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## Liquid Crystals

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## Dimethylmercury in mixtures of thermotropic nematogens

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The geometry of dimethylmercury was studied in several mixtures of the liquid crystals ZLI 1167 and phase 4. The variation of the geometry is not very large but systematic changes can be detected as a function of the liquid crystal composition. The anisotropies,  $\Delta\sigma$ , of the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{199}\text{Hg}$  shielding tensors were investigated by applying two methods based on mixing liquid crystals with opposite diamagnetic anisotropies and by applying various referencing methods. Apart from these, the anisotropy,  $\Delta J_{\text{HgC}}$ , of the  $^{199}\text{Hg}$ - $^{13}\text{C}$  spin-spin coupling tensor was studied in four mixtures of these liquid crystals, and was found to vary with the solvent.

### 1. Introduction

Dimethylmercury dissolved in liquid-crystalline environments has been an object of several N.M.R. studies [1-6]. However, no systematic investigation of the variation of the geometry with the liquid crystal solvent has been published until now. When studying structures of various small and medium sized molecules [7-13] it has become evident that the effects arising from the correlation between vibrational and reorientational motions on the geometry can be eliminated by using proper mixtures of thermotropic nematogens, i.e. mixtures of nematogens that give opposite dipolar  $^{13}\text{C}$ - $^1\text{H}$  splittings for methane, or by applying theoretical models [10, 12-15]. The investigations have also shown that the correlation effects will be enhanced if the degree of orientational order is low. The dimethylmercury molecule is well oriented in most liquid crystals, the order parameter  $S_{zz}^D$  (here the superscript D refers to the liquid crystal director) being of the order of 0.2. Therefore, the structural variations can be expected to be small. Due to the high accuracy in the experimental dipole-dipole coupling constants we have, however, been able to observe a systematic variation in the structure when changing the liquid crystal solvent.

Dimethylmercury is a favourable case for liquid-crystalline studies since it provides several magnetic parameters for inspection. In the present series of measurements, we have also studied the shielding anisotropies for proton, carbon-13 and mercury-199. The NEMIX [16] and ENEMIX [17] methods with internal methane- $^{13}\text{C}$  and TMS and external  $\text{CHCl}_3$  references were applied for proton and carbon-13 measurements. In contrast,  $\Delta\sigma_{\text{Hg}}$  was derived by the ENEMIX method only and by measuring the chemical shifts with respect to the spectrometer operating frequency. Furthermore, the chemical shift jumps experienced by the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei in methane- $^{13}\text{C}$  and TMS were measured for the critical mixture of ZLI 1167 and phase 4.

The anisotropy of the  $^{13}\text{C}$ - $^{199}\text{Hg}$  spin-spin coupling tensor has been studied earlier in the liquid crystals phase 4 [4], phase 5 [4] and in the mixture of EBBA and *p*-ethoxyphenyl-*p*-caproyloxybenzoate [2]. In the present work, the liquid crystals ZLI 1167 and phase 4 and their two mixtures (85 wt % ZLI 1167 and 58 wt % ZLI 1167)

were used. Previous investigation of methyl fluoride- $^{13}\text{C}$  yielded a very drastic variation in  $\Delta J_{\text{CF}}$  [10]. This variation was also explained on the basis of the correlation effects which contribute to the structure. The  $\Delta J_{\text{HgC}}$  is also found to be dependent on the liquid crystal solvent, but in this case the variation is less pronounced.

## 2. Experimental

Dimethylmercury,  $(\text{CH}_3)_2\text{Hg}$ , was supplied by Merck and it was used without further purification. Its  $^1\text{H}$  N.M.R. spectra with  $^{13}\text{C}$ -satellites and  $^{13}\text{C}$  N.M.R. spectra were recorded on a JNM-GX400 spectrometer. The liquid crystal solvents used are collected in table 1. The samples were prepared in coaxial double tubes (outer diameter 5 mm) with  $\text{CDCl}_3$  as a locking substance in the annulus. The  $^1\text{H}$  resonance, detectable from the undeuterated chloroform molecules, was used as an external reference for measuring  $^1\text{H}$  chemical shifts whereas the  $^{13}\text{C}$  signal from  $\text{CDCl}_3$  was used in the  $^{13}\text{C}$  spectra. Each sample was degassed and contained also a small amount of  $^{13}\text{CH}_4$  (*c.* 1 atm) and TMS as internal chemical shift references. The  $^{199}\text{Hg}$  and  $^{13}\text{C}$ - $^{199}\text{Hg}$  satellite N.M.R. spectra were recorded from 10 mm tubes on a JNM-FX100 spectrometer and the chemical shifts were measured with respect to the spectrometer operating frequency.

Table 1. Sample compositions in the study of the  $^1\text{H}$  and  $^{13}\text{C}$  N.M.R. spectra of dimethylmercury.

Sample	Liquid crystal composition†	Concentration of $(\text{CH}_3)_2\text{Hg}‡$
1	ZLI 1167	9.1
2	ZLI 1167 (85) + phase 4 (15)	9.2
3	ZLI 1167 (78) + phase 4 (22)	9.2
4	ZLI 1167 (58) + phase 4 (42)	11.8
5	ZLI 1167 (40) + phase 4 (60)	9.3
6	ZLI 1167 (20) + phase 4 (80)	9.3
7	phase 4	9.4

† The figures in parenthesis give the amount of the liquid crystal in wt %.

‡ In wt %. Each sample contained also  $^{13}\text{CH}_4$  and TMS.

The spectral analyses were carried out with the aid of the program LEQUOR [18] whereas the modified version of the program SHAPE [19] was used to determine the geometry.

## 3. Results and discussion

### 3.1. Structure

The dipole-dipole coupling constants  $D_{\text{HH}}$  and  $D_{\text{CH}}$  were derived from the carbon-13 satellites in the  $^1\text{H}$  N.M.R. spectra and only these were used in the analyses of the geometry. The experimental parameters are collected in table 2. Figure 1 shows the numbering of the nuclei. The couplings were corrected for harmonic vibrations by adopting the correction factors from [6]. The geometric parameters,  $r_{\text{CH}}/r_{\text{HgC}}$  and the HCH angle, and the order parameters,  $S_{zz}$ , based on these corrected coupling constants are given in table 3. The variation of the geometric parameters as a function of the liquid crystal composition is shown graphically in figure 2.

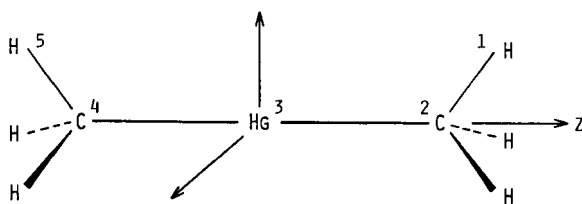


Figure 1. Numbering of the nuclei used in dimethylmercury.

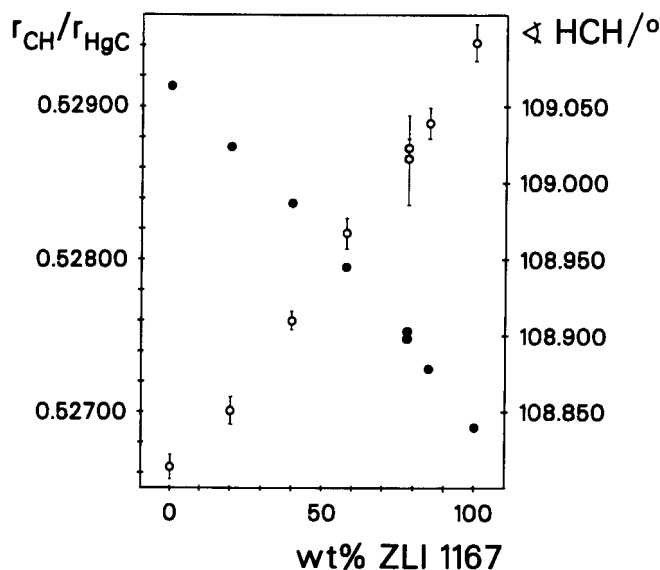
Figure 2. The bond length ratio  $r_{\text{CH}}/r_{\text{HgC}}$  (○) and HCH bond angle (●) of dimethylmercury as a function of the amount of ZLI 1167 in mixtures of ZLI 1167 and phase 4.

Table 2. Experimental H–H and C–H dipole–dipole couplings† for dimethylmercury in various liquid crystals.

Sample‡	$D_{11}/\text{Hz}$	$D_{12}/\text{Hz}$	$D_{14}/\text{Hz}$	$D_{15}/\text{Hz}$	$J_{15}\S/\text{Hz}$
1	−885.77(2)	−590.81(6)	24.23(9)	70.08(4)	0.46(7)
2	−924.41(2)	−618.25(5)	25.34(7)	73.07(3)	0.49(6)
3⊥	−950.89(6)	−637.05(16)	26.15(22)	75.15(9)	0.42(3)
3	1893.62(2)	1268.18(10)	−51.87(13)	−149.67(4)	0.41(3)
4	1660.71(5)	1115.83(13)	−45.70(18)	−131.15(5)	0.36(3)
5	1904.96(4)	1283.68(10)	−52.21(12)	−150.32(4)	0.38(3)
6	2162.23(6)	1460.79(15)	−58.98(19)	−170.42(6)	0.39(3)
7	2083.94(3)	1411.77(10)	−56.91(10)	−164.25(6)	0.45(11)

† These values must be corrected for harmonic vibrations. The correction factors are the following: 1.0416 for  $D_{11}$ , 1.0916 for  $D_{12}$ , 0.9975 for  $D_{14}$  and 1.0036 for  $D_{15}$ .

‡ See table 1.

§ Used as a free parameter in the iterative process. The other spin–spin coupling constants were kept unchanged:  $J_{12} = 129.5 \text{ Hz}$ ,  $J_{14} = -1.7 \text{ Hz}$  [4, 6] and  $J_{13} = -102.5 \text{ Hz}$  (measured from a liquid crystal sample heated to the isotropic phase).

⊥ Liquid crystal director perpendicular to the magnetic field.

|| Liquid crystal director parallel to the magnetic field.

Table 3. Bond length ratio  $r_{\text{CH}}/r_{\text{HgC}}$ , intramethyl HCH angle and order parameter  $S_{zz}$  of the symmetry axis for dimethylmercury in various liquid crystals. The results are based on coupling constants corrected for harmonic vibrations.

Sample†	$r_{\text{CH}}/r_{\text{HgC}}$	HCH/°	$S_{zz}$ §
1	0.52942(12)	108.8399(7)	-0.08868(6)
2	0.52889(10)	108.8784(6)	-0.09234(5)
3⊥	0.52866(30)	108.9032(17)	-0.09490(16)
3	0.52873(6)	108.8979(5)	0.18905(7)
4	0.52817(10)	108.9448(8)	0.16541(9)
5	0.52760(6)	108.9867(5)	0.18928(6)
6	0.52701(9)	109.0238(7)	0.21427(10)
7	0.52664(8)	109.0635(5)	0.20622(9)

† See table 1.

§ Based on  $r_{\text{HgC}} = 2.083 \text{ \AA}$  [20].

⊥ Director perpendicular to the magnetic field.

|| Director parallel to the magnetic field.

The results indicate that the maximum deviation (in the liquid crystals used) in the geometrical parameters are  $0.00278 \pm 0.00020$  and  $0.2236 \pm 0.0012^\circ$  for the bond length ratio and the HCH bond angle, respectively. These deviations are not large when compared to the accuracy achievable, for example, by electron diffraction or microwave spectroscopy, but they are large when compared to the error limits obtained in the present study or in liquid crystal studies in general. Moreover, the variation for both parameters is systematic so that  $r_{\text{CH}}/r_{\text{HgC}}$  increases while the HCH angle decreases with increasing amount of ZLI 1167 in the mixture. Mixture 4 with 58 wt % of ZLI 1167 and 42 wt % of phase 4 gives a vanishing dipolar splitting,  $D_{\text{CH}}(\text{CH}_4) = -0.30 \text{ Hz}$ , for methane- $^{13}\text{C}$  and has been found to result in well-determined structures for many molecules [7–13]. For the  $r_{\text{CH}}/r_{\text{HgC}}$  and the HCH angle, this particular mixture gives the values of  $0.52817 \pm 0.00010$  and  $108.9448 \pm 0.0008^\circ$ , respectively. Unfortunately, no complete geometries determined by techniques other than N.M.R. spectroscopy could be found for comparison. The only available study [20] reports the value of  $2.083 \pm 0.005 \text{ \AA}$  for the Hg–C bond length and  $2.712 \pm 0.018 \text{ \AA}$  for the Hg–H distance leading to the  $r_{\text{HgC}}/r_{\text{HgH}}$  ratio of  $0.768 \pm 0.007$ . The present liquid crystal data range from 0.77990 to 0.78196.

### 3.2. Chemical shift anisotropies for $^1\text{H}$ , $^{13}\text{C}$ and $^{199}\text{Hg}$

The nuclear chemical shifts for any nuclei in a linear molecule, such as dimethylmercury, dissolved in a liquid-crystalline environment is given by

$$\delta^{\text{exp}} = \delta^{\text{iso}} + \frac{2}{3} S_{zz} \Delta\sigma, \quad (1)$$

where  $\delta^{\text{iso}} = 1/3 \text{ Tr}(\delta)$ , one third of the trace of the chemical shift tensor,  $S_{zz}$  is the order parameter of the molecular symmetry axis (defined as the  $z$  axis) with respect to the magnetic field and  $\Delta\sigma = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$  is the anisotropy of the nuclear shielding tensor. In the NEMIX and ENEMIX methods,  $\Delta\sigma$  is calculated from

$$\Delta\sigma = \frac{3 \delta_{\parallel}^{\text{exp}} - \delta_{\perp}^{\text{exp}}}{2 S_{zz}^{\parallel} - S_{zz}^{\perp}}, \quad (2)$$

Table 4. Proton and carbon-13 chemical shift anisotropies for dimethylmercury derived by the ENEMIX and NEMIX methods using internal  $^{13}CH_4$  and TMS references and external  $CHCl_3$  reference. The other relevant parameters needed to calculate the  $\Delta\sigma$  values are also listed.

Parameter	Method	ENEMIX		NEMIX	
	Nucleus	$^1H$	$^{13}C$	$^1H$	$^{13}C$
$S_{zz}^{\parallel}$		0.1654	0.1608	0.1895	0.1896
$S_{zz}^{\perp}$		-0.1004	-0.0916	-0.0947	-0.0947
		Internal $^{13}CH_4$ reference			
$\delta_{\parallel}/p.p.m.$		0.523	-19.87	0.5793	-18.918
$\delta_{\perp}/p.p.m.$		-0.307	-28.72	-0.3307	-28.819
$\Delta\sigma/p.p.m.$		4.7(1)	52.6(3)	4.80(2)	52.3(1)
		Internal TMS reference			
$\delta_{\parallel}/p.p.m.$		0.23	-16.11	0.2514	-15.239
$\delta_{\perp}/p.p.m.$		-0.432	-24.46	-0.4574	-24.636
$\Delta\sigma/p.p.m.$		3.7(1)	49.7(3)	3.74(1)	49.6(1)
		External $CHCl_3/CDCl_3$ reference			
$\delta_{\parallel}/p.p.m.$		7.227	60.61	7.2315	61.411
$\delta_{\perp}/p.p.m.$		6.909	52.87	6.8617	52.644
$\Delta\sigma/p.p.m.$		1.8(2)	46.0(1)	1.95(1)	46.3(1)

where  $\parallel$  and  $\perp$  refer to the parallel and perpendicular orientations of the liquid crystal director, respectively. The two methods, however, use different mixtures of the liquid crystals with opposite diamagnetic anisotropies; in the NEMIX method the critical mixture is used, the ENEMIX method uses the mixture in which  $D_{CH}(CH_4) = 0$ . The  $\Delta\sigma_H$  and  $\Delta\sigma_C$  values obtained with the aid of these methods and with different reference compounds are listed in table 4 where the other relevant parameters are also given. The two methods give similar  $\Delta\sigma_H$  values independent of whether  $^{13}CH_4$  or TMS is used as a reference. In contrast, the two internal references lead to results deviating by about 1 p.p.m. (21 per cent) those obtained by TMS being lower. The situation is very similar for  $\Delta\sigma_C$ , relative changes being, however, only about 6 per cent.

The application of an external chloroform reference gives for  $\Delta\sigma_H$  and  $\Delta\sigma_C$  values which are remarkably smaller than the corresponding results obtained by using the internal methane- $^{13}C$  reference. Since the diamagnetic anisotropy of the liquid crystal mixture at the critical point, or more precisely near to the critical point, is small the bulk effect should be negligible and, consequently, the differences observed most likely arise from the local contributions that affect the reference molecules, too. For comparison,  $\Delta\sigma_H$  of  $3.70 \pm 0.03$  p.p.m. was obtained by using the smectic phase of HAB (4,4'-di-*n*-heptylazoxybenzene) with an external water reference [6], but this value includes the bulk effect.

The  $^{199}Hg$  shielding anisotropy was determined with the ENEMIX method only by measuring the chemical shifts with respect to the spectrometer operating frequency. This, of course, increases somewhat the uncertainty in the result but the problem is not very serious in cases where the anisotropy is large and the molecule is well

Table 5.  $^{199}\text{Hg}$  chemical shifts $\dagger$ , order parameters and the  $\Delta\sigma_{\text{Hg}}$  for dimethylmercury determined by the ENEMIX method.

Parameter	Value
$\delta_{\parallel}/\text{p.p.m.}$	-1110.1
$\delta_{\perp}/\text{p.p.m.}$	-2722.2
$S_{zz}^{\parallel}$	0.2206
$S_{zz}^{\perp}$	-0.1124
$\Delta\sigma_{\text{Hg}}/\text{p.p.m.}$	7260(90)

$\dagger$  Measured with respect to the spectrometer operating frequency, 17.80 MHz.

Table 6.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift changes for  $^{13}\text{CH}_4$  and TMS due to the rotation of the liquid crystal director from the parallel ( $\parallel$ ) to the perpendicular ( $\perp$ ) direction with respect to the magnetic field.

Nucleus	Molecule	$(\delta_{\parallel} - \delta_{\perp})/\text{p.p.m.}$
$^1\text{H}$	$^{13}\text{CH}_4$	-0.540
	TMS	-0.339
$^{13}\text{C}$	$^{13}\text{CH}_4$	-1.134
	TMS	-0.630

oriented. The relevant experimental parameters are shown in table 5. The resulting  $\Delta\sigma_{\text{Hg}}$  is  $7260 \pm 90$  p.p.m. which agrees with the value of  $7325 \pm 55$  p.p.m. obtained in the smectic HAB phase [6].

At suitable, inhomogeneous experimental conditions the use of a critical liquid crystal mixture makes it possible to detect simultaneously two spectra of the solute molecules which correspond to the director orientation parallel and perpendicular to the external magnetic field. This kind of experiment also reveals that the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei in the methane and TMS molecules experience changes in shielding when the director rotates by  $90^\circ$ . The chemical shift changes are given in table 6. The reasons for this observation are discussed in [17].

### 3.3. Spin-spin coupling anisotropy $\Delta J_{\text{HgC}}$

The experimental dipole-dipole coupling constants may include a contribution from the anisotropy of the corresponding indirect spin-spin coupling tensor so that

$$D_{ij}^{\text{exp}} = D_{ij}^{\text{dir}} + \frac{1}{2}J_{ij}^{\text{aniso}} + \text{vibrational contributions}, \quad (3)$$

where  $D_{ij}^{\text{dir}}$  is the pure dipole coupling

$$D_{ij}^{\text{dir}} = D_{ij}^{\text{calc}} = -K_{ij} \frac{S_{zz}}{r_{ij}^3}; \quad (4)$$

the factor  $K_{ij}$  is  $\mu_0\gamma_i\gamma_j\hbar/8\pi^2$ . For the molecule with a three- or higher-fold symmetry axis

$$J^{\text{aniso}} = (2/3)\Delta J S_{zz}, \quad (5)$$

where  $\Delta J = J_{zz} - \frac{1}{2}(J_{xx} + J_{yy})$  is the spin-spin coupling anisotropy. Thus

$$\begin{aligned} \Delta J &= (3/2)J^{\text{aniso}}/S_{zz}, \\ &= 3(D_{ij}^{\text{exp}} - D_{ij}^{\text{dir}})/S_{zz}, \end{aligned} \quad (6)$$

Table 7.  $J_{HgC}^{exp}$ ,  $D_{HgC}^{exp}$ ,  $D_{HgC}^{dir}$ ,  $S_{zz}$ ,  $\Delta J_{HgC}$  and the relative anisotropy  $R_{HgC} = \Delta J_{HgC}/J_{HgC}^{exp}$  determined for dimethylmercury in various liquid crystals.

Sample†	$J_{HgC}^{exp}/Hz$	$D_{HgC}^{exp}/Hz$	$D_{HgC}^{dir}/Hz$	$S_{zz}$	$\Delta J_{HgC}/Hz$	$R_{HgC}$
1	690.3	$23.2 \pm 1.1$	36.6	-0.06102	$655 \pm 56$	$0.95 \pm 0.08$
2	691.3‡	$27.1 \pm 0.7$	46.1	-0.07699	$744 \pm 27$	$1.08 \pm 0.04$
4	692.5	$-28.6 \pm 0.4$	-55.1	0.09201	$864 \pm 15$	$1.25 \pm 0.02$
7	693.8§	$-45.4 \pm 0.7$	-86.6	0.14445	$855 \pm 14$	$1.23 \pm 0.02$

† See table 1.

‡ Obtained by interpolation.

§ [4].

where  $\alpha$  indicates that the harmonic vibrational contributions are included in the  $D^{exp}$  value.

The  $D_{HgC}^{exp}$  can be measured from the  $^{199}Hg$  satellites in the  $^{13}C$  N.M.R. spectrum of partially oriented dimethylmercury. In this work,  $\Delta J_{HgC}$  was studied in the liquid crystals 1, 2, 4 and 7 (see table 1). The final results and other relevant parameters are collected in table 7. The anisotropy is found to vary from  $655 \pm 56$  Hz to  $864 \pm 15$  Hz, the smallest value being measured in the ZLI 1167 liquid crystal. The value  $855 \pm 14$  Hz in phase 4 is in fair agreement with  $795 \pm 50$  Hz derived earlier in this laboratory [4, 5]. The dependence of  $\Delta J_{HgC}$  on the liquid crystal solvent is relatively much less than that observed for  $\Delta J_{CF}$  in methyl fluoride- $^{13}C$  [10]. This, on the other hand, can be expected on the basis of the orientational behaviour.

The theoretical relative anisotropy of the  $^{199}Hg$ - $^{13}C$  coupling tensor was calculated on the non-iterative version of the programs REX [21, 22] and REXNMR [23-25], using the default hyperfine integrals for carbon and those given in [26] for mercury. The theoretical value of 1.34 appears to be in fair agreement with the experimental one of  $1.25 \pm 0.02$  determined in the liquid crystal mixture number 4.

#### 4. Conclusions

This N.M.R. study of dimethylmercury dissolved in mixtures of the liquid crystals Merck phase 4 and ZLI 1167 shows that the geometry is only slightly, but however detectably, dependent upon the liquid crystal solvent. The use of the proper mixture of the liquid crystals mentioned leads to the following best structural parameters:  $\angle HCH$   $108.9448 \pm 0.0008^\circ$ ;  $r_{CH}/r_{HgC}$   $0.5282 \pm 0.0001$ . The corresponding chemical shift anisotropies are:  $\Delta\sigma_H$   $4.7 \pm 0.1$  p.p.m.,  $\Delta\sigma_C$   $52.6 \pm 0.3$  p.p.m. and  $\Delta\sigma_{Hg}$   $7260 \pm 90$  p.p.m, and the Hg-C coupling anisotropy  $864 \pm 15$  Hz.

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