THE ULTRAVIOLET SPECTRA OF SILOCYCLOBUTANES

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The UV spectra of Si-substituted silocyclobutanes in vacuum were studied. The bathochromic shift of the absorption band, disclosed by comparison with bands of the corresponding acyclic compounds, can be explained by the highly strained state of the four-membered ring. This same principle in disilocyclobutanes leads to the reduction of the barrier effect of the methylene group, disrupting the interaction of the silicon atoms in the unstrained molecule.

Silocyclobutanes (I) are characterized by an exceptionally high reactivity of the endocyclic S—C bond.

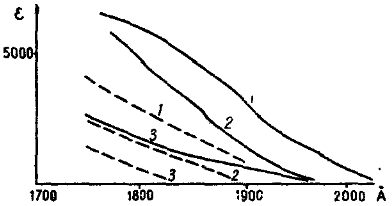
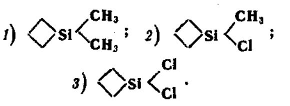


Fig. 1. UV spectra of monosilocyclobutanes (I) and ethylchlorosilanes. The broken lines correspond to: 1) $(C_2H_5)_4Si$; 2) $(C_2H_5)_3SiCl$; 3) $(C_2H_5)_2SiCl_2$. The solid lines correspond to:



This high reactivity is exhibited by the action of both electrophilic and nucleophilic reagents and also by the high reactivity of the silicon heteroatom in reactions of the S_{N_2} type. In addition, compounds of type (I) are increasingly important as they are a new type of organosilicon monomer, used for the preparation of polymers with the carbon silicon basic chain. The singular reactivity of I is usually explained by the strained condition of the ring and the accompanying steric effects.

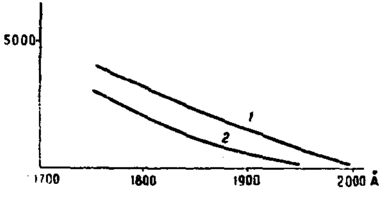


Fig. 2. UV spectra of the polymers: 1) $[Si(CH_3)_2CH_2]_n$; 2) $[Si(CH_3)_2CH_2CH_2CH_2]_n$. The absorption intensity is calculated on the basis of the group which contains the silicon atom.

Recently, a large amount of work has already been devoted to the synthesis and chemical conversion of I. On the other hand, study of the physical properties which could shed light on the special structure of these compounds has been almost neglected. We were interested in studying the UV spectra of the four-membered carbon silicon ring compounds since it is well known that the spectra are closely associated with the valence electron properties responsible for reactivity. Since the compounds I chosen for study are formally saturated compounds like the alkylsilanes, their spectra were obtained on the vacuum spectrophotometer SP-41, which was earlier used to determine the region of absorption of the alkylsilanes. (The solvent used in our experiment was a specially purified n-heptane.)

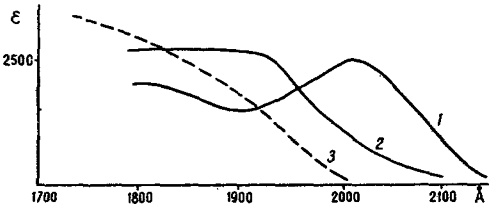
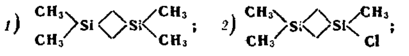
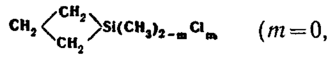


Fig. 3. UV spectra:



3) 1,3,5-trisilocyclohexane (III). The absorption intensity is calculated on the basis of the group which contains the silicon atom (in disilocyclobutane 1/2, in III 1/3 the actual measured value).

Figure 1 shows the absorption lines of tetraethylsilane and ethylchlorosilanes of the type

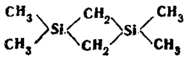


$(m=0,\ 1,\ 2)$.

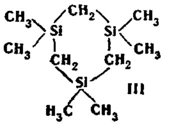
These lines indicate that in the spectra of I a significant bathochromic shift is observed; that is, a drawing together of the energy level of the ground and excited states occurs. The most probable reason for this seems to be a distortion of the C—Si—C angle from that of a regular tetrahedron and a corresponding excitation of the I molecule in the ground state.

The occurrence of the bathochromic shift in the strained cycloalkanes compared with n- and iso-alkanes is known. For example, according to our data the alkylcyclopropanes absorb in the region 1900–1800 Å and lower, while n- and iso-alkanes and also unstrained cyclanes (hexane, cyclohexane, heptane, etc.) with the same number of carbon atoms do not absorb down to 1700 Å.. This agrees with the singular behavior of cyclopropane compounds which has been explained by the distortion of the valence angles in the cyclopropane ring, which results in an unusual unsaturation of the carbon ring.

In the case of the four-membered carbonsilicon heterocyclic ring the bathochromic effect is commensurate with or even greater than in the case of the cyclopropane derivatives. This is apparently explained by the introduction into the ring of a silicon heteroatom. In connection with this we became interested in studying the UV spectra of cyclic compounds containing two heteroatoms of silicon. The spectrum of 1,1,3,3-tetramethyl-1,3-disilocyclobutane (II) is compared with the spectrum of the six-membered ring (III) and of the high molecular silomethylene polymer—$[(CH_3)_2SiCH_2]_n$ with ($n = 8 \cdot 10^4$) (IV) (see Figs. 2 and 3.)



II



III

III and IV have the same structural unit $Si(CH_3)_2CH_2$ as I and II, but it is likely that the most significant of the C—Si—C angles of their molecules are tetrahedral. The molecule III has an absorption band, the strength of which in the first approximation can be understood as a tripling of the absorption of $Si(C_2H_5)_4$. The small bathochromic shift of the band observed here bears witness to the weakness of the interaction of the group—$SI(CH_3)_2$—across the methylene cross link. It is possible to arrive at an analogous conclusion through the examination of the UV spectrum of IV. In spite of the very long length of its molecule, a strong shift, characteristic of even short chain molecules of the type $[Si(CH_2)_2]_n$ ($n = 2—55$)[2], is not observed. (The methylene cross link interferes with the interaction of silicon atoms in the chain. Even stronger "barriers" to the interaction of silicon atoms in the chain $[Si(CH_3)_2CH_2CH_2]_n$, (V) (Fig. 2) are the trimethylene groups, to which the hypsochromic shift in the spectra of polymers bears witness.)

As is evident from Fig. 3 the absorption band in the spectrum of II is observed in the region of ~2000 Å. Thus, it is obvious by comparison with (I) that the introduction of the second atom of silicon in the ring increases the bathochromic shift in the spectrum of four-membered rings. The singular structure of the four-membered ring leads us to believe that the methylene group here is not a "barrier" which disrupts the interaction of silicon atoms to the same extent to which this occurs in compounds with tetrahedral atoms.

The bathochromic shift of I and II is weakened (see Figs. 1 and 3) with the substitution of methyl groups on the silicon groups by chlorine atoms. The greater the number of chlorine atoms, the greater is the observed weakening. In this relationship I behaves in a manner analogous to the acyclic $(C_2H_5)_mSiCl_{4-m}$. Figure 1 is a visual illustration of this principle.

The UV spectra of I and II obtained in our work agree with earlier well-known factors about the unusually high level of the molecular refraction of these compounds [3]. This is not surprising, since both phenomena have a similar nature.

I was obtained as shown in [3]. II and III were synthesized from chloromethyldimethylchlorosilane and magnesium according to [4]; 1-chloro-1,3,3-tetramethyl-1,3-disilocyclobutane was obtained by A. V. Zelenoi by condensing chloromethyldimethylchlorosilane and chloromethylmethyldichlorosilane, using magnesium. The properties of these individual compounds agree with the given literature and the purity was verified by gas-liquid chromatography. The polymeric compounds IV and V were prepared according to [5] and [6].

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