

Direct and Indirect Sn–H Coupling Constants in MeSnCl_3 and Me_3SnCl Partially Oriented in Nematic Phases determined by the Dilution–Spinning Method

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Summary Direct and indirect coupling constants between Sn and H atoms in MeSnCl_3 and Me_3SnCl partially oriented in nematic phases are separated by the dilution–spinning method which utilizes dilution effects in addition to the conventional method of sample rotation, and structural parameters comparable to those in the gas phase are obtained for the SnCH_3 fragment.

DIRECT coupling constants (D) obtained from the n.m.r. spectra of molecules partially oriented in liquid crystals are known to provide valuable information about the structure of the molecules.¹ However (apart from the rarely occurring problem of anisotropic contributions) it is usually necessary, when deriving direct coupling constants, to separate the direct and indirect coupling constants in the ordered spectra. There are several ways of doing this, *e.g.*, i, substitution of data from other sources such as that available from isotropic media for the indirect coupling constant in a liquid crystal, ii, extrapolation in the variable temperature experiment with a liquid crystalline sample, and iii, extrapolation in the sample rotation experiment with a liquid crystalline sample. However, when the indirect coupling constants under consideration show considerable solvent and/or temperature dependence as in the case for organometallic compounds, methods i and/or ii become useless. Recently an example of this was reported for dimethylmercury.² We have been studying the ordered ^1H n.m.r. spectra of organotin compounds³ and have now evaluated the $^2J(\text{SnH})$ indirect coupling constants in MeSnCl_3 and Me_3SnCl oriented in a few nematic phases by utilizing dilution effects in addition to the conventional method of sample rotation. We have also evaluated $^2J(\text{SnH})$ in ZLI1167(Merck) where the method of sample rotation is invalid unless a superconducting magnet equipped with a special spinning apparatus which makes possible a controlled, slow, sample rotation is used.

N.m.r. spectra were measured with a Hitachi R-900M FT n.m.r. spectrometer operating at 90 MHz and at 34.1°C . A sample-spinning apparatus was made using a variable-speed Q-CON motor (Japan Servo Co. Ltd.). The spinning rate was read by a tachometer within an error of ± 0.1 count, and the variation in this rate was ≤ 0.1 count during the n.m.r. measurement. MeSnCl_3 and Me_3SnCl were purified by sublimation under reduced pressure and liquid crystals were distilled under high vacuum (*ca.* 10^{-5} Torr) using a vacuum line, since organotin compounds are liable to be hydrolysed by trace amounts of water in the liquid crystal. In the dilution experiment CCl_4 was used as a diluent.

The ^1H n.m.r. spectrum of MeSnCl_3 is a 1:2:1 triplet [splitting $3D(\text{HH})$] with two types of satellites due to ^{119}Sn and ^{117}Sn [splitting $2D(\text{SnH}) + J(\text{SnH})$].† From the

plots of $2D(\text{SnH}) + J(\text{SnH})$ vs. $3D(\text{HH})$, following extrapolation to $3D(\text{HH}) \rightarrow 0$, $J(\text{SnH})$ could be derived in the dilution and/or spinning experiments. The results are summarized in the Table for MeSnCl_3 in Nematic Phase IV, NP1052, and ZLI1167 (Figure), and for Me_3SnCl in Nematic

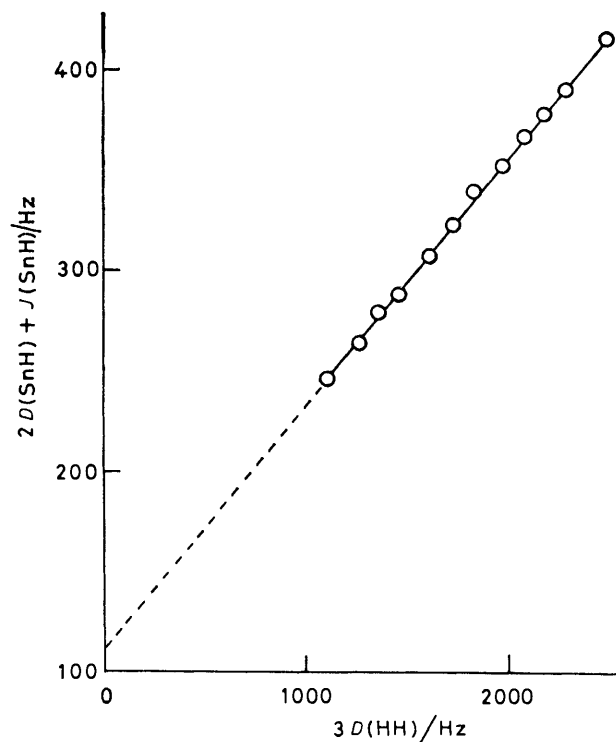


FIGURE. Determination of $J(\text{SnH})$, in MeSnCl_3 partially oriented in ZLI1167, by the dilution method.

Phase IV. In the latter case, $2D(\text{SnH}) + J(\text{SnH})$ was plotted against the separation of the two peaks which are produced by the direct coupling constants between intra- and inter-methyl protons and which lie near the satellite peaks. In all the cases treated here, because of the partial overlapping of the ^{119}Sn and ^{117}Sn satellites, the positions of these satellites were liable to be affected by the resolution of n.m.r. measurement. Therefore, averaged separations of the two types of satellites were plotted in the ordinate, and the value of the intercept was converted to $^2J(^{119}\text{SnH})$ and $^2J(^{117}\text{SnH})$ using the γ ratio.

The standard deviation in $D(^{119}\text{SnH})/D(\text{HH})$ as determined in each dilution–spinning experiment (Table, last column) was comparable with the error introduced from the

† See ref. 1, ch. 3, for the analysis of n.m.r. spectra of partially oriented molecules.

TABLE. Indirect coupling constants and the ratio of direct coupling constants in MeSnCl₃ and Me₃SnCl partially oriented in liquid crystal solvents.^a

	Liquid crystal	$J(^{119}\text{SnH})/\text{Hz}$	$J(^{117}\text{SnH})/\text{Hz}$	Method ^b	$D(^{119}\text{SnH})/D(\text{HH})$
MeSnCl ₃	Nematic Phase IV	108.9 ± 0.8	104.0 ± 0.8	S	0.1867 ± 0.0006
		109.1 ± 0.9	104.3 ± 0.9	D	0.1860 ± 0.0006
		109.5 ± 0.5	104.7 ± 0.5	D-S	0.1860 ± 0.0008
MeSnCl ₃	NP1052	109.6 ± 0.5	104.8 ± 0.5	D-S	0.1784 ± 0.0017
MeSnCl ₃	ZLI1167	112.4 ± 0.3	107.4 ± 0.3	D	0.1880 ± 0.0006
Me ₃ SnCl	Nematic Phase IV	60.5 ± 0.7	57.9 ± 0.7	D-S	0.1725 ± 0.0018

^a The concentration of the tin compound was *ca.* 0.1M and maximum concentrations of CCl₄ added in the dilution experiment were *ca.* 0.6M (Nematic Phase IV), *ca.* 0.1M (NP1052), and *ca.* 0.7M (ZLI1167). *Ca.* 10 data points were collected in each experiment, and the extrapolation and error analysis were made by a least squares method. ^b S = spinning, D = dilution, D-S = dilution-spinning.

$J(\text{SnH})$. Accordingly, the effect of dilution on the structural parameter is considered negligible. The $J(\text{SnH})$ values in the Table are reasonable considering the available values in isotropic media, *i.e.*, 99.9(95.4) Hz in CH₂Cl₂, 106.9(102.1) Hz in nitrobenzene, and 122.0(116.0) Hz in CH₂Cl₂ containing excess amounts of γ -picoline for MeSnCl₃, and 57.8(55.2) Hz in CCl₄ and 67.6(64.5) Hz in pyridine for Me₃SnCl [values in parentheses being those of $^2J(^{117}\text{SnH})$]. That $J(\text{SnH})$ in MeSnCl₃ dissolved in ZLI 1167 has a somewhat larger value than that obtained for MeSnCl₃ dissolved in the other two liquid crystals suggests that the former solvent has a relatively strong basicity. $D(\text{SnH})$ and $D(\text{HH})$ values are concluded to be positive as $J(\text{SnH})$ values are positive.⁴

The ratio $D(\text{SnH})/D(\text{HH})$ may be expressed as in equation (1), where θ is the Sn-C-H angle. From this

$$D(\text{SnH})/D(\text{HH}) = -\gamma_{\text{Sn}}/\gamma_{\text{H}}(d_{\text{HH}}/d_{\text{SnH}})^3[2 - 3(d_{\text{CH}}/d_{\text{SnH}})^2\sin^2\theta] \quad (1)$$

equation θ is derivable if the distances (d) of Sn-C and C-H are equated to the gas-phase values determined by

electron diffraction.⁵ The angle is 107.0 ± 0.2 in Nematic Phase IV, 108.6 ± 0.4 in NP1052, and $106.6 \pm 0.1^\circ$ in ZLI 1167 for MeSnCl₃ (the gas-phase reference value being $107.5 \pm 2.0^\circ$)⁵ and $111.1 \pm 0.4^\circ$ in Nematic Phase IV for Me₃SnCl (gas-phase reference value $113.4 \pm 1.4^\circ$)⁵.

The order parameter for the C_{3v} molecular axis is estimated as follows: $S_{c_3} = +0.0618$ (0.01M in Nematic Phase IV), $+0.0354$ (0.09M in NP1052), and $+0.0837$ (0.08M in ZLI 1167) for MeSnCl₃, and $S_{c_3} = -0.0488$ (0.13 in Nematic Phase IV containing 0.59M CCl₄) for Me₃SnCl.

In conclusion, we have established that dilution is useful for the separation of indirect and direct coupling constants in ordered n.m.r. spectra. The merits of this effect are i, applicability to liquid crystal solvents for which sample rotation proved useless, ii, enhancement of reliability of the derived results (when used together with the sample rotation) by shortening the range of extrapolation required, and iii, less line broadening than when sample rotation alone is used.

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¹ J. W. Emsley and J. C. Lindon, 'NMR Spectroscopy Using Liquid Crystal Solvents,' Pergamon, New York, 1975.

² J. Jokisaari and P. Diehl, *Org. Magn. Reson.*, 1980, **13**, 359.

³ H. Fujiwara, K. Takahashi, and Y. Sasaki, *J. Magn. Reson.*, 1980, **41**, 171.

⁴ J. D. Kennedy and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 1974, 983.

⁵ B. Beagley, K. McAloon, and J. M. Freeman, *Acta Crystallogr., Sect. B*, 1974, **30**, 444.