

# INVESTIGATION OF SILATRANES BY ULTRAVIOLET SPECTROSCOPY

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## Introduction

The silatranes ( $\overline{\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ ) have characteristic bond structure. A number of researchers have investigated their structure by various methods. It has been found that dative covalent bond was formed between the silicon and nitrogen atoms in silatranes. The spatial orientation of silicon atom corresponds to a trigonal bipyramid and the nitrogen atom is tetrahedral [1]. In this paper our study on the ultraviolet spectra is presented. We wanted to get answer for the question whether any information could be drawn for the Si←N bond, that is for the silatrane structure on the basis of the ultraviolet spectra.

## The review of literature

Till now only a few papers have dealt with the ultraviolet spectroscopic investigation of silatranes, since the investigations were impeded by the very limited solubility of the compounds. ПЕТУХОВ et al. [2] studied the UV spectra of alkyl and alkoxy silatranes ( $\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_2\text{H}_5\text{O}, (\text{CH}_3)_2\text{CHO}$ ) in aqueous solution in the wavelength region between 180 and 240 nm. It was found that the spectra of silatranes were shifted toward the shorter wavelengths in comparison to the spectrum of triethylamine. This hypsochromic effect was explained by the participation of the lone electron pair of the nitrogen of silatranes, in contrast with the nitrogen of triethylamine, in chemical bond. The formation of Si ← N bond increases the bond energy, and the energy of electronic transition decreases (it means a shift to the direction of shorter wavelengths). However, the information taken from this paper is insufficient since it presents only a sketch of the ultraviolet spectra, and the characteristic data of the spectra are not given.

VORONKOV et al. [3] studied the UV spectra of parasubstituted phenoxy silatranes ( $\text{R} = \text{p-XC}_6\text{H}_4\text{O}$ , where  $\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CH}_3\text{O}, (\text{CH}_3)_3\text{C}$ ) in aqueous solution in the range from 195 to 400 nm. The spectral data were compared

with those of organosilicon and organic compounds of similar composition ( $p\text{-XC}_6\text{H}_4\text{OSi}(\text{CH}_3)_3$  and  $p\text{-XC}_6\text{H}_4\text{OCH}_3$ ). Besides, quantumchemical calculations were carried out by PPP method, and conclusions were drawn on the existence and the magnitude of  $d\pi\text{--}p\pi$  bond formed in the phenoxy groups attached to the silicon atom. It was found that silatranes showed two characteristic maxima in the region of 215–225 and 270–288 nm, respectively, but the UV spectra in the investigated region did not give any information concerning the Si  $\leftarrow$  N bond. The common fault of both mentioned works is the use of water as solvent though it is well known that the water breaks up the Si  $\leftarrow$  N bond and the silatrane ring and splits off the substituent R. In addition to the above-mentioned two papers UV data can be found for phenylsilatrane in the work of BROWN and PRESCOTT [4]:  $\lambda_{\text{max}} = 269$  nm in chloroform. The published UV data of silatranes are summarized in Table 1.

Table 1

Data taken from the literature for the UV spectra of silatranes

$$\begin{array}{c} \text{R} \\ \text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N} \end{array}$$

| R  | $\lambda_{\text{max}}$ (nm) | $\epsilon$  | Lit. |
|--|-----------------------------|-------------|------|
| $\text{C}_2\text{H}_5$                           | 183*                        | $\sim 1020$ | [2]  |
| $\text{C}_3\text{H}_7$                           | 185*                        | $\sim 840$  | [2]  |
| $\text{C}_2\text{H}_5\text{O}$                   | 186*                        | $\sim 1140$ | [2]  |
| $(\text{CH}_3)_2\text{CHO}$                      | 196                         | $\sim 300$  | [2]  |
| $\text{C}_6\text{H}_5\text{O}$                   | 212                         | 6200        | [3]  |
|  | 270                         | 1300        |      |
| $p\text{-ClC}_6\text{H}_4\text{O}$               | 225                         | 11970       | [3]  |
|  | 280                         | 1710        |      |
| $p\text{-CH}_3\text{C}_6\text{H}_4\text{O}$      | 213                         | 8070        | [3]  |
|  | 270                         | 1400        |      |
| $p\text{-CH}_2\text{OC}_6\text{H}_4\text{O}$     | 223                         | 8520        | [3]  |
|  | 288                         | 2870        |      |
| $p\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{O}$ | 220                         | 6070        | [3]  |
|  | 275                         | 1350        |      |

\* Shoulder

### Experimental

For recording the ultraviolet spectra we chose isooctane as solvent which did not interact with the investigated compounds. Some difficulties were caused by the low solubility of silatranes: the  $p$ -nitrophenoxysilatrane could not be solved at all, in the case of phenyl- and  $o$ -aminophenoxysilatrane only

the shorter wavelength bond-maxima could be determined. The solubility data are given in Table 2. In order to interpret the UV spectra of silatranes,

Table 2  
Solubility of silatranes  $\overline{\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  in 25 °C

| R                               | mg/100 g<br>i-octane | R   | mg/100 g<br>i-octane |
|---------------------------------|----------------------|---|----------------------|
| CH <sub>3</sub>                 | 32.9                 | C <sub>6</sub> H <sub>5</sub>                     | 25.7                 |
| C <sub>2</sub> H <sub>5</sub>   | 5.7                  | C <sub>6</sub> H <sub>5</sub> O                   | 10.0                 |
| CH <sub>2</sub> =CH             | 5.0                  | p-ClC <sub>6</sub> H <sub>4</sub> O               | 9.3                  |
| C <sub>2</sub> H <sub>5</sub> O | 27.9                 | o-NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O | 4.3                  |

the spectra of triethoxysilanes with similar composition were also measured. The UV spectra of phenylsilatrane and phenyltriethoxysilane were recorded in chloroform, too, for determining the maximum of  $\alpha$ -band. A Carl Zeiss SPECORD UV VIS instrument was used for the measurements.

The investigated silatranes were prepared by reesterification reaction known from the literature [5, 6]. The triethoxysilane was synthesised as follows:

p-chlorophenoxytriethoxysilane ( $\text{p-ClC}_6\text{H}_4\text{OSi}(\text{OC}_2\text{H}_5)_3$ ):

A solution of 0.5 mol (64.3 g) p-chlorophenol in 30 cm<sup>3</sup> ethanol was added dropwise to 0.5 mol (104.2 g) tetraethoxysilane in the presence of a small amount of metallic sodium as catalyst. The mixture was under reflux for 8 hours and after removing the ethylalcohol by distillation the product was obtained by vacuum distillation. The physico-chemical data of the product: b.p. 123–124 °C/260 Pa,  $n_D^{25}$ : 1.4588,  $d_4^{25}$ : 1.097 g/cm<sup>3</sup>,  $\text{MR}_D$  (calc.): 71.91 cm<sup>3</sup>,  $\text{MR}_D$  (meas.): 72.44 cm<sup>3</sup>; the result of analysis:  $\text{Si}_{\text{calc}}$ : 9.66%,  $\text{Si}_{\text{exp}}$ : 9.10%.

p-nitrophenoxytriethoxysilane ( $\text{p-NO}_2\text{C}_6\text{H}_4\text{OSi}(\text{OC}_2\text{H}_5)_3$ ):

A solution of 0.15 mol (20.9 g) p-nitrophenol in 50 cm<sup>3</sup> ethanol was added dropwise to the solution of 0.1 mol (20.8 g) tetraethoxysilane in 150 cm<sup>3</sup> dry benzene in the presence of a small amount of metallic sodium as catalyst. The mixture was under reflux for 8 hours and after removing the solvent and the formed ethylalcohol by distillation, the product was obtained by vacuum distillation. The physico-chemical data of the product: b.p. 137 °C/60 Pa,  $n_D^{25}$ : 1.4590,  $d_4^{25}$ : 1.090 g/cm<sup>3</sup>,  $\text{MR}_D$  (calc.): 74.94 cm<sup>3</sup>,  $\text{MR}_D$  (meas.): 75.57 cm<sup>3</sup>; the result of analysis:  $\text{Si}_{\text{calc}}$ : 9.32%,  $\text{Si}_{\text{exp}}$ : 9.40%. The data of ultraviolet spectra for silatranes and triethoxysilanes are presented in Table 3, and the spectra are shown in Figs 1 and 2.

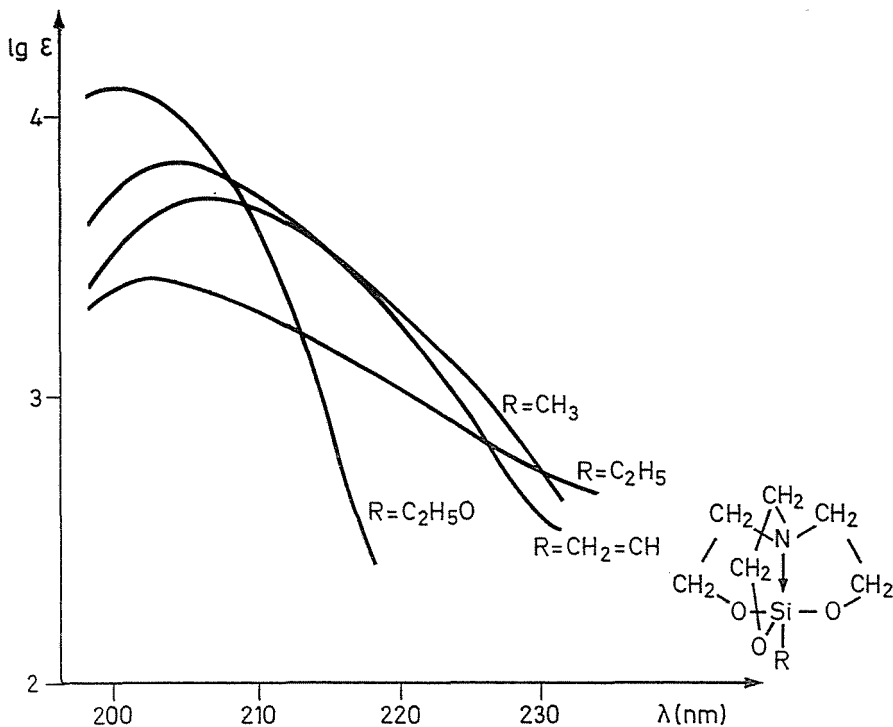


Fig. 1. Ultraviolet spectra of silatranes  $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2 = \text{CH}, \text{C}_2\text{H}_5\text{O}$ ). Solvent: *i*-octane

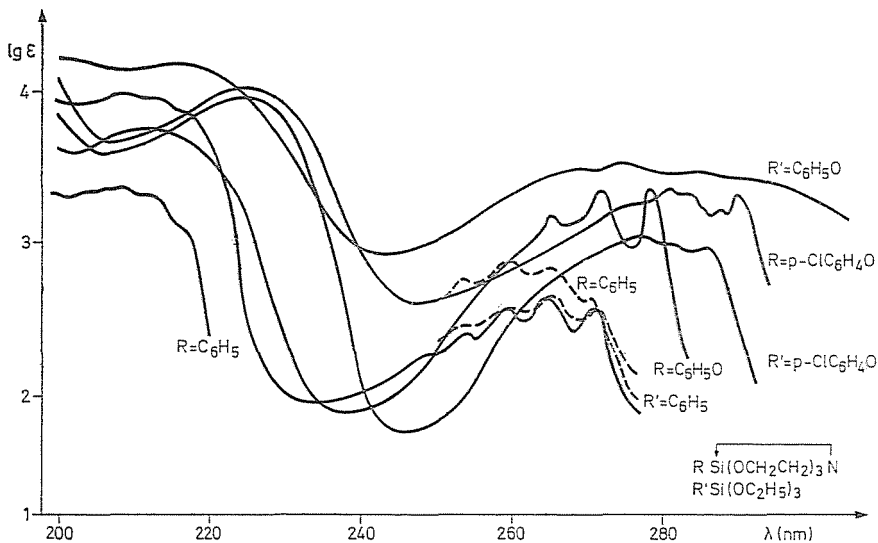


Fig. 2. Ultraviolet spectra of silatranes  $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$  and triethoxysilanes  $\text{R}'\text{Si}(\text{OC}_2\text{H}_5)_3$  ( $\text{R} = \text{R}' = \text{C}_6\text{H}_5, [\text{C}_6\text{H}_5\text{O}], \text{p-ClC}_6\text{H}_4\text{O}$ ). Solvent: — *i*-octane, — — — chloroform

**Table 3**  
 Experimental data of ultraviolet spectra of silatrenes and triethoxy-silanes  
 (in i-octane)

| R   | RSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> N |            |                      |            | RSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> |            |                      |            |
|---|---|------------|----------------------|------------|---|------------|----------------------|------------|
|   | $\lambda_{max}$ (nm)                                  | $\epsilon$ | $\lambda_{max}$ (nm) | $\epsilon$ | $\lambda_{max}$ (nm)                              | $\epsilon$ | $\lambda_{max}$ (nm) | $\epsilon$ |
| CH <sub>3</sub>                                   | 206   | 5290       |                      |            | —   |            |                      |            |
| C <sub>2</sub> H <sub>5</sub>                     | 202   | 2690       |                      |            | —   |            |                      |            |
| CH <sub>2</sub> =CH                               | 204   | 7010       |                      |            | —   |            |                      |            |
| C <sub>2</sub> H <sub>5</sub> O                   | 200   | 12920      |                      |            | —   |            |                      |            |
| C <sub>6</sub> H <sub>5</sub>                     | 209   | 2440       |                      |            | 210   | 10230      | 248*                 | 160        |
|   | 213*  | 2220       |                      |            | 213*  | 9660       | 254                  | 250        |
|   | 217*  | 1360       |                      |            | 217*  | 7450       | 259                  | 350        |
|   |   |            |                      |            |   |            | 264                  | 430        |
|   |   |            |                      |            |   | 271        | 370                  |            |
| C <sub>6</sub> H <sub>5</sub> **                  |   |            | 253                  | 650        |   |            | 254*                 | 310        |
|   |   |            | 259                  | 860        |   |            | 260                  | 420        |
|   |   |            | 265                  | 790        |   |            | 265                  | 510        |
|   |   |            | 270                  | 510        |   |            | 271                  | 430        |
| C <sub>6</sub> H <sub>5</sub> O                   | 212   | 6110       | 265                  | 1560       | 217   | 16100      | 262*                 | 2430       |
|   |   |            | 272                  | 2380       |   |            | 268                  | 3190       |
|   |   |            | 278                  | 2350       |   |            | 274                  | 3470       |
|   |   |            |                      |            |   |            | 284                  | 2960       |
| p-ClC <sub>6</sub> H <sub>4</sub> O               | 225   | 11210      | 276                  | 1800       | 223   | 9470       | 271*                 | 860        |
|   |   |            | 281                  | 2310       |   |            | 277                  | 1120       |
|   |   |            | 284*                 | 2240       |   |            | 286                  | 930        |
|   |   |            | 288*                 | 1630       |   |            |                      |            |
|   |   |            | 290                  | 2120       |   |            |                      |            |
| o-NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O | 209   | 2640       |                      |            |   |            |                      |            |
|   | 212*  | 2360       |                      |            |   |            |                      |            |
|   | 216*  | 990        |                      |            |   |            |                      |            |
| p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O |   |            |                      |            | 217   | 9500       | 284                  | 7090       |
|   |   |            |                      |            | 223*  | 8300       |                      |            |

\* Shoulder

\*\* In chloroform

### Discussion

On the basis of ultraviolet spectra the following conclusions were drawn. The ultraviolet spectra of identically substituted silatranes and triethoxysilanes ( $R = C_6H_5$ ,  $C_6H_5O$  and  $p-ClC_6H_4O$ ) exhibit curves of similar shape. The spectrum of phenylsilatrane shows a hypsochromic shift of small degree in comparison to that of phenyltriethoxysilane considering both measurements carried out in isoctane and chloroform, respectively. As far as the *p*-chlorophenoxy derivatives are concerned, in the case of silatrane compounds a slight bathochromic displacement and for the phenoxy derivatives a hypsochromic shift of larger extent was observed. These displacements of several nm indicate some changes in the strength of the Si—R bonds. The magnitude and direction of the observed shifts are not qualified, however, to decide whether the Si—R bond is weaker in silatranes than in triethoxysilanes. The similar shape of the UV spectra supports the opinion of VORONKOV et al. [3], that in the case of silatranes containing phenyl group, no information can be obtained from the spectra at the interval between 200 and 300 nm on the specific silatrane structure, on the presence of Si ← N bond.

A characteristic maximum around 200 nm was observed in the case of silatranes in which substituent R attached to the silicon atom does not contain phenyl group ( $R = CH_3$ ,  $C_2H_5$ ,  $CH_2=CH$ ,  $C_2H_5O$ ). On the other hand, the spectra of triethoxysilane homologues had no absorption maximum in this region. On the basis of these experimental findings it can be concluded that the absorption bands appearing at 200—206 nm were characteristic of silatranes, of the five-coordinated silicon atom and of the Si ← N bond. The UV spectra at the wavelength range below 200 nm can be expected to provide more information. Changing the R substituent in the series of silatranes a bathochromic shift was found in the case of the position of the  $\alpha$  and  $\rho$  bands in the following order:  $C_6H_5 < C_6H_5O < p-ClC_6H_4O$ . The tendency in the displacement of the absorption maxima was experienced to be the same for triethoxysilanes:  $C_6H_5 < C_6H_5O < p-ClC_6H_4O < p-NO_2C_6H_4O$ . These shifts are consistent with the known changes observed for compounds with formulae  $RSi(CH_3)_3$  [7] and reasonably explained by electronic effects. Our further investigations will be directed on the recording of the vacuum ultraviolet spectra below 200 nm.

### Summary

In this work the ultraviolet spectra of silatranes ( $\overline{\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ ) and triethoxysilanes ( $\text{RSi}(\text{OC}_2\text{H}_5)_3$ ) were studied. It was found that for compounds containing phenyl group ( $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{O}$ ,  $p\text{-ClC}_6\text{H}_4\text{O}$ ) the UV spectra of silatranes and triethoxysilanes were similar, the small shifts point to changes in the Si-R bond strength, the spectra were not suitable for the investigation of the Si-N bond in silatranes. In the case of compounds without phenyl group ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2 = \text{CH}$ ,  $\text{C}_2\text{H}_5\text{O}$ ) a maximum characteristic of silatranes was observed between 200 and 206 nm, this absorption band could not be detected in the spectra of the homologous triethoxysilanes.

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