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# Syntheses, Infrared and Raman Vibrational Spectra, Normal Coordinate Analyses and $^{29}$Si-NMR-Spectra of Halogenated Disilanes $X_nSi_2H_{6-n}$ (X = F, Cl, Br, I)

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## 1. INTRODUCTION

While the spectroscopic properties of halogenated ethanes have been studied quite extensively in the past, little is known of their Si analouges. The reason presumably is the high reactivity of halogenated disilanes, as they react vigorously with water and inflame spontaneously on contact with air. They may also decompose explosively on contact with metal surfaces Apart from these difficulties, they are also not easily synthesized. Reactions of $Si_2H_6$ with various halogenating agent such as $Cl_2$[1], $BCl_3$ [2], $SnCl_4$ [3], HBr [4], HI [5] or $BBr_3$ [6] and $SnBr_4$ [7] are not only dangerous, but they almost always lead to mixtures of disilanes that are difficult or impossible to separate.

## 2. SYNTHESES

All possible bromo and iododisilanes $Br_nSi_2H_{6-n}$ and $I_nSi_2H_{6-n}$ (n = 1,2,3,4,5), including isomers, and a number of chlorodisilanes were synthesized from $Ph_nSi_2H_{6-n}$ with either gaseous HCl, HBr and HI (catalyzed by $AlCl_3$, $AlBr_3$ or $AlI_3$) or liquid hydrogen halides.

$$Ph_nSi_2H_{6-n} + nHX \longrightarrow X_nSi_2H_{6-n} + nC_6H_6$$

However, disilanes with low boiling points (e.g. $BrSi_2H_5$, $BrH_2SiSiH_2Br$, $ClH_2SiSiH_2Cl$ or $Cl_2HSiSiHCl_2$) cannot be separated from benzene formed in the reaction because of the formation of azeotropic mixtures. In these cases, mesityldisilanes or naphthyldisilanes (mesityl: 2,4,6-trimethylphenyl) were used

$$\begin{aligned} NaphthH_2SiSiH_2Naphth + HBr &\longrightarrow BrH_2SiSiH_2Br \\ MesH_2SiSiH_2Mes + HCl_l &\longrightarrow ClH_2SiSiH_2Cl \\ Mes_2HSiSiHMes_2 + HCl_l &\longrightarrow Cl_2HSiSiHCl_2 \end{aligned}$$

## 3. VIBRATIONAL SPECTRA

Liquid phase and gas phase infrared spectra as well as liquid phase Raman spectra of all disilanes were measured. As an illustration, Figs. 1 and 2 show the spectra of $Cl_2HSiSiHCl_2$ and $BrH_2SiSiH_2$ Br

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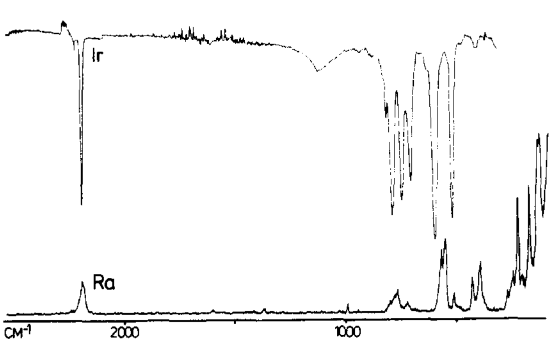

Fig. 1: Gas phase Ir spectrum and Raman spectrum (liquid) of $Cl_2HSiSiHCl_2$

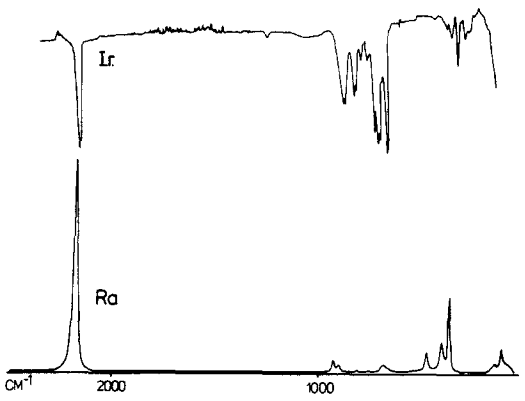

Fig. 2: Gas phase Ir spectrum and Raman spectrum (liquid) of $BrH_2SiSiH_2Br$

The number of observed lines clearly exceeds the number predicted for each single rotamer, proving the existencxe of both rotamers in the liquid and gas

$$\text{anti, } C_{2h} : \Gamma_{vib} = 6\,Ag(Ra) + 3\,Au(Ir) + 3\,Bg(Ra) + 5\,Bu(Ir)$$

$$\text{gauche, } C_2 : \Gamma_{vib} = 9\,A\,(Ra, Ir) + 8\,B(Ra, Ir)$$

phase at room temperature. Rotational isomerism of halogenated disilanes was also established by electron diffraction of $Br_2HSiSiHBr_2$ [8], $I_2HSiSiHI_2$ and $IH_2SiSiH_2I$ [9]. Energy differences between the rotamers are typically small (±2.5 $kJmol^{-1}$ from ED), with barrier heights ranging from 1-5 $kJmol^{-1}$ ($FSi_2H_5$: 4,4 $kJmol^{-1}$ [10]). As can be observed from Fig. 3, both rotamers of $BrH_2SiSiH_2$ Br are present in the liquid (298 K) as well as in the solid state (140 K).

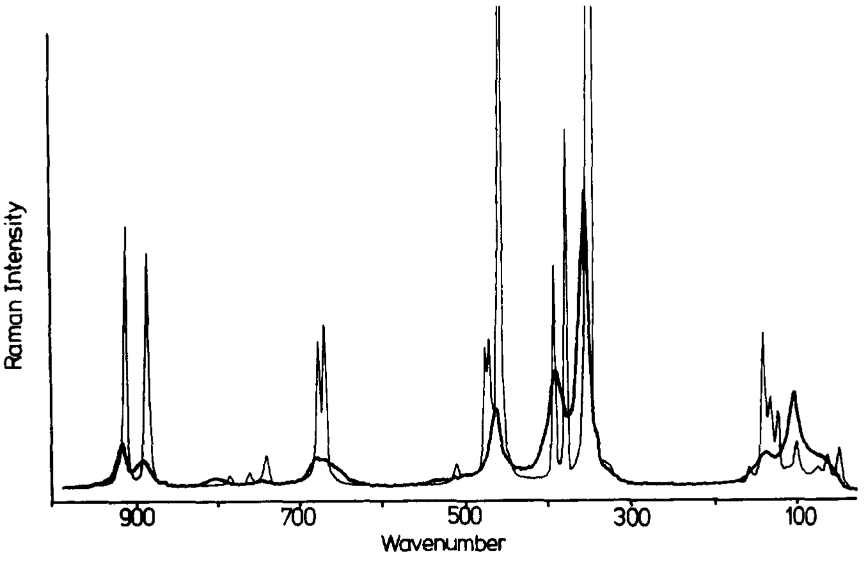

Fig. 3: Raman spectra of $BrH_2SiSiH_2Br$ at 298 K (bold) and 140 K

## 4. NORMAL COORDINATE ANALYSES

Normal coordinate analyses have been carried out for all disilanes using the FG method. Typically, the spectra of the anti rotamers (including the spectra of deuterated compounds in many cases) were calculated and the force constants obtained were used for the calculations of the gauche rotamers, using the correlation tables [11]. Local symmetry coordinates were used for $SiH_2$ ($\delta_s$, $\gamma$, $\tau$ and $\rho SiH_2$) or $SiX_2$ groups, and ab initio calculations of vibrational frequencies were performed to support the NCA. Table 1 summarizes the results for $BrH_2SiSiH_2Br$. The SiSi valence force constants generally increase with increasing number of halogen atoms in the molecule and decrease in the order F > Cl > Br > I. This is also nicely reproduced by ab initio calculations [12].

Table 1: Calculated and observed normal vibrations [$cm^{-1}$] of anti and gauche $BrH_2SiSiH_2Br$

| | | anti $BrH_2SiSiH_2Br$ | | | | gauche $BrH_2SiSiH_2Br$ | | |
|---|---|---|---|---|---|---|---|---|
| species | mode | exp. | NCA | ab initio* | species | exp. | NCA | ab initio* |
| $A_g$(Ra) | $\nu_sSiH_2$ | 2168 | 2168 | 2166 | A(Ra,Ir) | 2168 | 2168 | 2165 |
| | $\delta_sSiH_2$ | 925 | 921 | 946 | | 930 | 924 | 949 |
| | $\gamma SiH_2$ | 816 | 817 | 838 | | 790 | 806 | 825 |
| | $\nu SiSi$ | 471 | 477 | 457 | | 478 | 479 | 461 |
| | $\nu SiBr$ | 363 | 366 | 386 | | 363 | 341 | 347 |
| | $\delta SiSiBr$ | 112 | 108 | 107 | | 73 | 90 | 80 |
| $A_u$(Ir) | $\nu_{as}SiH_2$ | 2181 | 2181 | 2177 | | 2181 | 2181 | 2170 |
| | $\rho SiH_2$ | 397 | 400 | 360 | | 445 | 434 | 449 |
| | $\tau SiH_2$ | - | 649 | 646 | | 678 | 649 | 651 |
| $B_g$(Ra) | $\nu_{as}SiH_2$ | 2168 | 2168 | 2168 | B(Ra,Ir) | 2168 | 2168 | 2158 |
| | $\rho SiH_2$ | 520 | 517 | 550 | | 478 | 489 | 511 |
| | $\tau SiH_2$ | 685 | 686 | 689 | | 678 | 686 | 670 |
| $B_u$(Ir) | $\nu_sSiH_2$ | 2181 | 2181 | 2161 | | 2181 | 2181 | 2171 |
| | $\nu SiBr$ | 421 | 418 | 397 | | 386 | 414 | 382 |
| | $\delta_sSiH_2$ | 930 | 921 | 934 | | 875 | 918 | 922 |
| | $\gamma SiH_2$ | 739 | 738 | 748 | | 775 | 752 | 784 |
| | $\delta SiSiBr$ | 73 | 92 | 66 | | 148 | 141 | 135 |

*scaled by 0.92

## 5. $^{29}$Si-NMR-SPECTRA

$^{29}Si$ chemical shifts and $^{29}Si^{29}Si$- one bond ($^1J$) coupling constants were measured for all disilanes using INADEQUATE pulse sequences [13]. Table 2 summarizes the data.

Table 2: $^{29}Si$ chemical shifts [ppm, TMS] and SiSi coupling constants [Hz] of bromo- and iododisilanes

| | X = Br | | | X = I | | |
|---|---|---|---|---|---|---|
| compound | δ(Si)* | δ(Si) | $^1$J(SiSi) | δ(Si*) | δ(Si) | $^1$J(SiSi) |
| $XH_2Si^*SiH_3$ | -42,3 | -94,3 | 86,6 | -81,1 | -93,4 | 83.4 |
| $X_2HSi^*SiH_3$ | +5,0 | -85,1 | 98,6 | | | |
| $XH_2SiSiH_2X$ | | -45,2 | 98±2 | | -82,4 | 92,4 |
| $X_2HSi^*SiH_2X$ | -21,1 | -43,9 | 113,6 | -92,1 | -77,0 | 97,8 |
| $X_3Si^*SiH_3$ | -20,1 | -75,3 | 117,7 | -149,4 | -67,5 | 97,8 |
| $X_3Si^*SiH_2X$ | -29,4 | -40,1 | 138,8 | -155,1 | -69,2 | 107,5 |
| $X_2HSiSiHX_2$ | | -24,8 | 137,2 | | -89,7 | 106,9 |
| $X_3SiSiHX_2$ | -34,2 | -24,9 | 171,6 | -153,0 | -86,5 | 119,2 |

One bond SiSi coupling constants increase with increasing sum of the electronegativities of the substituents (ΣEN), a least square fit resulting in the relation

$$J(Hz) = 781{,}8 - 112{,}8\ (\Sigma EN) + 4{,}51\ (\Sigma EN)^2$$

Very large SiSi coupling constants are predicted for fluorodisilanes (491,6 Hz for $F_5Si_2H$)

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