ATRANES

XX. Ultraviolet Absorption Spectra of Silatranes and Germatranes*

V. A. Petukhov, L. P. Gudovich, G. I. Zelchan, and M. G. Voronkov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 6, pp. 968–969, 1969

UDC 546.287:543.422.6

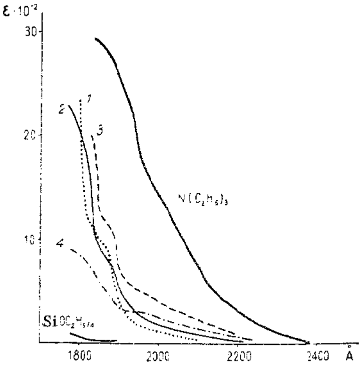
The UV absorption spectra in the 1800–2400 Å region of 1-alkylsilatranes and 1-alkylgermatranes have been studied, confirming the presence of Si ← N and Ge ← N bonds, respectively, in these compounds.

In the molecules of the atranes $M(OCH_2CH_2)_3N$, the heteroatom M and the nitrogen atom are linked by a donor-acceptor bond [2–8]. This bond is created by the transfer of electrons from the unshared pair of the nitrogen to the vacant orbitals of the M-atom. It appeared of interest to confirm the existence of the M ← N bond by means of UV absorption spectra. The absorption of light connected with the unshared pair of electrons of the N-atom or the M-atom is observed in the shortwave region which is difficult of access for standard instruments (of the SF-4 type), and, therefore, we used a vacuum spectrophotometer permitting spectra to be obtained in the liquid phase down to the limits of transmission of the solvent.

The absorption of the atranes is determined mainly by the two groups connected to the N- and M-atoms. According to our results, the absorption connected with the group of the N-atom is observed in the more accessible longer-wave region (λ ≃ 1900–2000 Å) than the absorption due to the group of the N-atom (λ ≃ 1700 Å). The formation of the M ← N bond must increase the bond energy of the unshared electron pair of the nitrogen atom which, in its turn, leads to a shift in the band of the amino group in the shortwave direction. Consequently, the spectrum of an atrane must be shifted in the shortwave direction as compared with the spectrum of free triethylamine, in which the unshared electron pair of the nitrogen atom is free.

The formation of the M ← N bond may affect the absorption of the group of the M-atom. Most frequently, the band of the group of the M-atom is shifted in the long-wave direction, since the density of the electron cloud surrounding the M-atom increases. However, the band of the group of the M-atom is unsuitable for observation, and, therefore, the hypothesis given above is somewhat provisional.

The experimental results that we have obtained confirm the considerations expressed above. The absorption bands of the 1-alkylsilatranes are shifted in the shortwave direction relative to the bands of triethlamine. Thus, (see the spectra of a number of silatranes in the figure) the UV spectra confirm the existence of a Si ← N bond in the silatranes.



UV spectra of the silatranes:

1 — $C_2H_5Si(OCH_2CH_2)_3N$;
2 — $CH_3CH_2CH_2Si(OCH_2CH_2)_3N$;
3 — $C_2H_5OSi(OCH_2CH_2)_3N$;
4 — $(CH_3)_2CHOSi(OCH_2CH_2)_3N$.

solvent was water.

Unfortunately, the spectra of 1-phenyl- and 1-benzylsilatranes are unsuitable for establishing the presence of a Si ← N bond in these compounds, since the strong bands of the benzene ring are superposed on the bands of the group of the N-atom and interfere with their observation.

The absorption bands of the 1-alkylgermatranes are shifted in the shortwave direction relative to the bands of the trialkylamines to a smaller extent than in the case of the 1-alkylsilatranes. This can be explained either by a lower strength of the Ge ← N bond or by the fact that the band of the group of the Ge atom is, as a rule, located in the shorter-wave region than the band of the corresponding group of the Si atom. For a definitive elucidation of the main cause of this phenomenon, we shall study the UV absorption spectra of $RGe(OC_2H_5)_3$ and $Ge(OC_2H_5)_4$

REFERENCES

1. M. G. Voronkov and S. V. Mikhailova, KhGS [Chemistry of Heterocyclic Compounds], 5, 795, 1969.

2. M. G. Voronkov and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 1, 51, 1965.

3. M. G. Voronkov, I. B. Mazheika, and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 1, 58, 1965.

---

*For part XIX, see [1].

4. A. N. Egorochkin, V. A. Pestunovich, M. G. Voronkov, and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], **1**, 300, 1965.
5. Yu. P. Egorov, M. G. Voronkov, T. B. Lutsenko, and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], **2**, 24, 1966.
6. M. G. Voronkov, Pure Appl. Chem., **13**, 35, 1966.
7. M. G. Woronkow, G. I. Seltschans, A. F. Lapsina, and W. A. Pestunowitsch, Z. Chem., **8**, 214, 1968.
8. M. G. Voronkov, Vestn. AN SSSR, no. 10, 48, 1968.

18 July 1967

Zelinskii Institute of Organic Chemistry AS USSR, Moscow

Institute of Organic Synthesis AS LatvSSR, Riga