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The Molecular Forms of the Rotational Isomers of Ethylmethylsilane

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In a previous note[1] on the rotational isomerism of ethylmethylsilane, the existence of two rotational isomers was reported. However, the molecular forms of the isomers could not be conclusively determined. In the gaseous state, one of the present authors has since found by microwave spectroscopy[2] that one of the isomers was in the *trans* form. However, since the microwave spectra of this substance were too weak for them to be assigned to another isomer, he could not find whether or not one of the isomers was in the *gauche* form.

In the present note, we will consider the unknown molecular form of the isomer, using the vibrational spectra of an asymmetrically-deuterated species of ethylmethylsilane.

Experimental

A sample of an asymmetrically-deuterated species of ethylmethylsilane was prepared by the method of reducing $CH_3CH_2SiCl_2CH_3$ with an equimolar mixture of $LiAlH_4$ and $LiAlD_4$ in *n*-butyl ether.[3] A mixture of $CH_3CH_2SiH_2$-CH_3, $CH_3CH_2SiD_2CH_3$, and $CH_3CH_2SiHDCH_3$ was thus obtained and was used for the measurements without further attempts at isolation. In order to find the assignments of the spectra, the corresponding mixture of dimethylsilane and $(CH_3)_2SiH_2$ and $(CH_3)_2SiD_2$ were also prepared from dimethyldichlorosilane by a similar method.

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[1] M. Hayashi, K. Ohno, and H. Murata, This Bulletin, **45**, 298 (1972).

[2] M. Hayashi and C. Matsumura, *ibid.*, **45**, 732 (1972).

[3] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

The infrared spectra in the region from 200 to 4000 cm^{-1} were recorded in the gaseous, liquid, and crystalline states with a Perkin-Elmer instrument (model 621), using the same technique as has been described in the previous note.

Results and Discussion

As is shown in Fig. 1, since the two *gauche* forms come not to be equivalent when one of the hydrogens of the SiH$_2$ group is replaced by a deuterium, the spectra of the *gauche* isomer are expected to be split into doublets, while the spectra of the *trans* isomer are singlets, without regard to the asymmetrical deuteration.

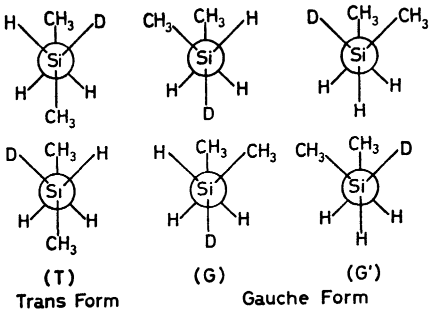

Fig. 1. Rotational isomers of CH$_3$CH$_2$SiHDCH$_3$.

In Fig. 2, the observed infrared spectra in the region from 300 to 600 cm^{-1} are shown for the mixture of CH$_3$CH$_2$SiH$_2$CH$_3$, CH$_3$CH$_2$SiD$_2$CH$_3$, and CH$_3$CH$_2$SiHDCH$_3$ species, where the solid and the dotted lines indicate the spectra in the liquid and in the crystalline states respectively. Since the pure sample of CH$_3$CH$_2$SiHDCH$_3$ can not be prepared at present, the spectra for this species must be found from the spectra of the mixture. For this purpose, the spectra in the liquid state for the corresponding species of dimethylsilane are considered as suitable references; they are also shown in Fig. 2.

The rocking mode of the SiH$_2$ group is expected around 480 cm^{-1}, which is probably well localized from the other modes; it is expected to be shifted to the region around 390 cm^{-1} for the deuterated species with the SiD$_2$ group. For dimethylsilane, it is found at 476 cm^{-1} for the SiH$_2$ species and at 385 cm^{-1} for the SiD$_2$ species. There are two additional bands at 496 and 415 cm^{-1} for the mixture besides the bands due to the SiH$_2$ and SiD$_2$ species. Therefore, they can be assigned to the SiHD deformation vibrations, which originate from the twisting and rocking modes.

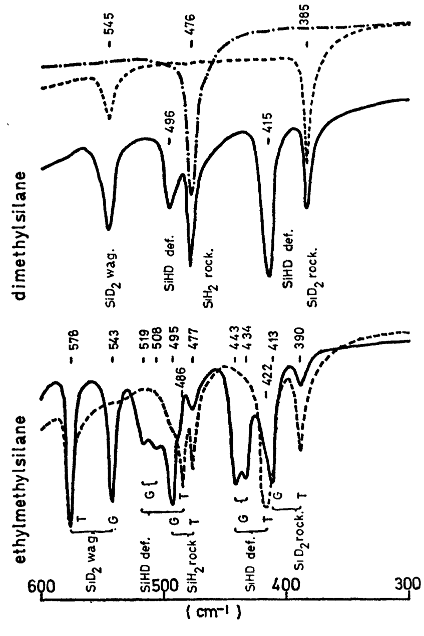

Fig. 2. Observed infrared spectra of dimethylsilane and ethylmethylsilane.

Upper: —— indicates the spectra of the mixture for (CH$_3$)$_2$SiH$_2$, (CH$_3$)$_2$SiD$_2$, and (CH$_3$)$_2$SiHD.
—·— indicates the spectra of (CH$_3$)$_2$SiH$_2$.
----- indicates the spectra of (CH$_3$)$_2$SiD$_2$.

Lower: Solid and dotted lines indicate the spectra of the mixture for CH$_3$CH$_2$SiH$_2$CH$_3$, CH$_3$CH$_2$SiD$_2$CH$_3$, and CH$_3$CH$_2$SiHDCH$_3$ in the liquid and the crystalline states respectively.

For ethylmethylsilane, in the spectra for the mixture four bands are seen, at 422, 438, 486, and 513 cm^{-1}, attributable to the CH$_3$CH$_2$SiHDCH$_3$ species; the bands at 422 and 486 cm^{-1} are shoulders of the strong bands due to the other species. In the crystalline state, the bands at 422 and 486 cm^{-1} persist, while the two other bands at 438 and 513 cm^{-1} vanish. The persisting bands are obviously singlets, while the vanishing bands are doublets with spacings of 9 and 11 cm^{-1} respectively.

Therefore, it can be concluded that the isomer persisting in the crystalline state is definitely the *trans* and that the other isomer vanishing in the crystalline state is not the molecular form with a plane of symmetry such as the *trans* and *cis* forms, but is probably a *gauche* form, in which two hydrogens attached to the Si atom come not to be equivalent for the asymmetrically-deuterated species.

For the other modes, the assignments of the observed spectra seem to be difficult since the spectra due to three different species overlap. Therefore, no obvious evidence is obtained for the molecular form from these modes of vibrations.