INFRARED ABSORPTION SPECTRA AND STRUCTURE OF 1, 1, 4, 4-TETRASUBSTITUTED 1, 4-DISILACYCLOHEXANES

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The IR absorption spectra of 1, 1, 4, 4-tetramethyl- and 1, 1, 4, 4-tetraphenyl-1, 4-disilacyclohexanes have been studied. The group spectral analysis of these compounds shows that the silicon atoms have "barene" properties. The presence at about 980 cm^{-1} of one strong band (and not two) of C—C stretching vibrations in agreement with the selection rules confirms the chair form of the heterocycle.

The spectral properties of heterocyclic organosilicon compounds, 1, 4-disilacyclohexanes, have been studied very little up to the present time [1–3]. Nevertheless, these heterocycles are interesting not only in respect of their chemical properties but also for spectroscopic investigations. With these as examples it is possible to trace the "barene" effect of silicon atoms [1, 4, 5] and to obtain the information necessary to answer the question on the conformation of such systems.

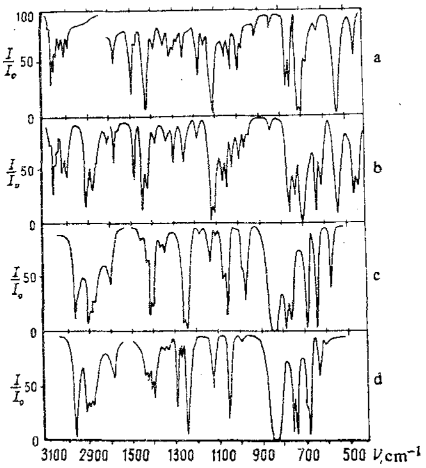
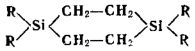


Fig. 1. IR spectra of: a) $(C_6H_5)_4$ Si (III); b) $(C_6H_5)_2$ Si $(CH_2CH_2)_2$ Si $(C_6H_5)_2$ (II) KBr tablets; c) $CH_3)_2$ Si $(CH_2CH_2)_2$ Si $(CH_3)_2$ (I); d) $(CH_3)_3$ Si CH_2CH_2 Si $(CH_3)_3$ (IV) crystals at −150° C.

In the present paper we describe the results of an investigation of the IR spectra of 1, 1, 4, 4-tetramethyl-1, 4-disilacyclohexane (I), 1, 1, 4, 4-tetraphenyl-1, 4-disilacyclohexane (II), and also tetraphenylsilane (III) and hexamethyldisilethane (IV). The vibrational spectra of complex molecules of organosilicon compounds of the type $R^1R^2R^3R^4Si$ are noteworthy by the fact that they are separated into the sum of the frequencies of the R_i fragments and the frequencies of the skeleton (stretching Si—C vibrations and deformation C—Si—C vibrations generally located below 700 cm^{-1}). This property, called the "barene" effect [1, 4, 5] greatly facilitates the identification of the spectrum of an unknown organosilicon compound.

Making use of this fact, we have carried out a group analysis of the IR spectrum of I (Fig. 1, c). Maxima at 690, 777, 820–855, 1247 and 1263, 1412, 2907, and 2967 cm^{-1} correspond, as is well known, to the frequencies of methyl groups attached to silicon atoms. Corresponding bands were observed in the spectrum of IV (Fig. 1, d). The remaining frequencies, 752, 978, 990 (very weak), 1060, 1076 (shoulder), 1132, 1410, and a doublet in the 2900 cm^{-1} region, belong to the heterocycle V.



A similar assignment of bands can be carried out in the case of the IR spectrum of II. From a comparison of the spectra of II and III (Fig. 1, a and b), it can be seen that they both contain a series of well-defined bands located above 700 cm^{-1} (707, 743, 857, 999, 1028, 1071, 1108, 1180, 1260, 1305, 1332, 1381, 1428, 1485, 1588, 3004, 3017, 3055 and 3066 cm^{-1}), relating to a phenyl radical attached to a silicon atom [7]. The remaining bands, 761, 976, 1055, 1115, 1412, and 2881, and 2910 cm^{-1}, characterize the heterocycle V. It is easy to identify them with the corresponding bands of compound I (Fig. 1, b and c).

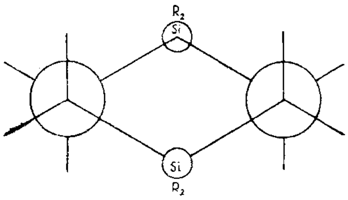


Fig. 2. Newman projection of the six-membered organosilicon heterocycle in the chair form.

In considering the structure of organosilicon heterocycles of type V, one must expect the presence of conformations analogous to the conformations of cyclohexane. Here the difference between the cyclic systems consists only in the fact that two (1, 4-) methylene groups of cyclohexane have been replaced in V by

$>Si(CH_3)_2$ groups, which also possess a tetrahedral arrangement of the bonds. As is well known, cyclohexane exists in the chair form and in the energetically less favorable boat form. The construction of the spatial model shows that the organosilicon heterocycle V most readily assumes a chair form free from internal stresses and consisting of two $-CH_2-CH_2-$ bridges in the gauche form connecting the silicon atoms (Fig. 2). The boat form is less likely since it consists of a system of two unstable ethylene bridges in the cis form. In addition, in this case it is spatially difficult to superpose two voluminous radicals (methyl or phenyl radicals) attached to the silicon atoms of the heterocycle. In actual fact, when the tetrahedral angles between the bonds of the C and Si atoms are observed, the distance between the closest ("bowsprit" [8]) points of the bonds of the Si—C radicals should be equal to the lengths of the C—C bond (1.54 Å). It is clear that neither two methyl groups [2 × 1.09 Å (2C—H) + 2 × 1.2 Å (2H) = 4.58 Å] nor, much less, two phenyl radicals can fit into this space. The difficulty is not eliminated even by a distortion of the boat with some internal rotation around the Si—C bonds of the ring.

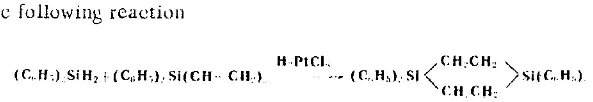
The above considerations are confirmed by spectroscopy. The object of the present work was not a complete interpretation of the frequencies of the compounds studied but only a consideration of the vibrations reflecting the conformation of the heterocycle. As these we may select the C—C stretching vibrations in the 1000 cm^{-1} region. In actual fact, the heterocycle V in the chair form is described by the symmetry group C_{2h} with a center of inversion. According to the selection rules, only one antisymmetric stretching vibration of the C—C type A_u is active in the IR spectrum of V and a symmetrical one of type A_g in the Raman spectrum. The conformation in the boat form is described by the symmetry group C_{2v} and that of a distorted boat by C_2. In this case both the symmetrical vibration A_1 and the antisymmetrical vibration B_2 of the C—C bond (for the C_2 group symmetry, A and B, respectively) are forbidden in the IR spectrum. Thus, the chair form is characterized by a single band of the C—C stretching vibrations and the boat form by two. In the spectrum of I (Fig. 1, c) there is a strong frequency of 978 cm^{-1} with a weak shoulder at 990 cm^{-1}. The convoluted ethylene bridges of the heterocycle V interact little with one another because of the "barene" property of the silicon atoms, thanks to which the IR spectrum is characteristic for the $SiCH_2CH_2Si$ moiety in the gauche form.

Let us now turn our attention to the 900–1050 cm^{-1} region in the IR spectrum of (IV) (Fig. 1, d) assuming the trans form with a zigzag arrangement of the atoms of the skeleton in the crystalline state. The conformation of this molecule belongs to the symmetry group C_{2h}, for which the stretching vibration of the C—C bond is not permitted and does not appear in the IR spectrum. The small peak at 992 cm^{-1} is apparently due to a combination frequency. In this region I has only one strong band, at 978 cm^{-1}, which characterizes the stretching vibrations of the C—C bond. The shoulder at 990 cm^{-1} is, as in the IR spectrum of IV, a combination frequency. The presence of only one strong band of the C—C vibration is in favor of the chair form of the heterocycle V considered. A corresponding band at 976 cm^{-1} also appears in the spectrum of II (Fig. 1, b). Thus, the stretching vibration of the C—C bond can be used as a convenient method for determining the conformation of chains of the XCH_2CH_2X type.

EXPERIMENTAL

1, 1, 4, 4-Tetramethyl-1, 4-disilacyclohexane (I) was obtained from 1, 2-bis(trimethylsilyl)ethane by a previously published method [1]. The structure of this compound was shown by a chromatographic comparison with a reference sample prepared from ethylene and dichlorodimethylsilane [6].

1, 1, 4, 4-Tetraphenyl-1, 4-disilacyclohexane (II) was obtained by the following reaction



$$(C_6H_5)_2SiH_2 + (C_6H_5)_2Si(CH=CH_2)_2 \xrightarrow{H_2PtCl_6} (C_6H_5)_2Si{<}^{CH_2CH_2}_{CH_2CH_2}{>}Si(C_6H_5)_2$$

The II was isolated from the reaction mixture by recrystallization from benzene and had mp 207.5°–208.5° C.* Found: C 79.76; 80.08; H 6.59; 6.49; Si 13.25; 13.62%. Calculated for $C_{28}H_{28}Si_2$, %: C 80.00; H 6.64; Si 13.3. At room temperature, compounds I and IV are liquids and II and III are solids.

A cryostat was used to obtain the spectra of I and IV in the crystalline state. Samples of II and III were prepared in the form of appropriate tablets with KBr. The recording of the IR spectra was carried out on a UR-10 infrared spectrometer (with a resolving power at 1000 cm^{-1} of 1.5 cm^{-1}).

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* The structure of 1, 1, 4, 4-tetraphenyl-1, 4-disilacyclohexane has been assigned to a material with mp 131°–134.5° C obtained from vinyldiphenylsilane [2]. However, it was later found that it was a mixture of different compounds.