

# Proton and Deuterium Magnetic Resonance Studies of Methylsilane and Methylgermane Dissolved in a Nematic Liquid Crystal

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**Abstract:** Proton and deuterium magnetic resonance spectra are reported for  $\text{CD}_3\text{SiH}_3$ ,  $\text{CH}_3\text{SiD}_3$ ,  $\text{CD}_3\text{GeH}_3$ , and  $\text{CH}_3\text{GeD}_3$  dissolved (under pressure) in the nematic phase of EBBA. From the results we have calculated several molecular parameters such as the ratio of interatomic distances, bond angles, and deuterium quadrupole coupling constants. The results are in good agreement with microwave and other data for these molecules. We were, however, unable to deduce the predominant conformation of these molecules and determine the sign of  $J_{\text{HD}}$ . The proton chemical shift anisotropies in the  $-\text{CH}_3$ ,  $-\text{SiH}_3$ , and  $-\text{GeH}_3$  groups are estimated from measurements of the proton chemical shifts in the nematic and isotropic phases.

The analysis of the nuclear magnetic resonance (nmr) spectra of molecules dissolved in the nematic phase of liquid crystals may provide us with data on their molecular structure, quadrupole coupling constants ( $e^2qQ$ ), and the anisotropy of the chemical shift.<sup>1-7</sup> Information obtained in this manner complements data derived from other techniques such as microwave spectroscopy (molecular geometry and  $e^2qQ$ 's), solid state nmr ( $e^2qQ$  and chemical shift anisotropy), nuclear quadrupole resonance ( $e^2qQ$ ), etc. The interpretation of the nmr spectra of fairly complicated molecules dissolved in liquid crystals is relatively simple and this is an advantage over other techniques, in particular microwave spectroscopy. On the other hand the information contained in the nmr spectra is incomplete and the precision of the results is usually lower.

In this paper we report the measurements and interpretation of the nmr spectra of methylsilane and methylgermane dissolved in the nematic and isotropic phases of a liquid crystal (EBBA).<sup>8</sup> Since the interpretation is greatly facilitated by partial deuteration, we have prepared and measured the spectra of  $\text{CD}_3\text{SiH}_3$ ,  $\text{CH}_3\text{SiD}_3$ ,  $\text{CD}_3\text{GeH}_3$ , and  $\text{CH}_3\text{GeD}_3$ . Some measurements were also performed on  $\text{CH}_3\text{GeH}_3$ . The results are compared with microwave data which are available for these molecules.<sup>9-11</sup>

## Experimental Section

**Materials.**  $\text{CH}_3\text{SiD}_3$  was synthesized from the commercially available (Fluka)  $\text{CH}_3\text{SiCl}_3$  by reduction with  $\text{LiAlD}_4$ .<sup>12</sup>  $\text{CD}_3\text{SiH}_3$  was obtained by the Grignard reaction of  $\text{SiH}_3\text{Br}$  with  $\text{CD}_3\text{Br}$  (Merck).  $\text{SiH}_3\text{Br}$  was obtained by the bromination of silane.<sup>13</sup>

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$\text{CD}_3\text{GeH}_3$  was obtained by the Grignard reaction of  $\text{GeH}_3\text{Br}$  with  $\text{CD}_3\text{Br}$ .  $\text{GeH}_3\text{Br}$  was obtained by the bromination of  $\text{GeH}_4$ .<sup>14</sup>  $\text{GeH}_4$  was obtained by the reduction of  $\text{GeO}_2$  with  $\text{KBH}_4$  in acidic medium.<sup>15</sup>  $\text{GeD}_3\text{CH}_3$  was prepared by the Grignard reaction of  $\text{GeD}_3\text{Br}$  and  $\text{CH}_3\text{Br}$ .  $\text{GeD}_3\text{Br}$  was obtained by bromination of  $\text{GeD}_4$ .<sup>14</sup>  $\text{GeD}_4$  was prepared from  $\text{GeH}_4$  and  $\text{D}_2\text{O}$  in the presence of KOD at 70°.  $\text{CH}_3\text{GeH}_3$  was obtained by the Grignard reaction of  $\text{GeH}_3\text{Br}$  with  $\text{CH}_3\text{I}$ . All final products were purified by vacuum distillation at low temperature.

All compounds were dissolved in *p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA, obtained from Vari-Light Corp.) under pressures of 6 to 25 atm. The EBBA was carefully thaw-freeze degassed before the materials were introduced. Samples were sealed in 5-mm o.d. Pyrex tubes (504 PP from Wilmad Corp.).

Measurements in samples where the solute concentration is low (*i.e.*, the total pressure in the sample tube is low) have the advantage that spectral resolution is better and consequently the precision in determining the line position is higher. Whenever possible (spectra of the main proton lines) this procedure was adopted and the total pressure in the sample tubes was kept at 6-10 atm. On the other hand, increase of the pressure increases the solute concentration and thus the signal/noise ratio is improved. For some measurements (such as proton satellite spectra or deuterium spectra) the application of high pressures (20-25 atm) was advantageous. In the following section where the results are reported (Tables I and II) these two sets of experiments will be denoted as "low (or high) pressure samples."

**Nmr Measurements.** All spectra were taken on a Bruker HFX-10 nmr spectrometer. Proton spectra were recorded at 90 MHz using  $\text{CF}_3\text{COOH}$  contained in an eccentric 10-mm o.d. tube or in a capillary, as external lock. In the isotropic phase measurements were performed in 5-mm o.d. tubes using one of the liquid crystal resonances for internal lock. In some cases, in the isotropic phase, the samples were also spun. The proton satellites due to  $^{13}\text{C}$  and  $^{29}\text{Si}$  were recorded with the aid of a Varian C-1024 CAT (200-500 passages). In some cases the deuterons were decoupled with a broad-band decoupler operating at 13.82 MHz. We have failed to observe the satellites due to  $^{73}\text{Ge}$  ( $I = 9/2$ ) in  $\text{CD}_3\text{GeH}_3$ . Deuterium spectra were recorded at 13.82 MHz without the use of a lock. The temperature was kept constant with the aid of the Bruker B-ST 100/700 temperature controller. All samples were allowed to equilibrate in the probe for a few hours before the spectra were recorded.

## Results and Discussion

In all compounds, except for  $\text{CH}_3\text{GeH}_3$ , the proton spectra consist of a 1:2:1 triplet where each resonance is further split into a 1:3:6:7:6:3:1 septet by the interaction with the deuterons. Also observed are the

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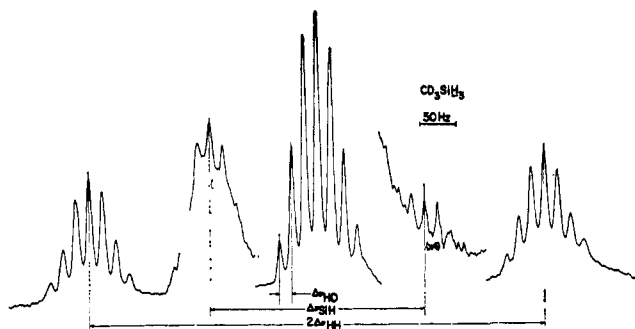


Figure 1. Proton nmr spectrum of  $\text{CD}_3\text{SiH}_3$  in EBBA at  $19^\circ$ . The notations for the splittings are indicated.

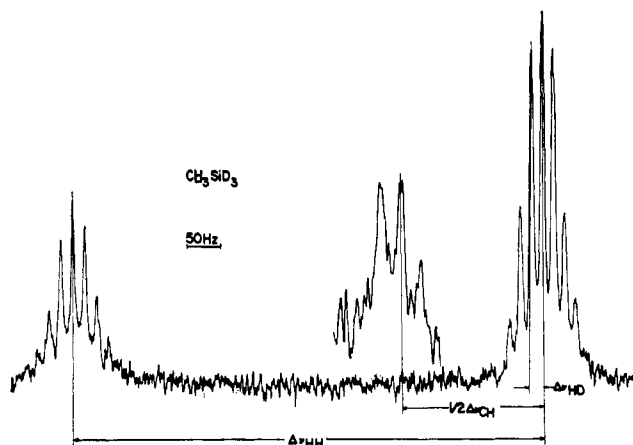


Figure 2. Proton nmr spectrum of  $\text{CH}_3\text{SiD}_3$  in EBBA. The high-field resonances of the triplet and of the  $^{13}\text{C}$  satellites are not shown ( $t = 19^\circ$ ).

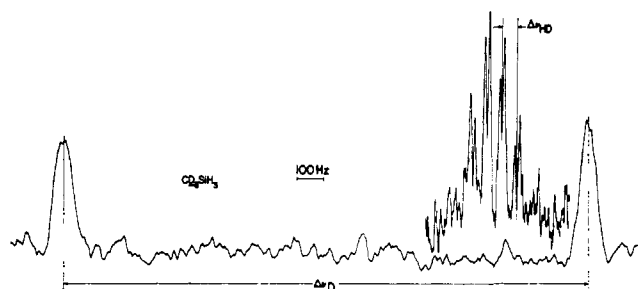


Figure 3. Deuterium nmr spectrum of  $\text{CD}_3\text{SiH}_3$  in EBBA. The expanded (slow passage) spectrum of one of the resonances is included and shows the splittings into a quartet due to the interactions with the protons ( $t = 19^\circ$ ).

satellites due to the interaction with  $^{13}\text{C}$  or  $^{29}\text{Si}$  which consist of a doublet, each component of which is split into a septet by the deuterons. Deuterium spectra consist of a 1:1 doublet where each line is further split into a quartet by the interaction with the protons. The proton spectrum of  $\text{CH}_3\text{GeH}_3$  in the nematic phase consists of about 36 lines.

Figures 1–5 show some of the proton and deuterium spectra of  $\text{CD}_3\text{SiH}_3$ ,  $\text{CH}_3\text{SiD}_3$ ,  $\text{CD}_3\text{GeH}_3$ , and  $\text{CH}_3\text{-GeD}_3$ . The notations of the splittings used in the interpretation are shown in the figures. Schematic diagrams of the  $\text{CH}_3\text{SiD}_3$  and  $\text{CD}_3\text{SiH}_3$  molecules are shown in Figure 6. Similar diagrams hold for  $\text{CH}_3\text{-GeD}_3$  and  $\text{CD}_3\text{GeH}_3$ . The notations of the distances and angles are marked in the figure.

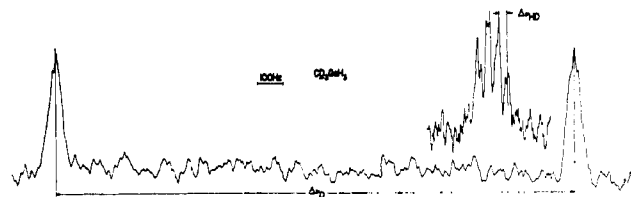


Figure 4. Deuterium nmr spectrum of  $\text{CD}_3\text{GeH}_3$  in EBBA at  $19^\circ$ . One resonance is expanded to show the splittings.

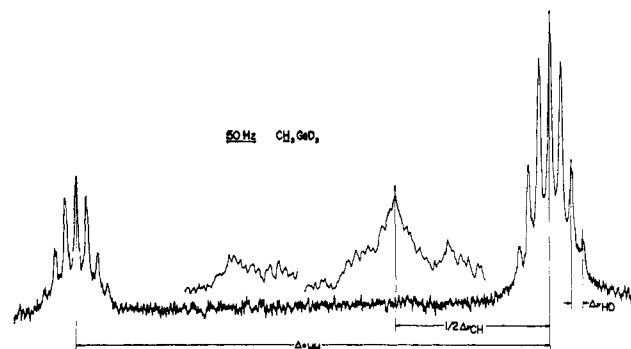


Figure 5. Proton nmr spectrum of  $\text{CH}_3\text{GeD}_3$  in EBBA at  $26^\circ$ .

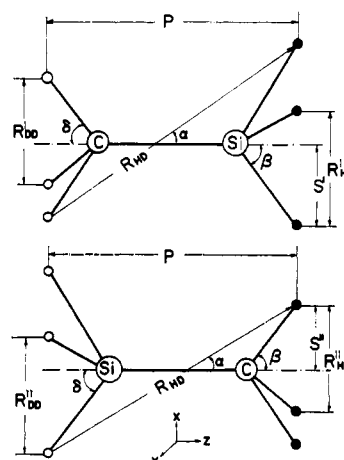


Figure 6. Schematic diagrams of  $\text{CD}_3\text{SiH}_3$  (top) and  $\text{CH}_3\text{SiD}_3$  (bottom) showing the notations of interatomic distances and angles used in the text. An analogous diagram can be drawn for  $\text{CD}_3\text{GeH}_3$  and  $\text{CH}_3\text{GeD}_3$  where the same notations were used.

In the interpretation of the spectra of molecules with  $C_{3v}$  symmetry of the type  $\text{CH}_3\text{YD}_3$  or  $\text{YH}_3\text{CD}_3$  ( $\text{Y} = \text{Si}$  or  $\text{Ge}$ ), the following general expressions apply<sup>1-3</sup>

$$\Delta\nu_{\text{HH}} = \left(\frac{3}{2}\right)D_{\text{HH}} \quad (1)$$

where

$$D_{\text{HH}} = (\hbar\gamma_{\text{H}}^2/2\pi R_{\text{HH}}^3)S_{zz} \quad (1a)$$

$R_{\text{HH}}$  is the interproton distance and  $S_{zz}$  is the ordering parameter of the  $C_{3v}$  axis

$$\Delta\nu_{\text{HD}} = D_{\text{HD}} + J_{\text{HD}} \quad (2)$$

where

$$D_{\text{HD}} = -(\hbar\gamma_{\text{H}}\gamma_{\text{D}}/2\pi) \left\langle \frac{(3 \cos^2 \alpha - 1)}{R_{\text{HD}}^3} \right\rangle S_{zz} \quad (2a)$$

$\langle \rangle$  denotes the average over the angle  $\alpha$  and the proton-deuterium distance,  $R_{\text{HD}}$ . The angle  $\alpha$  is shown in

**Table I.** Experimentally Measured Quantities (Splittings Given in Hz and Temperatures in °C)

Compd	Nematic phase					Isotropic phase		
	<i>t</i>	$\Delta\nu_{\text{HH}}$	$\Delta\nu_{\text{HD}}$	$\Delta\nu_{\text{CH}}$ OR $\Delta\nu_{\text{SiH}}$	$\Delta\nu_{\text{D}}$	<i>t</i>	$J_{\text{HD}}$	$J_{\text{CH}}$ OR $J_{\text{SiH}}$
CD <sub>3</sub> SiH <sub>3</sub>	19	315.1 ± 0.8	18.0 ± 0.1	298.3 ± 0.4 <sup>a</sup>	1955 ± 8	27		-191 ± 0.6 <sup>a</sup>
	26	585.5 ± 1.0 <sup>b</sup>	34.4 ± 0.1 <sup>b</sup>			37		-191 ± 0.6 <sup>a</sup>
CH <sub>3</sub> SiD <sub>3</sub>	19	688.5 ± 0.8	16.2 ± 0.1	413.7 ± 0.5 <sup>a</sup>	891 ± 5	26	+0.69 ± 0.04	+121.2 ± 0.3 <sup>a</sup>
	26	1310 ± 5 <sup>b</sup>	31.6 ± 0.2 <sup>b</sup>			26	+0.69 ± 0.04	
CD <sub>3</sub> GeH <sub>3</sub>	19	275 ± 1	15.8 ± 0.1		2037 ± 8		+0.65 ± 0.01 <sup>c</sup>	
	26	447.5 ± 1.0 <sup>b</sup>	27.0 ± 0.2 <sup>b</sup>					
CH <sub>3</sub> GeD <sub>3</sub>	26	874 ± 3	19.2 ± 0.2	535 ± 1 <sup>a</sup>	1061 ± 5		+0.65 ± 0.01 <sup>c</sup>	+128.9 ± 0.5 <sup>a</sup>
Mixture of 1:1 CH <sub>3</sub> SiH <sub>3</sub> - CH <sub>3</sub> SiD <sub>3</sub>	19	252.0 ± 1.5						
Mixture of 1:1 CD <sub>3</sub> GeH <sub>3</sub> - CH <sub>3</sub> GeD <sub>3</sub>	18	382 ± 2						
		1053 ± 4						

<sup>a</sup> Taken with a CAT. <sup>b</sup> Low-pressure samples. <sup>c</sup> Calculated using  $J_{\text{HD}} = (\gamma_{\text{D}}/\gamma_{\text{H}})J_{\text{HH}}$  from the value of  $J_{\text{HH}}$  measured in CH<sub>3</sub>GeH<sub>3</sub> at 42°.

Figure 6.  $J_{\text{HD}}$  is the indirect spin-spin coupling constant between H and D atoms. This value is measured in the isotropic phase; however, its sign could not be determined from our nmr data (a detailed exposition of this problem is given in the Appendix). We have therefore used the assignment given by Schumann and Dreeskamp<sup>17</sup> who found that  $J_{\text{HD}} > 0$  in compounds similar to ours

$$\Delta\nu_{\text{CH}} = D_{\text{CH}} + J_{\text{CH}} \quad (3)$$

where

$$D_{\text{CH}} = -(\hbar\gamma_{\text{H}}\gamma_{\text{C}}(3 \cos^2 \beta - 1)/2\pi R_{\text{CH}}^3)S_{zz} \quad (3a)$$

$J_{\text{CH}}$  is the indirect spin-spin coupling constant between <sup>13</sup>C and <sup>1</sup>H (measured in isotropic phase) and  $\beta$  is the angle shown in Figure 6. The sign of  $J_{\text{CH}}$  is well known to be positive.<sup>18</sup> Analogous expressions hold for  $\Delta\nu_{\text{SiH}}$  and  $D_{\text{SiH}}$  (with the quantities  $J_{\text{SiH}}$ ,  $\gamma_{\text{Si}}$ ,  $R_{\text{SiH}}$ ). The anisotropy of the spin-spin coupling,  $\Delta J$ , which adds a term  $(2\Delta J_{\text{CH}}/3)S_{zz}$  (or  $(2\Delta J_{\text{SiH}}/3)S_{zz}$ ) to eq 3 has been neglected. In eq 1-3 the effects of molecular vibrations on the interatomic distances and bond angles are also neglected

$$\Delta\nu_{\text{D}} = \frac{3}{2}(e^2q_{zz}Q/\hbar)S_{zz} \quad (4)$$

and

$$(e^2qQ/\hbar)_{\text{C-D}} = [1/2(3 \cos^2 \beta - 1)]^{-1}(e^2q_{zz}Q/\hbar) \quad (4a)$$

In eq 4 and 4a it was assumed that field gradient  $eq$  is axially symmetric along the C-D bond, *i.e.*, that the asymmetry parameter  $\eta = 0$ . Analogous expressions hold for  $\Delta\nu_{\text{D}}$  measured in Si-D and Ge-D bonds with  $\delta$  replacing  $\beta$ .

The measured quantities appearing in eq 1-4 were used in the computations and are shown in Table I. Also given in Table I are the values of  $J_{\text{HD}}$  and  $J_{\text{CH}}$  (or  $J_{\text{SiH}}$ ) which were measured in the isotropic phase. It should be noted that  $\Delta\nu_{\text{HH}}$  and  $\Delta\nu_{\text{HD}}$  were also measured in "low-pressure samples" (*cf.* Experimental Section).

From the data given in Table I and using eq 1-4, the ordering parameters ( $S_{zz}$ ) and the geometrical parameters

(17) C. Schumann and H. Dreeskamp, *J. Magn. Resonance*, **3**, 204 (1970).

(18) J. H. Goldstein, V. S. Watts, and L. S. Rattet, *Progr. Nucl. Magn. Resonance Spectrosc.*, **8**, 1 (1972).

of the molecules may be calculated. The following procedures were applied.

(a) The first step in our calculations involves the determination of the absolute signs of the  $D$ 's and of  $S_{zz}$ . We start from eq 3 and 3a. From  $J_{\text{CH}} > 0$  it follows that  $D_{\text{CH}} > 0$ , otherwise the  $\beta$  appearing in eq 3a would deviate drastically from the known microwave value. Also since  $3 \cos^2 \beta - 1 < 0$  and  $D_{\text{CH}} > 0$  we must conclude that  $S_{zz} > 0$ . This implies that our molecules are oriented such that their symmetry axis lies in the direction of the magnetic field. This agrees well with other results for molecules with similar structures dissolved in nematic liquid crystals.<sup>1,5</sup> Since  $\gamma_{\text{Si}}$  has an opposite sign to  $\gamma_{\text{C}}$ , it follows, by the same arguments as above, that  $J_{\text{SiH}} < 0$  and  $D_{\text{SiH}} < 0$ . Turning now to eq 1 and 1a it follows that both  $S_{zz}$  and  $D_{\text{HH}}$  have the same sign, *i.e.*, positive. The value of  $D_{\text{HD}}$  (eq 2 and 2a) is negative because  $\langle (3 \cos^2 \alpha - 1)/R_{\text{HD}}^3 \rangle$  is positive.

(b) All the molecules studied contain two fragments which may have different relative conformations (staggered, eclipsed, etc.) or may rotate freely around the central Si-C or Ge-C bonds. The computed values of  $Q^{1/2} \equiv p/s$  (*cf.* Figure 6) depend on the conformational model which is chosen. In more detail, the values taken by the angle  $\phi$ , which is the angle between the C-H(D) and the Si-H(D) or Ge-H(D) bonds, determine the conformation. If the two parts of the molecule are rotating freely with respect to each other,  $\phi$  must be averaged over all angles between 0 and  $2\pi$ . Otherwise,  $\phi$  takes the values of  $\pi/3$ ,  $\pi$ ,  $5\pi/3$  or 0,  $2\pi/3$ ,  $4\pi/3$  radians for the staggered and eclipsed conformations, respectively. For CH<sub>3</sub>SiD<sub>3</sub> we have tried<sup>8</sup> four models: (A) free rotation, (B) staggered, (C) eclipsed, (D) staggered and eclipsed. It was found that the results for  $Q$  correspond closely to the microwave data only for models A or B. Hence, in present computations, we shall restrict our consideration to models A and B, *i.e.*, to the free rotation or the staggered conformations.

(c) From eq 1 and 3 the following expression may be derived

$$\frac{\Delta\nu_{\text{CH}} - J_{\text{CH}}}{\frac{2}{3}\Delta\nu_{\text{HH}}} = \frac{D_{\text{CH}}}{D_{\text{HH}}} = \frac{\gamma_{\text{C}}}{\gamma_{\text{H}}} \left( \frac{R_{\text{HH}}}{R_{\text{CH}}} \right)^3 \left[ \left( \frac{R_{\text{HH}}}{R_{\text{CH}}} \right)^2 - 2 \right] \quad (5)$$

(with an analogous expression for the terms containing  $R_{\text{SiH}}$ ). From eq 5 the ratio  $R_{\text{HH}}/R_{\text{CH}}$  or  $R_{\text{HH}}/R_{\text{SiH}}$  was

Table II. Molecular Parameters Obtained in This Work with the Corresponding Microwave (MW) Data<sup>9-11</sup>

	CD <sub>3</sub> SiH <sub>3</sub>	CH <sub>3</sub> SiD <sub>3</sub>	CD <sub>3</sub> GeH <sub>3</sub>	CH <sub>3</sub> GeD <sub>3</sub>
$R_{HH}/R_{CH}$		1.613 ± 0.001		1.626 ± 0.003
MW		1.615 ± 0.013		1.622 ± 0.014
$R_{HH}/R_{SiH}$	1.615 ± 0.022			
MW	1.620 ± 0.012			
$\angle HCH$		107° 34' ± 10'		108° 48' ± 22'
MW		107° 40' ± 30'		108° 25' ± 30'
$\angle HSiH$	107° 48' ± 20'			
MW	108° 15' ± 30'			
$R_{HH'}/R_{HH''}$		1.349 ± 0.005	1.402 ± 0.007	
MW		1.363 ± 0.006	1.419 ± 0.008	
$Q^{1/2}$				
Free rotation	2.00 ± 0.02 <sup>a</sup>	2.69 ± 0.02 <sup>a</sup>	1.97 ± 0.02 <sup>a</sup>	2.75 ± 0.03
	2.01 ± 0.03 <sup>b</sup>	2.71 ± 0.04 <sup>b</sup>	2.01 ± 0.02 <sup>b</sup>	
Staggered	1.94 ± 0.02 <sup>a</sup>	2.61 ± 0.02 <sup>a</sup>	1.90 ± 0.02 <sup>a</sup>	2.67 ± 0.03
	1.95 ± 0.03 <sup>b</sup>	2.60 ± 0.04 <sup>b</sup>	1.94 ± 0.02 <sup>b</sup>	
MW	2.01 ± 0.02	2.73 ± 0.03	1.89 ± 0.02	2.79 ± 0.03
$R_{Si-C}^c$		1.831 ± 0.007 Å		
MW		1.867 ± 0.000 Å		
$R_{Si-H}^c$		1.474 ± 0.007 Å		
MW		1.485 ± 0.005 Å		

<sup>a</sup> Low-pressure samples. <sup>b</sup> High-pressure samples. <sup>c</sup> Calculated from molecular geometry obtained by nmr; assuming  $R_{C-H} = 1.093$  Å<sup>9, 10</sup> and taking  $Q^{1/2} = 2.71$ .

obtained by a numerical solution. The HCH (or HSiH) angle was then obtained from

$$\frac{R_{HH}}{R_{CH}} = 2 \sin(\angle HCH/2) \quad (6)$$

(with an analogous expression for  $\angle HSiH$ ). The ratio of interproton distance in the CH<sub>3</sub> and SiH<sub>3</sub> (or the GeH<sub>3</sub>) groups denoted as  $n$  is given by

$$n = R_{HH'}/R_{HH''} = \{\Delta\nu_{HH}(\text{CH}_3)/\Delta\nu_{HH}(\text{SiH}_3)\}^{1/3} \quad (7)$$

(with an analogous expression containing  $\Delta\nu_{HH}(\text{GeH}_3)$ ). The quantities on the right-hand side of eq 7 are measured in a 1:1 mixture of CH<sub>3</sub>SiD<sub>3</sub> and CD<sub>3</sub>SiH<sub>3</sub> or CH<sub>3</sub>GeD<sub>3</sub> and CD<sub>3</sub>GeH<sub>3</sub>. The ratio  $p/s \equiv Q^{1/2}$  may now be obtained from eq 1 and 2. First  $R_{HH}$ ,  $\langle R_{HD} \rangle$ , and  $\langle \cos \alpha \rangle$  are expressed in terms of  $Q$ ,  $n$ , and  $\langle \cos \phi \rangle$ . For CH<sub>3</sub>YD<sub>3</sub> molecules the relations are

$$R_{HH'} = 3^{1/2}s' \quad (\text{or } R_{HH''} = 3^{1/2}s'') \quad (8a)$$

$$\langle R_{HD}^2 \rangle = p^2 + s'^2 \{n^2 + 1 - 2n\langle \cos \phi \rangle\} \quad (8b)$$

$$\langle \cos^2 \alpha \rangle = \langle p^2/(R_{HD}^2) \rangle \quad (8c)$$

In the case of the YH<sub>3</sub>CD<sub>3</sub> molecule  $1/n$  and  $s''$  replace  $n$  and  $s'$  in (8b). Substituting eq 8 in eq 1 and 2 we obtain for the CH<sub>3</sub>YD<sub>3</sub> molecules

$$\frac{\Delta\nu_{HD} - J_{HD}}{\Delta\nu_{HH}} = \frac{D_{HD}}{D_{HH}} = -2(3)^{1/2} \left( \frac{\gamma_D}{\gamma_H} \right) \left( \frac{2Q - (n^2 + 1 - 2n\langle \cos \phi \rangle)}{\{Q + n^2 + 1 - 2n\langle \cos \phi \rangle\}^{1/2}} \right) \quad (9)$$

(For the YH<sub>3</sub>CD<sub>3</sub> molecules  $1/n$  is substituted for  $n$  in eq 9.) The best values of  $Q$  are obtained by a numerical solution of eq 9. For the free rotation model the right-hand side of eq 9 is integrated over all values of  $\phi$  (0–2 $\pi$ ) while in the staggered model  $\phi$  takes discrete values of  $\pi/3$ ,  $\pi$ , and  $5\pi/3$ .

(d) The values of  $J_{CH}$  (or  $J_{SiH}$ ) (eq 5) or  $J_{HD}$  (eq 9) which we used were measured in the isotropic phase of the same liquid crystal and their values are given in Table I. Our values compare well with data measured by others. For CH<sub>3</sub>SiH<sub>3</sub>:  $J_{CH} = 122.1 \pm 0.8$  Hz,

$J_{SiH} = 194.2 \pm 0.6$  Hz,  $J_{HH} = 4.68 \pm 0.02$  Hz<sup>19a</sup> or  $J_{CH} = 122.5$  Hz,  $J_{SiH} = 194.2$  Hz, and  $J_{HH} = 4.72$  Hz.<sup>19b</sup> For CH<sub>3</sub>GeH<sub>3</sub>:  $J_{HH} = 4.22$  Hz<sup>20a</sup> or  $J_{HH} = 4.33$  Hz,  $J_{CH} = 129$  Hz<sup>20b</sup> or  $J_{HH} = 4.2$  Hz, and  $J_{CH} = 127.8$  Hz.<sup>20c</sup>

(e) For the calculation of  $(e^2qQ)_{C-D}$  the value of  $S_{zz}$  is required. This value was computed from eq 1 using  $R_{HH}$  values taken from microwave data:<sup>9-11</sup>  $R_{HH} = 2.406$ , 1.765, 2.493, and 1.756 Å for CD<sub>3</sub>SiH<sub>3</sub>, CH<sub>3</sub>SiD<sub>3</sub>, CD<sub>3</sub>GeH<sub>3</sub>, and CH<sub>3</sub>GeD<sub>3</sub>, respectively. The calculated errors in  $e^2qQ$  take into account the errors in the  $R_{HH}$  microwave data and the errors in the measurements of  $\Delta\nu_D$  and  $\Delta\nu_{HH}$ . However, the dipolar interaction between the deuterons has been neglected.

The calculated molecular geometrical parameters and the corresponding values from microwave data<sup>9-11</sup> are given in Table II.

Inspection of Table II shows that in general there exists a very good agreement between our results and the microwave gas-phase data. This agreement justifies the approximations that we have made such as the neglect of terms involving  $\Delta J$  or the neglect of corrections for molecular vibrations. The results for  $Q^{1/2}$ , in comparison with the microwave data, do not seem to enable us to distinguish between the conformation of the molecules although a slight preference to the free rotation prevails. This contradicts the microwave data for CH<sub>3</sub>SiH<sub>3</sub><sup>9</sup> and our conclusion for CH<sub>3</sub>SiD<sub>3</sub> given in a previous report<sup>9</sup> where  $J_{HD}$  was assumed to be negative. The barriers to internal rotation have been determined by microwave spectroscopy<sup>9-11</sup> and are about 1.7 and 1.2 kcal/mol for the Si and Ge compounds, respectively.

Table III complements the calculated quantities and gives the value of the quadrupole coupling constants  $e^2qQ$ , for the deuterons in C–D, Si–D, and Ge–D bonds and also the ordering parameters,  $S_{zz}$ , of the compounds. The  $e^2qQ$ 's obtained for the deuterium bonded to carbon

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**Table III.** Quadrupole Coupling Constants and Ordering Parameters

	CD <sub>3</sub> SiH <sub>3</sub>	CD <sub>3</sub> GeH <sub>3</sub>	CH <sub>3</sub> SiD <sub>3</sub>	CH <sub>3</sub> GeD <sub>3</sub>
$e^2qQ/\hbar$ , kHz	176 ± 4	175 ± 4	91 ± 2	82 ± 2
$S_{zz}$	+0.0244 ± 0.0003 <sup>a</sup>	+0.0237 ± 0.0003 <sup>a</sup>	+0.0210 ± 0.0002 <sup>a</sup>	+0.0263 ± 0.0003 <sup>b</sup>

<sup>a</sup> At 19°. <sup>b</sup> At 26°.

fit well with similar data such as for CH<sub>3</sub>CD<sub>3</sub> where the value is 167 ± 12 kHz.<sup>6</sup> The values of  $e^2qQ$  in Si-D or Ge-D are quite a bit lower and compare well with other data: SiD<sub>4</sub>, 94 kHz;<sup>21</sup> C<sub>6</sub>H<sub>5</sub>SiD<sub>3</sub>, 91 ± 2 kHz;<sup>22</sup> GeD<sub>4</sub>, 82 ± 5 kHz.<sup>23</sup>

**Chemical Shift Anisotropy.** The magnitude of the chemical shift anisotropy of a particular nucleus in a molecule may be estimated from the chemical shift between its resonances in the oriented and random states. In the case of molecules having axial symmetry, the following expression applies

$$\sigma(\text{nematic}) - \sigma(\text{isotropic}) = \frac{2}{3}S_{zz}\Delta\sigma$$

where  $\Delta\sigma = \sigma_{\perp} - \sigma_{\parallel}$ . It is, however, necessary to obtain  $\sigma(\text{nematic})$  and  $\sigma(\text{isotropic})$  at the same temperature. The best procedure to achieve this seems to be the measurement of the difference in resonance positions in nonrotating and rotating samples at such a temperature in which the nematic phase exists.<sup>24</sup> In another procedure the chemical shifts are measured relative to a standard such as tetramethylsilane (TMS), as a function of the temperature in both the nematic and isotropic phases. The latter value is then extrapolated to a nematic temperature. In the second procedure solvent effects interfere severely with the reliability of the results. We have applied both methods to estimate the proton chemical shift anisotropy in CD<sub>3</sub>SiH<sub>3</sub> and CD<sub>3</sub>GeH<sub>3</sub>. For CH<sub>3</sub>SiD<sub>3</sub> the first method is unapplicable since the TMS, which serves as reference, and the CH<sub>3</sub> resonances are very close (*ca.* 15 Hz) and overlap. For the same reason the frequency difference between the central CH<sub>3</sub> peak in CH<sub>3</sub>SiD<sub>3</sub> and TMS could not be measured precisely when TMS was used as a lock. The  $S_{zz}$  values were obtained in each case from  $\Delta\nu_{\text{HH}}$  (*cf.* eq 1), with lock on TMS, using the  $R_{\text{HH}}$  value taken from microwave data.

The results are summarized in Table IV. It should be noted that solvent effects may change the values of  $\Delta\sigma$  appreciably.<sup>5,7</sup> Taking into account this effect the value of  $\Delta\sigma$  in CH<sub>3</sub>SiD<sub>3</sub> may be considerably lower than that given in Table IV. The results for CD<sub>3</sub>SiH<sub>3</sub> and

**Table IV.** Proton Chemical Shift Anisotropies in Ppm

	CH <sub>3</sub> SiD <sub>3</sub>	CD <sub>3</sub> SiH <sub>3</sub>	CD <sub>3</sub> GeH <sub>3</sub>
Spinning-nonspinning technique (26°)		+2.1 ± 0.4	+4.7 ± 0.7
Slope of $\sigma(\text{nematic}) - \sigma(\text{isotropic})$ vs. $S_{zz}$	+11 ± 2	+4 ± 2	+6 ± 1.5

CD<sub>3</sub>GeH<sub>3</sub> obtained by the spinning-nonspinning procedure are presumably less affected by solvent effects. It is also reasonable to assume that solvent effects will be less important in CD<sub>3</sub>SiH<sub>3</sub> and CD<sub>3</sub>GeH<sub>3</sub> which is indeed manifested in the results shown in Table IV. On the other hand, a value of  $\Delta\sigma = +10$  ppm has recently been quoted as an average value for  $\Delta\sigma$  of aliphatic protons.<sup>25</sup>

### Appendix

The cause of the difficulty in determining the sign of  $J_{\text{HD}}$  is its small value as compared to  $D_{\text{HD}}$  (eq 2). To demonstrate this we have calculated  $D_{\text{HD}}$  (eq 2a) for the different molecules using microwave data for the structural parameters and  $S_{zz}$  obtained from the proton spectra (eq 1 and 1a). The results together with the experimental  $D_{\text{HD}}$  values, taken from Table I, are given in Table V. It is clearly evident from Table V that

**Table V.** Calculated and Experimental Values of  $D_{\text{HD}}$  (Hz)

	CD <sub>3</sub> SiH <sub>3</sub>	CH <sub>3</sub> SiD <sub>3</sub>	CD <sub>3</sub> GeH <sub>3</sub>	CH <sub>3</sub> GeD <sub>3</sub>
	Calculated			
Staggered	17.9 <sup>a</sup> 33.3 <sup>b</sup>	15.5 <sup>a</sup> 29.5 <sup>b</sup>	15.2 <sup>a</sup> 24.8 <sup>b</sup>	18.3
Free rotation	18.8 <sup>a</sup> 34.9 <sup>b</sup>	16.2 <sup>a</sup> 30.8 <sup>b</sup>	16.5 <sup>a</sup> 26.8 <sup>b</sup>	19.3
	Experimental			
$J_{\text{HD}} > 0$	18.7 ± 0.1 <sup>a</sup> 35.1 ± 0.2 <sup>b</sup>	16.9 ± 0.2 <sup>a</sup> 32.3 ± 0.3 <sup>b</sup>	16.4 ± 0.1 <sup>a</sup> 27.6 ± 0.2 <sup>b</sup>	19.8 ± 0.2
$J_{\text{HD}} < 0$	17.4 ± 0.1 <sup>a</sup> 33.7 ± 0.2 <sup>b</sup>	15.5 ± 0.2 <sup>a</sup> 30.8 ± 0.3 <sup>b</sup>	15.1 ± 0.1 <sup>a</sup> 26.3 ± 0.2 <sup>b</sup>	18.5 ± 0.2

<sup>a</sup> Low-pressure samples. <sup>b</sup> High-pressure samples.

within our experimental accuracy the sign of  $J_{\text{HD}}$  cannot be determined. Analysis of the proton spectra of the fully protonated species might solve the problem in our case.

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