INFRARED SPECTRA OF SOME SILACYCLOBUTANE DERIVATIVES AND THE STRUCTURE OF THE SILACYCLOBUTANE RING

V. T. Aleksanyan, G. M. Kuz'yants, V. M. Vdobin, P. L. Grinberg, and O. V. Kuz'min UDC 541.65

The IR spectra of a series of simple derivatives of silacyclobutane have been studied. The observed splitting of the Q-branches of Si-H and Si-D valence vibrations indicates that the silacyclobutane ring has a nonpolar structure.

It has been customary for a long time to assume that in compounds having a saturated four-membered carbon ring, and in their simple heterocyclic analogs, the ring has a planar configuration. This assumption is a natural consequence of the Baeyer strain theory. Bell [1] was the first to suggest the possibility of a non-planar dihedral structure for the skeleton of four-membered rings. The instability of the planar configuration was attributed by Bell to the conformation stress arising from repulsion between hydrogen atoms on adjacent methylene groups. In recent years the problem of the structure of four-membered rings has attracted greater attention and is the subject of numerous investigations. There is now no doubt that the molecules of cyclobutane and some of its simple alkyl and halogen derivatives do indeed have a non-planar carbon skeleton [2-4]. In other cases (cyclobutanone, methyl-ene cyclobutane) it has been established that their rings are planar [5, 6]. Information also exists on the structure of simple heterocyclic analogs of cyclobutane. Thus oxetane, 3-methyleneoxetane, and β -propiolactone have a planar configuration [7-9] whereas in thietane the ring is nonplanar [10].

There is at present very little information in the literature on the structure of that interesting cyclobutane analog, silacyclobutane, which contains one atom of silicon in the ring. Available electron-diffraction data [11] indicates a non-planar structure for the skeleton of 1-silacyclobutane and 1,1-dichloro-1-silacyclobutane. The non-planar structure of silacyclobutane has also been established by a study of its long wave infrared spectrum [12].

In the present work we have studied the IR spectra of silacyclobutane and some of its simple derivatives in order to clarify their structures. In analyzing the spectra obtained, particular attention has been given to the regions corresponding to the Si-H and Si-D valence vibrations. In practice, the non-planar ring structure leads to conformational isomerism owing to the resulting nonequivalence of the exocyclic bonds of the carbon and silicon atoms. By analogy with cyclohexane it is possible to speak of axial and equatorial positions for the C-Hand Si-H bonds. If thering inversion frequency, or, in other words, the frequency of the interchange between one conformation and the other, is not too great, absorption bands due to the valence vibrations of axial and equatorial Si⁻H bonds may be observed in the vibrational spectrum. We have taken as a model compound 1-deutero-1silacyclobutane, the two conformations of which must be thermodynamically almost equivalent, and therefore present in the mixture in approximately the same concentrations. From what has been said, it can be expected that in the IR spectra the Si-H and Si-D bands will be split into two components of approximately equal intensity.* It should be noted that, strictly speaking, the absence of splitting cannot be considered as evidence for a planar ring structure, since this may be a consequence of small differences between the frequencies of axial and equatorial Si-H and Si-D bonds. In the case of 1-monosubstituted compounds of silacyclobutane the splitting, although possible, may fail to be observed, but for a different reason: the concentration of one of the conformers may prove to be low because of a large difference in enthalpy between the axial and equatorial conformations. Of course, the splitting effects may be detected in other absorption bands as well, but the absorption region corresponding to v_{Si-H} and v_{Si-D} valence vibrations is most convenient for this investigation, since in this region overlap from bands due to other fundamental vibrations of the molecule does not occur. We have studied the

•Neglecting the possible small difference in the absorption intensities arising from the different modes of vibration of the axial and equatorial Si-H and Si-D bonds.

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TABLE 1

Compound	Frequency, cm ⁻¹
K SI D	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
	2166 (v_{Si-H}) 2169 (v_{Si-H}) 1545 (v_{Si-H})
Si CH3	$1548 (v_{Si-D})$ 1548 (v_{Si-D})
Si Cl	2169 (v_{Si-H}) 2172 (v_{Si-H})
Si CH ₃	2128 (v _{Si—H}) 2131 (v _{Si—H})





Fig. 1. IR-spectrum of gaseous 1-deutero-1-silacyclobutane in the Si-H valence vibration region.



Fig. 2. IR-spectrum of gaseous 1-deutero-1-silacyclobutane in the Si-D valence vibration region.

IR spectra at high resolution of the following substances in the gaseous form: 1-deutero-, 1-chloro-, 1-bromo-, 1-methyl, and 1-methyl-1-deutero-1-silacyclobutane. A preliminary study of the Q-branches in the compounds listed showed that they should not exceed 1 cm⁻¹ in width. The results of the completed study show that in all the compounds the Q-branches of the v_{Si-H} and v_{Si-D} valence vibration bands are split into two components of approximately equal intensity. The extent of the splitting amounts to 3-5 cm⁻¹ (Figs. 1-3 and Table 1). The splitting of the Q-branches into two components is also observed for most of the other fundamental bands. Hence, the observed pattern of the IR-spectra shows good qualitative agreement with that predicted for the non-planar model of the silacyclobutane ring structure.

Before drawing the final conclusion, other possible explanations for the splitting of the O-branches in the spectra under investigation should be considered.

One of the most probable causes of splitting is Fermi resonance of the v_{Si-H} vibration with an overtone or combination vibration. However, the experimental facts (small difference in frequencies of the components and their similarity in intensity) do not agree well with this hypothesis. In fact, where the resonance is sharp, a significantly greater separation between the resonating levels would be expected. Further, since the splitting is also observed for the majority of the other absorption bands, it must be supposed that for each of these vibrations there must be a corresponding adjacent resonating level, which is not very probable.

Another possible explanation for the splitting of absorption bands is the existence of transitions of the type $v_i + v_j - v_j$, where v_i is one of the fundamental vibrations and v_j is a low-frequency vibration of the same molecule (a "hot" transition). Such transitions may be rather intense in IR-spectra if v_j is very small and lie, with rare exceptions, on the long-wave side of the fundamental band (due to anharmonicity).

In fact, as can be seen in Figs. 1-3 (a similar behavior is shown by the other compounds studied), the less intense components has a higher rather than a lower frequency. Hence, the suggestion that "hot" transitions may be a cause of the observed Q-branch splitting is likewise not in good agreement with the experimental data.

It can thus be assumed that the most probable reason for the splitting of the Q-branches in the IR-spectra is axial-equatorial isomerism, the presence of which implies that the silacyclobutane ring in all the compounds studied has a non-planar configuration.

EXPERIMENTAL

The samples of 1-deutero-1-silacyclobutane, 1-methyl-1silacyclobutane and 1-deutero-1-methyl-1-silacyclobutane examined in the present work were obtained by reducing the corresponding chlorides with lithium deuteride, lithium aluminum hydride and lithium aluminum deuteride by the standard method [13]. Samples of 1-chloro- and 1-bromo-1-silacyclobutane were obtained by substituting halogen for hydrogen according to the general scheme:



Fig. 3. IR-spectrum of gaseous 1-methyl-1-silacyclobutane in the Si-H valence vibration region.



All the compounds obtained were purified by distillation in a fractionating column. The sample purity was checked by gasliquid chromatography; it amounted to not less than 98.5-99.5%. The IR-spectra were recorded on a Hitachi-Perkin-Elmer 225 grating spectrometer. The spectral slit width was 0.9 cm⁻¹ near 2140 cm⁻¹ and 0.7 cm⁻¹ near 1560 cm⁻¹. Calibration of the instrument was carried out in the usual way, with the aid of water vapor and deuterium chloride spectra. The error in measuring wavelength did not exceed 1 cm⁻¹. The IR-spectra of the gases were obtained using a standard 10 cm gas cell with KBr windows.

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