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Proton Magnetic Resonance Studies of Methylmercuric Halides in Isotropic and Nematic Liquid Crystal Solutions†

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Abstract—The PMR spectra of methylmercuric halides (chloride, bromide and iodide) including the spectra of the isotopic species containing ^{199}Hg and ^{13}C in the natural abundance have been investigated. Measurements on mixed solutions show that there is a rapid exchange of the halogen atoms. The relative bond distance $R_{HgC} : R_{CH}$ and the bond angles HCH and HHgC are determined. The HCH angle is $(110.00 \pm 0.04)°$ for methylmercuric chloride, $(110.10 \pm 0.03)°$ for bromide and $(110.20 \pm 0.03)°$ for iodide. Within limits of experimental accuracy the ratio R_{HgC}/R_{CH} is the same for all the studied compounds (1.828 ± 0.005).

The proton chemical shift anisotropies are found to be 2.4, 2.6 and 2.8 ppm for the chloro, bromo and the iodo compound respectively.

1. Introduction

Several workers[1–4] have studied the PMR spectra of methylmercuric halides dissolved in isotropic solvents. The compounds in natural abundance contain about (1) 82% molecules with ^{12}C and Hg isotopes of spin 0 or $\frac{3}{2}$ (2) 17% $^{12}CH_3{}^{199}HgX$ (Spin of $^{199}Hg = \frac{1}{2}$) (3) 1% molecules with ^{13}C (Spin $= \frac{1}{2}$) and Hg isotopes of spin 0 or $\frac{3}{2}$ and (4) a negligible fraction of $^{13}CH_3{}^{199}HgX$. The PMR spectrum in isotropic solution consists of a strong central line (species (1)), a doublet placed symmetrical to the central line (the isotopic effects on the chemical shift are negligible) due to (2) with a separation equal to the coupling constant (J_{HgH}) between ^{199}Hg and ^{1}H and a much weaker doublet

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due to species (3) with a separation equal to J_{CH} where J_{CH} is the indirect spin-spin coupling constant between ^{13}C nuclei and ^{1}H.

The line-widths of the ^{199}Hg–H doublets for the chloro and the bromo compounds have been found to be less than 1.0 Hz whereas for the iodo compound exceptionally large line-widths (5–16 Hz) depending upon the solvent and the temperature, have been obtained. The spectra of the mixtures of different methylmercuric halides consist only of one set of lines[1–3] with the chemical shift and the two scalar spin-spin coupling constants equal to the weighted means of those for the individual species. The results have been interpreted by assuming an exchange of the methyl groups [1–3] and the exchange rates have been calculated from the line-width of the Hg–H doublet.[1] In a later study[4] it has been found that the temperature dependence of the line-width cannot be explained by an exchange of the methyl groups and it was concluded that instead an exchange of the halogens takes place. In fact only such an exchange can easily explain the observation of the mean values for the J-couplings in mixtures.

A study of the proton spectrum of partially oriented methylmercuric chloride dissolved in a nematic phase has also been made.[5] Such a spectrum consists of a triplet with an intensity ratio of 1 : 2 : 1 due to species (1). The total splitting of the triplet gives $|6D_{HH}|$ where D_{HH} is the direct dipolar coupling[9] within the protons of the methyl group. Symmetrical to each component of the triplet, there is a doublet due to the interaction of ^{199}Hg with ^{1}H (species 2), the splitting between the components of the doublet being equal to $|2D_{HgH} + J_{HgH}|$. In addition, ^{13}C–H interactions (species 3), give rise to doublets (but much weaker in intensity due to low natural abundance of ^{13}C) around each component of the triplet, with separation equal to $|2D_{CH} + J_{CH}|$. The ^{13}C–H satellites can be observed in the natural abundance by accumulating a few hundred spectra. The direct dipolar coupling constants give the relative bond distances and the bond angles. From the earlier NMR studies on methylmercuric chloride in a nematic solvent, a value of the HCH angle equal to $(106.2 \pm 0.6)°$ had been obtained.[4] The result is surprising since the normal value for the HCH angle of CH_3 groups is nearly 110°.

The present studies on methylmercuric chloride, bromide and iodide were undertaken with a view to check the earlier results and to

look for the influence of different substituents on the structure of the mercury methyl moiety. Studies on the mixtures of the various halides provide some additional information on the exchange.

2. Experimental

Methylmercuric halides were obtained from commercial sources. The spectra were recorded on a Varian XL-100† spectrometer. For time averaging, a Varian Computer (C-1024) was used.

(1) Spectra in the Isotropic Media

About 10 weight % solutions of the methylmercuric halides containing some tetramethylsilane (TMS) were studied in benzene solutions. Equal volumes of the solutions of the chloro and the iodo compounds were mixed and the spectra of the mixtures were also recorded. A similar mixture of the solutions of the bromo compound and the iodo compound was also studied.

(2) Spectra in the Nematic Phase

About 8 mole % solutions of the mercury compounds were made in a mixture 80% (by weight) *N*-(*p*-ethoxybenzylidene)-*p'*-*n*-butylaniline (*a*) and 20% (by weight) *O*-carbobutoxy-*p*-oxybenzoic acid ethoxy phenyl ester (*b*).

The freshly prepared solutions gave the spectra of the dissolved compounds with rather broad lines (width $\simeq$ 40 Hz at the wings). The samples (in 5 mm NMR sample tubes) were stored horizontally at about 30 °C for a few days before spectra with line-widths of less than 7 Hz could be obtained. The samples were placed in the probe for about a day before recording and accumulating the spectra. The central component of the triplet was used as the " lock-signal ". For measuring the total splitting, the high frequency component of the CH_3-triplet was first recorded with a sweep width of 1000 Hz. The sweep off-set was then changed to such an extent that the low frequency component could be recorded and positioned close to the earlier one. From the change in the sweep off-set and the distance

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between the signals, the total splitting was determined and hence $|D_{HH}|$ obtained.

The ^{199}Hg–H satellites could be observed in a single scan spectrum but only with a relatively low signal to noise ratio. About 400–800 scans were made to finally record the ^{199}Hg–H and ^{13}C–H satellites.

The corresponding indirect couplings were determined from the spectra in the isotropic solutions. The samples were heated above the clearing point and the spectra recorded at several temperatures in order to take into account any temperature dependence of the indirect coupling constants. It was found that J_{CH} did not have any noticeable temperature dependence but J_{HgH} decreased by about 0.5 Hz per 10 °C increase of temperature for the chloro compound and 0.2 Hz per 10 °C increase of temperature for the bromo compound. The temperature dependence for the iodo compound was not determined because of the large line-width of the Hg–H satellites in this case. (The extrapolated values of J_{HgH} are included in Table 1).

TABLE 1 Spectral Parameters for Methylmercuric Halides Dissolved in Benzene

Compound	Chemical Shift in ppm relative to TMS†	$\|J_{HgH}\|$ (Hz)†	J_{CH} (Hz)	Line-width of the Hg–H Satellites (Hz)
CH_3HgCl	-0.047 ± 0.005	204.5 ± 0.3	138.0 ± 1.0	1.0 ± 0.2
CH_3HgBr	-0.115 ± 0.005	199.5 ± 0.3	139.0 ± 1.0	1.0 ± 0.2
CH_3HgI	-0.202 ± 0.005	185.0 ± 2.0	140.0 ± 2.0	10.0 ± 2.0
CH_3HgCl + CH_3HgI	-0.090 ± 0.005 (-0.112 ± 0.01)	199.0 ± 1.0 (196.2 ± 2.3)	138.0 ± 1.0	4.0 ± 1.0
CH_3HgBr + CH_3HgI	-0.148 ± 0.005 (-0.155 ± 0.01)	196.0 ± 1.0 (193.0 ± 2)	139.0 ± 0.5	4.0 ± 1.0

† Values within the parentheses are calculated values.

The measurements of the chemical shifts of the methyl group with respect to TMS were complicated because in the nematic solution, the central component of the triplet was very close to the TMS-line (which was much more intense). Consequently for the determination of the chemical shift, the center of the triplet was determined from the outer components. In the isotropic solution, measurements were

made at several temperatures and the isotropic chemical shift at the room temperature was determined by linear extrapolation.

For the study of the chemical exchange equal volumes of the solutions of the iodo and the bromo compounds were mixed and the spectra were recorded at room temperature. Similar experiments were performed for the mixture of all the three compounds.

3. Results and Discussions

(1) Solutions in Benzene

The values of the chemical shifts, the indirect ^{199}Hg–H and the ^{13}C–H coupling constants of the mercury compounds dissolved in benzene are given in Table 1. The line-widths of the ^{199}Hg–H satellite resonances are included in the last column of the table. For the mixture of the chloro with the iodo compound and the bromo with the iodo compound, only one set of resonances due to $^{12}CH_3$ group and the ^{199}Hg–H and ^{13}C–H satellites was observed for each case. The values of the derived parameters for the mixture are also included in Table 1. These are intermediate compared to the corresponding values for the individual components of the mixtures. In the table, the calculated values of the chemical shift and the coupling constant (J_{HgH}) are given within parentheses.

The appearance of the spectra with average values of the parameters for the mixtures of the methylmercuric halides establishes the presence of an exchange in these systems as reported earlier.[1] However, as far as the site of the exchange and the correlation of the exchange rate with the line-width of the ^{199}Hg–H satellites are concerned, the earlier results[1] need to be re-interpreted. If the exchange between the methyl groups attached to ^{199}Hg and those attached to other isotopes of mercury takes place, one cannot expect to get an average value of the ^{199}Hg–H coupling constant. The observation of the intermediate value of J_{HgH} establishes that the exchange involves the halide group. Such conclusions for methylmercuric iodide[4] have also been drawn from a study involving the temperature dependence of the PMR spectrum. There is in general no simple correlation between the exchange rate and the line-width of the ^{199}Hg–H satellites.

(2) Solutions in the Nematic Phase

(a) *Molecular structure*

The molecules of the type CH_3HgX possess a 3-fold axis of symmetry passing through C, Hg and X nuclei.[6] The spectra of molecules with a CH_3 group and hetero nuclei have been thoroughly investigated.[7–10] The equation relating the structure with the direct dipolar coupling is:[7–10]

$$\frac{D_{XH}}{D_{HH}} = \left(\frac{\gamma_X}{\gamma_H}\right)\left(\frac{r_{HH}}{r_{XH}}\right)^3 \left\{\left(\frac{r_{HH}}{r_{XH}}\right)^2 - 2\right\} \tag{1}$$

where X stands for ^{13}C or ^{199}Hg and other symbols have their usual meanings. From the ratios (r_{HH}/r_{XH}), the angles HCH (α) and H HgC (β) can be calculated with the help of Eqs (2) and (3).

$$\frac{r_{HH}}{r_{CH}} = 2 \sin \frac{\alpha}{2} \tag{2}$$

$$\frac{r_{HH}}{r_{HgH}} = \sqrt{3} \sin \beta \tag{3}$$

The analysis of the spectra in the nematic and the isotropic phases provides only the absolute values of the couplings in these cases. Their signs are determined from the following considerations: Since $\alpha > 90°$, D_{CH} and D_{HH} have the same sign but D_{HgH} and D_{HH} have the opposite signs since β is certainly less 32°. This limit is obtained by assuming that $r_{CH} \leqslant 1.2$ Å, $r_{HgC} \geqslant 1.9$ Å and $\angle HgCH \geqslant 90°$.

The ratio (r_{HH}/r_{HgH}) and the angle β were calculated with both possible sign combinations of D_{HgH} and J_{HgH}. It was found that only the combinations with the same signs for D_{HgH} and J_{HgH} give reasonable molecular structures. The other combinations have no solution with $0 \leqslant \beta \leqslant 32°$.

We assume that the symmetry axis of the molecules is oriented preferentially parallel to the direction of the magnetic field (and accordingly a positive sign of D_{HH}) as is found for similar compounds.[7–11] It follows from this that $D_{HgH} < 0$, $J_{HgH} < 0$ and $D_{CH} > 0$. J_{HgH} has in fact been found negative for similar compounds[11–13] and, therefore, it confirms the assumption of the positive S-value for the symmetry axis.

The sign of J_{CH} is positive[7] for a $^{13}CH_3$ group. The (r_{HH}/r_{CH}) values and the angle α were accordingly calculated assuming that D_{CH} and J_{CH} have the same signs. The opposite sign combination of D_{CH} and J_{CH}, however, gives a value of α which is only about 1° larger and hence it would not be possible to discard it for structural reasons alone.

The values of the direct and the indirect coupling constants are given in Table 2.

TABLE 2 The Direct and the Indirect Coupling Constants (in Hz) for Methylmercuric Halides Dissolved in the Nematic Phase of (a) + (b), at Room Temperature

Compound	J_{HgH}	J_{CH}	D_{HH}	D_{HgH}	D_{CH}
CH_3HgCl	-204.0 ± 0.5	137.5 ± 1.0	2137.43 ± 0.8	-195.5 ± 0.75	1616.75 ± 3.5
CH_3HgBr	-198.1 ± 0.2	139.0 ± 1.0	2182.83 ± 0.7	-199.95 ± 0.60	1661.5 ± 2.5
CH_3HgI	-184.0 ± 0.7	138.6 ± 0.5	1900.88 ± 0.7	-174.3 ± 0.85	1456.5 ± 2.5

The geometrical information derived is given in Table 3. γ_{Hg}/γ_H and γ_C/γ_H used were 0.17827 and 0.25144 respectively. (r_{HgC}/r_{CH}) values given in Table 3 were calculated from the other geometrical data.

TABLE 3 Geometrical Parameters in Methylmercuric Halides

Compound	r_{HH}/r_{HgH}	r_{HH}/r_{CH}	r_{HgC}/r_{CH}	∠HCH (α) in degrees	∠HHgC (β) in degrees
CH_3HgCl	0.6972 ± 0.0013	1.6383 ± 0.0004	1.8266 ± 0.005	110.00 ± 0.04	23.74 ± 0.05
CH_3HgBr	0.6976 ± 0.0010	1.6393 ± 0.0003	1.8278 ± 0.005	110.10 ± 0.03	23.75 ± 0.04
CH_3HgI	0.6979 ± 0.0016	$1.6403 + 0.0003$	1.8296 ± 0.007	$110.20 + 0.03$	23.76 ± 0.06

The table shows that the angle HCH has the normal value of about 110° for all these compounds. The value of the angle slightly increases from the chloro to the iodo compound. We consider that this

reflects a real change in the molecular structure since the neglected vibrational correction will be practically equal for these compounds. The change may be connected with the decrease of the ionic character of the Hg–X bond. Differences in the other geometrical data for the three compounds were found to be negligible within experimental errors. (We cannot explain the low value ($106.2 \pm 0.06°$) of the HCH bond angle obtained in the earlier PMR studies on the chloro compound.) Microwave studies[16, 17] within error limits give a constant value of 2.074 ± 0.015 Å for the Hg–C distance in these compounds. This value with the NMR data given in Table 3 gives $r_{CH} = 1.135 \pm 0.013$ Å for all the compounds. This is rather high but it is known from the earlier NMR studies[8, 14, 15] (where a value of about 1.125 Å was found) that the neglect of the influence of molecular vibrations is usually reflected in an apparent increase of about 2% of the C–H bond distance.

A comparison of the HHgC angle for these compounds with the corresponding angle of 23° 5′ for dimethyl mercury[11] indicates that although a halogen substitution does not produce any detectable change in this angle, a methyl substitution does produce a change. Differences in the Hg–C distances between methylmercuric halides and dimethylmercury have in fact been observed by electron diffraction and microwave spectroscopic studies.[6] It was found that this distance increases by about 0.1 Å which could account for the decrease in β.

(Recently, we repeated Englert's studies[11] on dimethylmercury in the above described nematic mixture. We also studied the ^{13}C-satellite spectrum. Because of the disturbing overlap, we could observe only those satellite lines which appear outside the range of the spectrum of the ^{12}C-species. For that reason we were able to determine only the ^{13}C–H coupling constant for the directly bonded nuclei. The J-couplings determined in the sample heated to the isotropic phase were $|J_{HgH}| = 102.3 \pm 0.2$ Hz and $|J_{CH}| = 129.4 \pm 0.2$ Hz. In the nematic phase at 30 °C, the degree of order along the symmetry axis was $S = 0.1701 \pm 0.0001$ (assuming $r_{HH} = 1.80$ Å). We find $\beta = 23.10 \pm 0.03°$ and the bond angle HCH $= 108.36 \pm 0.03°$. This corresponds to the ratio $r_{HgC}/r_{HH} = 1.844 \pm 0.003$ which is about 1% larger than the ratio in the methylmercuric halides. Accordingly, the decrease in β is mainly due to the change in the HCH bond

angle and only to a minor degree to a change in relative bond lengths.)

(*b*) *Chemical shift anistropies*

The values of the proton chemical shifts measured relative to TMS added as the internal standard are given in Table 4 together with the D_{HH} values in such solutions. As mentioned earlier, the chemical shifts in the isotropic solutions were measured by heating the samples above the clearing points. It was found that the methyl proton resonance shifted to the lower field by 6.5 Hz for the chloro, 6.1 Hz for the bromo and 5.5 Hz for the iodo compound as a result of changing the temperature from 66 °C to 102 °C. Assuming a linear change of the chemical shift with temperature, the values of the isotropic shifts at 30 °C and 50 °C were calculated and are included in Table 4. The validity of the assumption of the linear change of the chemical shift with temperature was checked by calculating the chemical shift anisotropies at both the temperatures.

The proton chemical shift anisotropy ($\Delta\sigma$) ($=\sigma_{\parallel} - \sigma_{\perp}$ where $\sigma_{\parallel}$ is the shielding measured along the 3-fold axis of symmetry and $\sigma_{\perp}$ perpendicular to it) is obtained from the shift difference ($\Delta\delta$) between the center of spectra in the nematic and the isotropic phases and with the help of Eq. (4):

$$\Delta\sigma = \frac{3}{2}\frac{\Delta\delta}{S_{C_3}} \tag{4}$$

The proton resonances were found to be at higher fields in the nematic solutions compared to those in the isotropic solutions.

The values of $\Delta\sigma$ obtained both at 30 °C and 50 °C are given in Table 4. They are the same within experimental errors (± 0.1 ppm).

The proton chemical shift anisotropy increases slightly outside the experimental error (± 0.1 ppm, the systematic error of the method may be assumed to be the same for all the compounds), from the chloro to the iodo compound. A similar trend of the proton chemical shift anisotropy is found for the methyl halides[9, 18] although the differences for methyl halides are larger than for methylmercury halides.

TABLE 4 Proton Chemical Shifts, the Direct Couplings, S_{C_3} Values and the Proton Chemical Shift Anisotropies in Methylmercuric Halides

Compound	Isotropic Chemical Shift in ppm relative to TMS				Chemical Shift (ppm) Relative to TMS in the Nematic Phase		D_{HH} (Hz)		S_{C_3}†		$\Delta\sigma$ (ppm)‡	
	102° C	66 °C	50 °C (extrapolated)	30 °C (extrapolated)	50 °C	30 °C	50 °C	30 °C	50 °C	30 °C	50 °C	30 °C
CH_3HgCl	−0.511 ± 0.001	−0.446 ± 0.002	−0.417 ± 0.002	−0.381 ± 0.002	−0.135 ± 0.008	−0.03 ± 0.01	1705 ± 3	2135.5 ± 0.9	0.1778 ± 0.0003	0.2227 ± 0.0001	2.38	2.36
CH_3HgBr	−0.597 ± 0.001	−0.536 ± 0.002	−0.509 ± 0.002	−0.475 ± 0.002	−0.229 ± 0.007	−0.12 ± 0.01	1567 ± 4	1994.7 ± 0.8	0.1637 ± 0.0004	0.2083 ± 0.0001	2.57	2.56
CH_3HgI	−0.703 ± 0.001	−0.648 ± 0.002	−0.624 ± 0.002	−0.593 ± 0.002	−0.330 ± 0.005	−0.234 ± 0.01	1498 ± 4	1841.7 ± 0.8	0.1567 ± 0.0004	0.1927 ± 0.0001	2.81	2.79

† Calculated with r_{HH} = 1.843, 1.844 and 1.845 Å respectively.

‡ Experimental error is ±0.01 ppm. The total error, however, is estimated to be around 1 ppm if the uncertainty in combining the isotropic and the nematic shifts for the calculation of $\Delta\sigma$ is taken into consideration.[8]

(c) *The Halide exchange*

The mixture of the solutions of equal volumes of the bromo and the iodo compounds dissolved in the nematic phase gave a spectrum with average values of the parameters (without any noticeable change in the line-widths). The total triplet splitting was between that for the solutions of the separate compounds (12063 Hz for the bromide solution, 11230 Hz for the iodide solution and 11845 Hz for the mixture). The value of $|2D_{Hg}+J_{HgH}| = 555.5$ Hz was also in between (598 Hz for the bromo and 533 Hz for the iodo compound). A mixture of the chloro, the bromo and the iodo compound also exhibited a similar behavior.

The fact that we cannot observe separate spectra in the mixtures and that there is no increase in the line-widths indicates that the halogen exchange rate is faster than 1000 sec^{-1}.

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