

## NMR OF ORIENTED ORGANO-MERCURY COMPOUNDS

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The results obtained from NMR studies of organomercury compounds such as methyl mercury halides, methyl mercury nitrate, dimethyl mercury, 1,1,1-trifluoromethyl methyl mercury, bis(cyclopentadienyl) mercury and phenyl mercury chloride are summarised. The structural information derived is discussed. A rapid halogen exchange in methyl mercury halides has been observed. The structure of bis(cyclopentadienyl) mercury corresponds to the  $\sigma$ -bonded type only if there is a bond shift or an exchange. The importance of the use of mixed liquid crystals of opposite diamagnetic anisotropies for the study of organomercury compounds is emphasized.

**Key Words :** Organometallic Compounds; Dipolar Couplings; Indirect Couplings; Chemical Shift Anisotropy

### INTRODUCTION

NMR studies of molecules dissolved in liquid crystalline solvents are extremely useful in the determination of structure and conformation of organometallic compounds. From the NMR experiments, the information on the metal-carbon bond can be directly obtained if the metal nuclei have non-zero (specially  $1/2$ ) spins. The studies involve the use of metal and/or proton magnetic resonance. The complexes of metals such as Sn, Se, Te, Hg, Mn, Os, Fe, W, Pt, Ni, Ge, As, Ru, Re, Cd, Sb and Cr have so far been examined using NMR spectroscopy of oriented systems.<sup>1</sup> The present contribution is aimed to provide an up-to-date information of the mercury compounds. The <sup>199</sup>Hg-isotope has a natural abundance of 17 per cent and a nuclear spin of  $1/2$ . It is, therefore, a very suitable nucleus from the NMR point of view. Furthermore, in view of the rich coordination chemistry, the toxicological importance and the recognition of the role of the organomercury compounds in environmental pollution, their studies have become of considerable interest.

### RESULTS AND DISCUSSION

The compounds studied are methyl mercury halides,<sup>2-4</sup> methyl mercury nitrate,<sup>5,6</sup> dimethyl mercury,<sup>2,7-11</sup> 1,1,1-trifluoromethyl methyl mercury,<sup>12</sup> bis(cyclopentadienyl) mercury<sup>13</sup> and phenyl mercury chloride.<sup>14</sup> The derived information is summarised below :

#### 1. Methyl Mercury Halides

These are perhaps the simplest mercury compounds studied from NMR spectroscopy of oriented systems. The compounds in the natural abundance

contain about (1) 82 per cent molecules with carbon and mercury isotopes with 0 or 3/2 nuclear spins (2) 17 per cent  $^{12}\text{CH}_3$   $^{199}\text{HgX}$ , where  $X$  is a halogen atom (spin of  $^{199}\text{Hg}$  is 1/2) (3) 1 per cent molecules with  $^{13}\text{C}$  (spin = 1/2) and Hg isotopes of spins 0 and 3/2 and (4) negligible fraction of  $^{13}\text{CH}_3$   $^{199}\text{HgX}$ . The proton spectra of the molecules including the  $^{13}\text{C}$  and the  $^{199}\text{Hg}$  satellites have been investigated. The spectra of molecules without the satellites consist of a triplet with intensity ratio of 1 : 2 : 1 with a total separation of  $|6 D_{\text{HH}}|$ , where  $D_{\text{HH}}$  is the intramolecular HH dipolar coupling constant. Symmetrical to each component of the triplet, there is a doublet due to the interaction of  $^{199}\text{Hg}$  with  $^1\text{H}$  (species 2), the doublet separation being  $|J_{\text{HgH}} + 2D_{\text{HgH}}|$ , where  $J_{\text{HgH}}$  and  $D_{\text{HgH}}$  are the indirect and direct HgH coupling constants respectively. In addition, the species (3) give rise to doublets (but with much weaker intensity due to lower natural abundance of  $^{13}\text{C}$ ) symmetrically placed around each component of the triplet with separation equal to  $|J_{13\text{CH}} + 2D_{13\text{CH}}|$ , where  $J_{13\text{CH}}$  and  $D_{13\text{CH}}$  are the indirect and the direct dipolar coupling between  $^{13}\text{C}$  and  $^1\text{H}$ . The indirect spin-spin couplings can be derived from the spectra in the isotropic media. The spectra in the nematic phase thus provide the values of  $D_{\text{HH}}$ ,  $D_{199\text{HgH}}$  and  $D_{13\text{CH}}$ . They are related<sup>2</sup> to the geometrical parameters by equations (1-3) :

$$D_{\text{XH}}/D_{\text{HH}} = (\gamma_X/\gamma_{\text{H}})(r_{\text{HH}}/r_{\text{XH}})^2 [(r_{\text{HH}}/r_{\text{XH}})^2 - 2], \quad \dots(1)$$

$$r_{\text{HH}}/r_{\text{CH}} = 2 \sin \alpha/2 \quad \dots(2)$$

and  $r_{\text{HH}}/r_{\text{HgH}} = \sqrt{3} \sin \beta, \quad \dots(3)$

where  $\gamma_i$  is the magnetogyric ratio of the  $i$ -nucleus ( $i$  is  $^{13}\text{C}$ ,  $^{199}\text{Hg}$  and  $^1\text{H}$  in this case)  $r_{ij}$  is the distance between nuclei  $i$  and  $j$ ,  $X$  stands for nuclei  $^{13}\text{C}$  or  $^{199}\text{Hg}$ ,  $\alpha$  is the HCH bond angle and  $\beta$  represents the HHgC angle.

The HCH bond angles in the chloro, bromo and the iodo compounds have thus been determined as 110.00, 110.10 and 110.20° respectively with an error of about 0.03°. The angle slightly increases from the chloro to the iodo compound and this change has been considered as the real change since the neglect of the vibrational corrections in this case has a similar effect on the bond angles in the three cases. In a latter study,<sup>4</sup> it has been actually found that the vibrational corrections change the HCH bond angle by about 0.7° in each case such that an application of such corrections increases the angles. The change is attributed to the change of ionic character of the Hg-X bond. The HHgC angle has been determined as  $23.75 \pm 0.05^\circ$  in each case. An application of the vibrational corrections reduces the value by about 0.2°.

The mixtures of the solutions of the methyl mercuric halides dissolved in the nematic phase give spectra with average values of the parameters without noticeable changes in the line-widths. For example, for a mixture of solution with equal volumes of the bromo and the iodo compounds, the total triplet separation

was 11,845Hz compared to 12,063Hz for the bromo and 11,230Hz for the iodo compound. These facts indicate the halogen exchange in these compounds with an exchange rate faster than  $1000 \text{ sec}^{-1}$ .

## 2. Methyl Mercury Nitrate

A procedure similar to that discussed above for the methyl mercury halides has been followed for the study of the structure of methyl mercury nitrate.<sup>5</sup> The proton and the  $^{13}\text{C}$ -NMR spectra of the compound dissolved in a thermotropic and a lyotropic phase<sup>5,6</sup> have been investigated. The vibrationally corrected values of the angles  $\alpha$  and  $\beta$  have been determined as  $110.58^\circ$  and  $23.67^\circ$  in the thermotropic and  $111.45^\circ$  and  $23.4^\circ$  in the lyotropic solvent. Values of the angles in the *nitro* compound in the thermotropic solvent are only slightly different from those in the methyl mercury halides. The differences between the values in the thermotropic and the lyotropic solvents are, however, significant. The Hg-C bond distance in the halides and the *nitro* compound are 204.4 and 203.0 pm in the thermotropic solvents.

## 3. Dimethyl Mercury and 1,1,1-Trifluoromethyl Methyl Mercury

These are the most exhaustively investigated organomercury compounds since the complete structures of the systems can be determined. In addition, the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{199}\text{Hg}$  chemical shielding and the indirect spin-spin coupling anisotropies have been derived.

The system dimethyl mercury possesses a 3-fold axis of symmetry since the two methyl groups are freely rotating and the nuclei  $\text{CHgC}$  are colinear. The various dipolar couplings are related to the geometrical parameters by the following equations :

$$(D_{ij}/(D_{ii})_{\text{intra}} = -3\sqrt{3} \gamma_j/\gamma_i \sin^3 \theta (2-3 \sin^2 \theta); \quad \dots(4)$$

$$\text{and} \quad (D_{ii})_{\text{inter}}/(D_{ii})_{\text{intra}} = 3\sqrt{3} / \pi \int_0^{2\pi} (a^2/b^2 + \cos \phi - 1)/((a^2/b^2) - 2 \cos \phi + 2)^{5/2} d \phi, \quad \dots(5)$$

where  $D_{ij} = ^{13}\text{CH}$  or  $^{199}\text{HgH}$  direct dipolar coupling  $D_{ii} = \text{HH}$  dipolar coupling and the symbols inter and intra represent the dipolar coupling between the inter and intra methyl protons,  $a$  is the distance between the planes containing the methyl protons and  $b$  is the distance of the methyl protons from the  $\text{C}_3$ -axis of symmetry.

The  $^{13}\text{C} - ^{199}\text{Hg}$  and the  $(\text{HH})_{\text{intra}}$  dipolar couplings ( $D_{\text{HgC}}$  and  $(D_{\text{HH}})_{\text{intra}}$ ) are related to the Hg-C and the  $\text{HH}(r_{\text{HgC}}$  and  $r_{\text{HH}})$  distances by equation (6).

$$(D_{\text{HgC}}/D_{\text{HH}}) = 2\gamma_{\text{Hg}} \gamma_{\text{C}}/\gamma_{\text{H}}^2 (r_{\text{HH}})_{\text{intra}}/r_{\text{HgC}}^3 \quad \dots(6)$$

Equations (4-6) have been used to determine the various geometrical parameters. The vibrational corrections to the observed dipolar couplings have been applied and the vibrationally corrected ( $r_w$ ) structure determined. The values have

been determined in various solvents and found to be practically solvent-independent. A value of  $207.97 \pm 0.05$  pm has been determined for the HgC-distance. The value is about 1 per cent larger than that in the methyl mercury halides. Similarly, a methyl substitution produces a reduction in the HCH bond angle by  $1.5-1.7^\circ$  compared to the value in methyl mercuric halides.

The vibrationally corrected  $r_\alpha$ -structure of 1,1,1-trifluoromethyl methyl mercury has also been determined similarly but the precision of determination of some of the geometrical parameters particularly the FCF bond angle and the FHg C angle was low ( $\pm 9-10^\circ$ ). This has been attributed to the low degree of order of the compound in some of the liquid crystal solvents.

#### 4. *Bis(cyclopentadienyl) Mercury*

Though several  $\pi$ -bonded complexes of cyclopentadienyl metal tricarbonyls<sup>15-21</sup> or nitrosyl<sup>12</sup> have been investigated, the study on the  $\sigma$ -bonded complex is perhaps restricted to bis (cyclopentadienyl) mercury. If the structure is of the  $\sigma$ -bonded type, the spectrum can be analysed as an AA'BB'C type provided the inter-ring

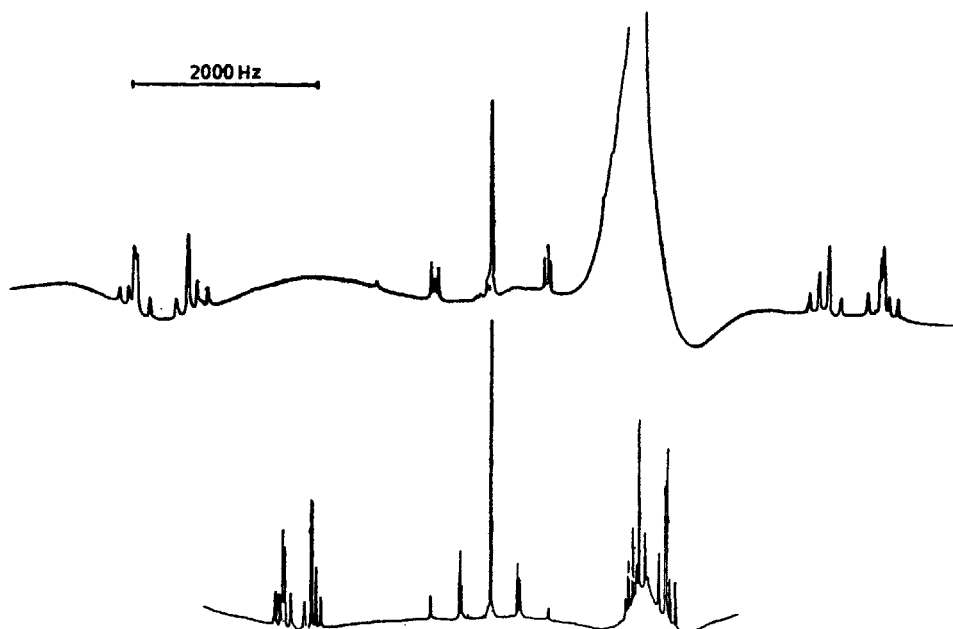


FIG 1 The 270 MHz proton magnetic resonance spectra of 2.6 wt per cent solution of phenyl mercuric chloride oriented in a 1:1 mixture of ZLI-1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile) and TNC-1132 (mixture of three phenyl cyclo hexanes and one biphenyl cyclohexane). The top trace (at 306 K) corresponds to the preferential alignment of the optic axis of the liquid crystal along the direction of the magnetic field and the bottom trace to that orthogonal to it.

Number of transients : 14,000 and 40,000 for the upper and the lower trace respectively. Spinning speed : 20Hz.

proton proton couplings are neglected. The results indicate that the structure is  $\sigma$ -bonded only if there is some kind of averaging in the molecule such that it leads to the effective 5-fold symmetry. The lines are broad in this case perhaps due to the unresolved inter-ring dipolar couplings. The required symmetry can also be achieved by an exchange process e.g. between the  $\sigma$ -bonded cyclopentadienyl units and the free cyclopentadienyl anions.

### 5. Phenyl Mercury Chloride

The use of mixed liquid crystals of opposite diamagnetic anisotropies in organometallic compounds has earlier been made in the selenium compounds<sup>22,23</sup> for obtaining information which otherwise cannot be obtained from the spectra of oriented molecules. At a critical concentration and temperature of the two liquid crystals, two spectra due to two different molecular orientations "coexist" such that the dipolar couplings corresponding to one orientation differ by a factor of  $-2$  compared to those in the other.<sup>24</sup> The experiments permit the separate evaluation of the indirect and the direct dipolar couplings—an information which otherwise cannot be obtained from the same spectrum. Phenyl mercury chloride is the first mercury compound where such experiments have been undertaken.<sup>14</sup> Typical spectra just above and below the critical point are shown in Fig. 1.

The proton spectra have been studied including the  $^1\text{H}$ - $^{199}\text{Hg}$ -satellites. The results provide the value of the Hg-C bond distance as 202pm.

It may be emphasised that the experiments not only permit the determination of NMR parameters which otherwise cannot be obtained from a single experiment but they also provide the molecular structure with minimal distortions.<sup>25</sup>

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