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MICROWAVE SPECTRA OF cis- AND skew-METHYLVINYLSILANE

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Microwave spectra of cis and skew isomers of methylvinylsilane were studied in relation to their molecular structures, dipole moments and barriers to internal rotation of the methyl group. The results were compared with those of cis and skew isomers of butene-1.

Recently, we have measured microwave spectra of cis and skew isomers of methylvinylsilane in order to compare the results with those of butene-1[1)] which is one of related molecules.

For each isomer, thirty-six transitions with $J \leqq 10$ were assigned. Some of the observed spectra exhibited doublet structures due to internal rotation of the methyl group. The rotational constants listed in Table 1 were obtained so as to fit the observed frequencies of transitions with $J \leqq 3$ in a rigid rotor expression. The centrifugal distortion effects were neglected in the calculation. The "A" component frequencies were used if the spectra were doublets.

The rotational constants were calculated for a model which has a set of

Table 1. Rotational Constants and Structural Parameters

cis isomer	obsd[a)]	δ(I)[b)]	δ(II)[b)]	δ(III)[b)]	skew isomer	obsd[a)]	δ(I)[b)]
A	9599.33(20)	0.77	-0.03	-0.29	A	13728.17(8)	0.02
B	3984.69(5)	-1.79	-0.20	-0.48	B	3048.78(7)	-0.26
C	2962.59(4)	-1.12	-0.20	-0.42	C	2825.27(2)	-0.34

Structural Parameters for δ(I)

Skeleton; r(C=C)=1.347Å, r(CH-Si)=1.853Å, r(CH$_3$-Si)=1.867Å, α(CSiC)=110°59', and α(CCSi)=122°53'; CH$_3$; r(CH$_s$)=r(CH$_a$)=1.095Å, α(SiCH$_s$)=α(SiCH$_a$)=110°56', α(H$_s$CH$_a$) =α(H$_a$CH$_a$)=108°; SiH$_2$; r(SiH)=1.483Å, α(HSiC)=109°30', α(HSiH)=107°50'; =CH; r(CH) =1.094Å, α(C=CH)=117°59', α(SiCH)=119°8'; CH$_2$; r(CH)=1.097Å, α(HCH)=119°4', α(H$_t$C=C)=120°38', α(H$_c$C=C)=120°18'; H$_t$ and H$_c$ are H atoms at the trans and cis positions against the Si atom, respectively.

For δ(II), δ(CCSi)=124°38'. For δ(III), δ(CSiC)=112°14'.

a) In MHz. Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviation.

b) $\delta(X) = 100(R_{obsd} - R_{calctd})/R_{obsd}$. R = A, B, or C. X = I, II, or III.

structural parameters transferred from the reported r_s structures of dimethylsilane2) and vinylsilane3) and has dihedral angles of 0° and 120° for the cis and skew isomers, respectively. In Table 1, δ(I) indicates the deviations of the calculated rotational constants from the observed in %. The agreement between the observed and calculated rotational constants is excellent for the skew isomer, while it is worse for the cis isomer. However, a better agreement is also obtained for the cis isomer, if we assume a slightly larger value for either the CCSi or CSiC angle than the transferred value (δ(II) and δ(III) in Table 1). Similar increases in the angles of the cis isomer from those of the skew isomer were also reported for butene-1.

From the observed splittings of the spectra, barriers to internal rotation of the methyl group were calculated to be 1800 ± 20 and 1585 ± 15 cal/mol for the cis and skew isomers, respectively, assuming Structure I. The barrier for the cis isomer is higher than that for the skew isomer by about 215 cal/mol in a similar manner to the isomers of butene-1.

Dipole moments were determined by Stark effect measurements of transitions. For the cis isomer, the dipole moment was $\mu_a = 0.222 \pm 0.005$, $\mu_b = 0.692 \pm 0.007$ and $\mu_{total} = 0.727 \pm 0.008$ D making an angle of 17°47' with the "b" inertial axis and making an angle of either 12°15' (Direction A) or 47°49' (Direction B) with the bisector of the HSiH angle. Since the dipole moment of vinylsilane makes an angle of about 13° with the symmetry axis of the SiH_3 group, Direction A is probably the correct one for cis-methylvinylsilane. For the skew isomer, the Stark coefficients for the observed transitions contain only slight dependences on μ_a and μ_c components of the dipole moment so that the determination of these components is difficult at present. However, if the direction of the dipole moment is nearly along the bisector of the HSiH angle, μ_a and μ_c values are estimated to be less than 0.07 D. Assuming μ_a and $\mu_c = 0$, μ_b was obtained as $\mu_b = 0.665 \pm 0.008$ D and μ_{total} can be estimated to be 0.68 D at most. Then, the dipole moment of the cis isomer is probably larger by about 0.05 D than that of the skew isomer. A similar tendency of the dipole moments was also reported for butene-1.

The work is in progress on the other isotopic species.

References

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