculation (the first set of bond moments) lowers this value to 1.9 D.

Inasmuch as the distance between the nitrogen and silicon atoms in I is 2.1-2.2 Å [10], the indicated $\mu_{\text{Si} \leftarrow \text{N}}$ value corresponds to charge transfer from the nitrogen atom to the silicon atom (to the extent of 0.2 e).

Thus, without repudiating the earlier conclusions regarding the determining effect of the Si \leftarrow N coordinate bond in silatrane molecules on many of their properties [2-4] (including also the dipole moments [5]), our results demonstrate only the erroneousness of the existing concepts of the exceptionally high polarity of this transannular bond.

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