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Review

NMR SPECTRA AND STRUCTURE OF ORGANOMERCURY COMPOUNDS

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I. Introduction

Organic derivatives of mercury, besides their extensive application in medicine, agriculture and industry, are widely used as model compounds in studying regularities of various types of chemical reactions [123]. In the latter case it is very important to have detailed information on the structure of compounds under investigation.

Fifteen years ago it was shown for the first time [18, 23, 83] that high resolution NMR spectroscopy is a very valuable tool for the study of the structure of organomercury compounds. These molecules contain ^{1}H, ^{13}C, ^{199}Hg and, very often, ^{19}F nuclei which are detectable in NMR. All these nuclei have spins I 1/2 and (except for ^{13}C) high natural abundances (^{1}H 99.9%, ^{13}C 1.1%, ^{19}F 100%, ^{199}Hg 16.8%). Relative sensitivities for an equal number of nuclei at constant field are high for ^{1}H (1.00) and ^{19}F (0.83), but low for ^{13}C ($1.59\ 10^{-2}$) and ^{199}Hg ($5.67\ 10^{-3}$). Nevertheless, as will be shown below, with the development of the technique of high resolution NMR it became possible to have ^{13}C and ^{199}Hg spectra of good quality which give, when combined with ^{1}H and ^{19}F spectra, further valuable information on the structure of organomercurials.

To the best of our knowledge, this review includes all data on NMR spectra of various organic derivatives of mercury and summarizes the 15 years of application of NMR spectroscopy in organomercury chemistry. We gave preference to a contemporaneous discussion of ^{1}H, ^{13}C, ^{19}F and ^{199}Hg NMR spectra for various types of organomercury compounds.

II. Alkylmercury compounds

A. Methyl derivatives

1. Dimethylmercury. Several works of various authors were devoted exclusively to the study of this molecule [79, 22, 101]. In other papers [23, 29, 133, 41, 121, 40, 134, 151, 106, 145, 35, 153] it was one of a number of compounds studied.

NMR parameters for liquid dimethylmercury are given below:

$\delta(^1H) \pm 5.5$ (from external benzene reference) [23]; $\delta(^{13}C)$ 169.3 (from internal CS_2 reference) [151]; $\delta(^{199}Hg)$ −2460 ppm (from external water solution of $Hg(NO_3)$ [133].

$J(^1H{-}^{13}C)$ 129.6 [22]; $J(^{13}C{-}^{199}Hg)$ 687.4 [22]; $J(^1H{-}C{-}^{199}Hg)$ −101.5 [22]; $J(^1H{-}C{-}Hg{-}^{13}C)$ −1.9 [22]; $J(^1H{-}C{-}Hg{-}C{-}^1H)$ 0.45 Hz [22].

On the basis of the difference between the ^{199}Hg chemical shifts for Me_2Hg and Et_2Hg (+ 330 ppm)* it was concluded [23] that the hyperconjugation shown below is not important in dialkylmercury compounds because if this were the case, the mercury nucleus should be more shielded in Me_2Hg than in higher homologs.

It was shown in our laboratory [101, 106] that the parameters of ^1H NMR spectra of Me_2Hg [$\delta(^1H)$ and $J(^1H{-}C{-}^{199}Hg)$] change substantially on going from solutions in inert solvents to solutions in strongly coordinating solvents, as shown in Table 1.

Analysis of the data given in Table 1 shows that there is no correlation between changes in $J(^1H{-}C{-}^{199}Hg)$ and $\delta(^1H)$. It was concluded [106] that various factors such as the dispersion interaction of solute and solvent, magnetic anisotropy of the solvents, and the solvation of Me_2Hg affect the $\delta(^1H)$ parameter, whereas only the solvation of Me_2Hg influences the $J(^1H{-}C{-}^{199}Hg)$ spin—spin coupling constants. Therefore we have placed the solvents in Table 1 in order of increasing $J(^1H{-}C{-}^{199}Hg)$, which, from our viewpoint, is the order of electron-donor power; we shall consider below the origin of complexes formed through the examples of diethyl- and dibenzyl-mercury.

2. *CH_3HgX compounds.* In 1963 Hatton, Schneider and Siebrand [41] reported the results of measurements of $\delta(^1H)$ and $J(^1H{-}C{-}^{199}Hg)$ constants in CH_3HgX compounds. The values of these parameters for 5 mol-% solutions in pyridine are summarized in Table 2. Analysis of the data shows that there is an approximate correlation of $J(^1H{-}C{-}^{199}Hg)$ and $\delta(^1H)$, and a rough correlation of both these parameters with the electronegativity of the group attached to mercury.

It was shown also [41] that the effect of solvent on $J(^1H{-}C{-}^{199}Hg)$ constants in CH_3HgX molecules is much smaller (Table 3) than that of the substituent. The authors [41] concluded that for the slightly dissociated MeHgOAc the $J(^1H{-}C{-}^{199}Hg)$ constants increase with increase in polarity of the solvents. As

---

* 304 ppm in ref. 145 and 280 ppm in ref. 133.

TABLE 1

^{1}H NMR PARAMETERS FOR SOLUTIONS OF Me_2Hg IN VARIOUS SOLVENTS [101, 106]

Solvent	$J(^1H—C—^{199}Hg)$ (Hz)	$\delta(^1H)$ (ppm)
Cyclohexane	101.0	1.13
CCl_4	102.0	1.16
$CHCl_3$	102.0	1.14
CH_2Cl_2	102.0	1.16
Dioxane	103.0	1.16
Acetone	104.0	1.21
1,2-Dimethoxyethane (DME)	104.0	1.23
Tetrahydrofuran (THF)	104.0	1.25
Tetrahydrothiophene (Tiophan)	104.0	1.16
Hexamethylphosphoric acid triamide (HMPT)	105.0	1.25
Diethoxyethane (DEE)	105.0	1.20
Triethylamine (TEA)	106.5	1.25
Tetramethylethylenediamine (TMED)	106.5	1.25
Pyridine	107.5	1.14
Diethyl sulfide (DES)	108.0	1.21
Dimethylformamide (DMF)	108.5	1.25
Dimethylsulfoxide (DMSO)	109.0	1.28

for $MeHgNO_3$ or $MeHgClO_4$, they may exist [41] in pyridine or D_2O solutions as $MeHgPy^+$ or $MeHgOD_2^+$ cations, and the value of $J(^1H—C—^{199}Hg)$ for a benzene solution of $MeHgClO_4$ is due to high hygroscopic properties of this compound and to formation of the $MeHgOD_2^+$ ion.

It should be noted also that it was concluded recently [3] on the basis of

TABLE 2

$\delta(^1H)$ AND $J(^1H—C—^{199}Hg)$ OF CH_3HgX IN PYRIDINE [14]

Compound	$J(^1H—C—^{199}Hg)$ (Hz)	$\delta(^1H)^a$ (ppm)
Me_2Hg	104.3	1.110
$MeHgCH{=}CH_2$[b]	106.7	1.070
$MeHgC_6H_5$[c]	109.0	1.957
$MeHgC{\equiv}CH$[d]	150.6	0.855
$(MeHg)_2S$	156.6	0.750
MeHgCN	178.0	0.650
MeHgY	200.0	0.317
MeHgSCN	208.0	0.383
MeHgBr	212.0	0.317
MeHgOH	214.2	0.442
MeHgCl	215.2	0.425
$(MeHg)_2C_2O_4$	215.2	0.412
$(MeHg)_2SO_4$	216.0	0.418
$(MeHg)_3PO_4$	220.5	0.575
MeHgOAc	220.8	0.525
$MeHgNO_3$[e]	227.0	0.362
$MeHgClO_4$	233.2	0.170

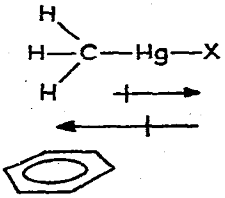
[a] $\delta(^1H)$ are measured with respect to internal cyclohexane. [b] Neat compound, ref. 146. [c] $CDCl_3$ solution, ref. 121. [d] See also ref. 155. For DMSO solution $J(^1H—C—^{199}Hg)$ — 149 Hz [5]. [e] For D_2O solution $J(^1H—C—^{199}Hg)$ —258 Hz and $J(^{13}C—^{199}Hg)$ + 1800 Hz [5].

TABLE 3

$J(^1H—C—^{199}Hg)$ CONSTANTS (Hz) FOR CH_3HgX IN VARIOUS SOLVENTS [41]

Compound	Solvent		
	Benzene	Pyridine	D_2O
MeHgCN	176.0	178.0	
MeHgOH	204.0	214.2	
$(MeHg)_2SO_4$	205.0	216.0	
$(MeHg)_2C_2O_4$	205.0	215.2	
MeHgOAc	214.3	220.8	233.4
$(MeHg)_3PO_4$		220.5	233.2
$MeHgNO_3$	240.6	227.0	259.2
$MeHgClO_4$	259.8	233.2	259.6

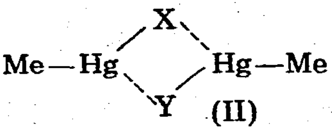
data for benzene solutions of MeHgX compounds that there is an intermolecular coordination in solutions (I).



(I)

It was also shown [41] that the two satellites of the methyl proton resonance, both the satellites arising from spin coupling of ^1H and ^{199}Hg, are very sharp (< 0.5 Hz) in the majority of compounds studied. Exceptional behavior was observed for the bromide, the iodide, and the thiocyanate for which the satellites were broadened without broadening of the central methyl resonance. The authors concluded that "fast alkyl exchange in which methyl groups attached to ^{199}Hg exchange with groups attached to non-magnetic mercury atoms would cause broadening". However, it was shown later [40, 38, 138, 82] that this broadening of the satellites is significant only for MeHgI and is better explained by fast relaxation of the ^{199}Hg nuclear spin. The large quadrupole moment of iodine is probably responsible for this relaxation.

Anion exchange was demonstrated [40, 38, 138, 82, 61] in various MeHgX—MeHgY systems, explainable as in II:

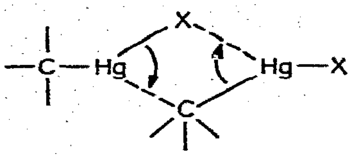


(II)

However, it was shown also [82] that pyridine favors the formation of Me_2Hg.

$$2MeHgX \xrightarrow{\text{pyridine}} Me_2Hg + HgX_2$$

This may be explained in terms of the transition state III proposed formerly [121].



(III)

It is very interesting that the rates of anion exchange decrease in the series Br > Cl > I, i.e., the transition state for MeHgBr is the most stable.

The experimental values of $J(^1H—C—^{199}Hg)$ given in Table 2 were rationalized by the authors [41] in terms of a simplified model for contact interaction employing optical hyperfine structure constants. Qualitative arguments were employed to assess the relative importance of spin—orbit interaction and the dipole—dipole term. It was concluded that "the spins of mercury and hydrogen nuclei in alkylmercuric compounds are coupled mainly through Fermi contact interaction. Spin coupling arising from electron orbital motion is negligible, whereas dipole—dipole contribution may be important."

Recently [42] an extended Hückel procedure for calculation of $J(^1H—C—^{199}Hg)$ constants was outlined and on the basis of the data obtained it was suggested that all the major features of $J(^1H—C—^{199}Hg)$ constants in alkylmercury compounds can be accounted for in terms of a Fermi contact mechanism and little use of mercury 5*d* orbitals in the bonding. It was shown recently [73] by means of Pulse Fourier Transform ^{199}Hg NMR spectroscopy that the screening constants for ^{199}Hg nuclei in MeHgX compounds increase in the series Cl < Br < Y and depend strongly on the nature of the solvent used. In all the cases studied the ^{199}Hg nuclei are much more shielded in DMSO than in pyridine. The present authors believe that these data strongly support the conclusions derived from ^{1}H, ^{13}C and ^{19}F NMR data for various organomercury compounds, that DMSO has greater electron-donor power than has pyridine (see Sections II. A.1, 4., II. B.1 and others).

3. *Bis(trifluoromethyl)mercury.* In its physical and chemical properties bis(trifluoromethyl)mercury differs from its simple methyl analog [24]. X-ray data [28] for solid $(CF_3)_2Hg$ indicate a linear C—Hg—C skeleton, and on the basis of infrared and Raman spectra it was concluded [24] that the molecule retains its linear shape when in solution. ^{19}F NMR spectra of bis(trifluoromethyl)mercury [24, 121] in various solvents consist of a single line with the two types of satellites due to $^{19}F—^{199}Hg$ and $^{13}C—^{19}F$ couplings. The spectral parameters are given in Table 4. The results can be rationalized if we assume that weak complexes of the type $(CF_3)_2Hg \cdot D$ (D= solvent) are formed in solutions. The effects are appreciable for CF_3HgX compounds (see below).

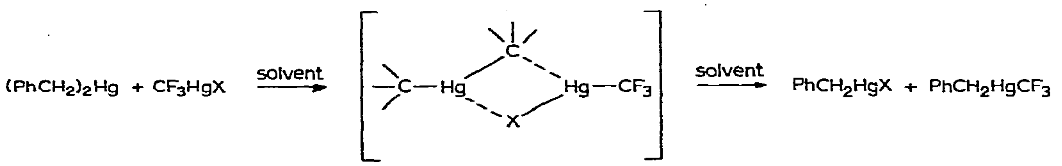
4. *CF_3HgX compounds.* These compounds are widely used [136] as convenient reagents for the preparation of $PhHgCF_3$, a useful difluorocarbene precursor, and in our laboratory [109, 110] as model compounds for a study of the effect of solvent upon the rates and mechanisms of organometallic reactions. The kinetics of these reactions (see below) can be easily studied by means of ^{1}H or ^{19}F NMR spectroscopy.

TABLE 4

^{19}F NMR SPECTRAL PARAMETERS FOR SOLUTIONS OF $(CF_3)_2Hg$

Solvent	$\delta(^{19}F)$ (ppm)	$J(^{19}F—C—^{199}Hg)$ (Hz)	$J(^{13}C—^{19}F)^a$ (Hz)
$CDCl_3$	-42.7^b	1253.0^d	
Benzene	-42.0^b; 36.4^c	1259.0^d; 1324.5^e	356.3^e
Pyridine	33.8^c	1259.9^d	358.4^e
CH_3OH	-40.2^b; 36.6^c	1323.0^d; 1312.1^e	
Water	-41.6^b	1324.0^d	

[a] The $^{13}C—^{19}F$ satellites consist of quartets with a splitting of 5.3 Hz (benzene solution) or 3.8 Hz (pyridine solution). [b] External CF_3COOH (ref. 121). [c] Internal $CFCl_3$ (ref. 24). [d] Ref. 121. [e] Ref. 24.



The ^{19}F NMR spectral parameters for various CF_3HgX compounds are given in Table 5. Analysis of the data in Table 5 shows that $J(^{19}F—C—^{199}Hg)$ constants increase with electron-acceptor properties of X. This observation can be rationalized if we assume [114] that $J(^{19}F—C—^{199}Hg)$ constants are proportional to the *s*-electron densities on ^{19}F and ^{199}Hg nuclei and that the increase of electron-acceptor properties of X leads to redistribution of 6*sp*-hybridized electrons in the Hg—CF_3 and Hg—X sites, so that the relative content of *s*-electrons increases in Hg—C bonds as does the relative content of *p*-electrons in Hg—X bonds.

We have studied the temperature- and concentration-dependences of $J(^{19}F—C—^{199}Hg)$ constants for CF_3HgX (X = I, Cl, $OCOCF_3$) molecules in various

TABLE 5

^{19}F NMR SPECTRAL PARAMETERS FOR CF_3HgX COMPOUNDS IN $CHCl_3$ [136]

X in CF_3HgX	$J(^{19}F—C—^{199}Hg)$ (Hz)	$\delta(^{19}F)^a$ (ppm)
CH_3	932^b	-41.8^b
$C_6H_5CH_2$	952^c	
C_6H_5	1008	−124.7
p-FC_6H_4	1031	−124.6
m-FC_6H_4	1046	−124.5
CF_3	1250	−126.0
I	1710^c 1769^b	-43.4^b
Br	1766, 1928^b	−130.4
Cl	1800	−130.9
$OCOCF_3$	2208	−132.4

[a] Downfield from internal hexafluorobenzene, unless otherwise stated. [b] In CH_3OH [121]; $\delta(^{19}F)$ from external CF_3COOH. [c] In CH_2Cl_2 [112, 113].

solvents [112]. The results suggest that these molecules in the solid state are associated through the X· · · · Hg bridge bonds. The rupture of these intermolecular bonds by inert solvent dilution leads to dissociation of $(CF_3HgX)_n$ units to monomeric (X = Cl) and dimeric (X = I, $OCOCF_3$) molecules. In strongly coordinating solvents there are mainly $CF_3HgX \cdot 2D$ complexes. In pyridine solutions an equilibrium between the 1/1 and 1/2 complexes exists. Complexes of the type $CF_3HgX \cdot D$ are T-shaped and have higher relative content of *s*-electrons in the Hg—C—F site, compared with tetragonal $CF_3HgX \cdot 2D$ complexes. The electron-donor power of solvents studied changes in the series (X = Cl, I); DMSO > DMF > acetone > THF > pyridine, whereas for $CF_3HgOCOCF_3$ this series is somewhat different; DMSO > acetone > DMF > THF > pyridine.

5. *Other methyl derivatives of mercury.* A good correlation between the $J(^1H—C—^{199}Hg)$ coupling constants in CH_3HgX (X = OR, SR, OCOR) compounds and the p*K* values of the parent HX compounds was observed [30, 144]. It was shown earlier [7] that the correlation between the $J(^1H—C—^{199}Hg)$ constants in $(RR'CH)_2Hg$ compounds and the pK_a values of the hydrocarbons $RR'CH_2$ can be successfully used for estimation of pK_a values for various hydrocarbons according to the equation: $pK_a = -0.298J(^1H—C—^{199}Hg) + 71.17$.

Various methylmercury derivatives of carboranes [32], carboranecarboxylic acids [49] and carboclosododecaboranes(11) [33] were studied by means of ^1H NMR spectroscopy.

PMR was also used in a study of complexation of various methylmercury systems [95, 137, 122], whereas in a study of complexation of bis(trinitromethyl) mercury [46] PMR was combined with ^{13}C and ^{14}N NMR techniques.

B. *Ethylmercury compounds*

1. *Diethylmercury.* This compound has been studied by various authors [23, 29, 133, 41, 145, 35, 153, 83, 84, 108, 132]. All the spectral parameters for a solution of Et_2Hg in CCl_4 are given below.

$\delta(^1H)CH_3$ 1.27, $\delta(^1H)CH_2$ 1.01 (with respect to internal TMS) [108]; $\delta(^{13}C)CH_3$ —13.0, $\delta(^{13}C)CH_2$ —36.0 (from internal TMS) [35]; $\delta(^{199}Hg)$ 304.0 ppm (with respect to internal Me_2Hg) [145].
$J(^1H—C—C—^1H)$ 7.6 [145]; $J(^1H—C—^{199}Hg)$ 97.0 [145], 98.0 [108];
$J(^1H—C—C—^{199}Hg)$ 126.6 [145], 127.5 [108]; $J(^{13}C—^{199}Hg)$ 642.0 [35];
$J(^{13}C—C—^{199}Hg)$ 25.0 [35].

It should be emphasized that these spectral parameters, especially $\delta(^{199}Hg)$, depend strongly on the concentration of Et_2Hg in solution [145]. The dependence of these parameters on the nature of the solvents is much more pronounced, as shown in Table 6.

^1H and ^{13}C chemical shifts (Table 6) do not depend strongly on the nature of solvents, whereas substantial changes are observed for $J(^1H—C—^{199}Hg)$ and $J(^{13}C—^{199}Hg)$ coupling constants. Assuming that these changes are due to solvation of Et_2Hg by the solvents, we have concluded [108, 114] that this solvation process is not followed by changes in *s*-electron densities in mercury, because if this were the case, $J(^1H—C—C—^{199}Hg)$ and $J(^{13}C—C—^{199}Hg)$ constants should have been changed as well as $J(^1H—C—^{199}Hg)$ and $J(^{13}C—^{199}Hg)$. The changes in the

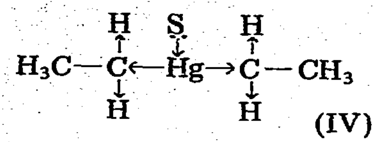
TABLE 6

NMR SPECTRAL PARAMETERS[a] FOR Et_2Hg IN VARIOUS SOLVENTS [108, 35]

Solvent	$\delta(^1H)CH_3$ (ppm)	$\delta(^1H)CH_2$ (ppm)	Δ^b (ppm)	$J(^1H{-}C{-}^{199}Hg)$ (Hz)	$\delta(^{13}C)CH_3$ (ppm)	$\delta(^{13}C)CH_2$ (ppm)	$J(^{13}C{-}^{199}Hg)$ (Hz)
CCl_4	−1.27	−1.01	0.26	98.0	−36.0	−13.0	642.0
$CHCl_3$	−1.27	−1.00	0.27	98.0	−35.3	−13.2	648.0
CH_2Cl_2	−1.26	−0.98	0.28	98.0			
Dioxane	−1.27	−0.98	0.29	101.0			
DME	−1.28	−0.97	0.31	101.0	−35.1	−13.3	663.0
Pyridine	−1.28	−0.96	0.32	102.0	−35.3	−13.8	679.0
DMF	−1.28	−0.93	0.35	102.5			
DMSO	−1.25	−0.90	0.35	104.5	−34.7	−13.5	688.0
HMPT	−1.26	−0.89	0.37	104.5			

[a] δ in ppm, J in Hz; $J(^1H{-}C{-}C{-}^{199}Hg)$ 127.5 Hz and $J(^{13}C{-}C{-}^{199}Hg)$ 25.0 Hz in all solvents studied. [b] $\Delta = \delta(^1H)CH_3 - \delta(^1H)CH_2$.

latter are due to changes in s-electron densities in the methylene hydrogens and carbons because of the inductive influence, shown in IV. It is very interesting



$$H_3C-\underset{\overset{\downarrow}{H}}{\overset{\overset{H}{\uparrow}}{C}}\leftarrow\overset{\overset{S}{\downarrow}}{Hg}\rightarrow\underset{\overset{\downarrow}{H}}{\overset{\overset{H}{\uparrow}}{C}}-CH_3$$

(IV)

that $J(^1H—C—^{199}Hg)$ constants and Δ-values are changed in the same series of solvents; this may be explained in terms of the general mechanism of solvation given above.

It should be emphasized that whenever we discuss the changes in spin—spin coupling constants we speak about absolute values of these constants. It is very important, however, to know the algebraic value of every constant. As for coupling of mercury nuclei with protons and carbons, it was shown in the case of Me_2Hg [22] (see above) that $J(^1H—C—^{199}Hg)$ is negative, whereas $J(^{13}C—^{199}Hg)$ is positive. On the other hand, it was concluded [83] on the basis of analysis of an ABX-system that $J(^1H—C—^{199}Hg)$ and $J(^1H—C—C—^{199}Hg)$ constants in Et_2Hg have opposite signs. Then we may assume that $J(^1H—C—C—^{199}Hg)$ is positive, as it was shown [5] for EtHgCl molecule (see below).

2. *C_2H_5HgX compounds.* It was shown [29, 41] that on going from Et_2Hg to EtHgX compounds there are substantial changes in the chemical shifts of methylene protons and in spin-spin coupling constants of methyl and methylene protons with mercury nuclei (Table 7).

Table 7 shows [41] that the linear correlation between $\delta(^1H)CH_2$ and $J(^1H—C—^{199}Hg)$ exists, as was shown for CH_3HgX compounds (see above). There is, however, no correlation between chemical shifts of the methyl protons and the corresponding mercury—proton coupling constant. The changes in chemical shifts of the methyl and methylene protons were explained by the authors [41] in terms of the electronic effects of the substituent which, however, do not extend beyond the CH_2 group. On the other hand, the magnetic anisotropy effect of the Hg—X bonds was also assumed [29] to be important. As for the larger value of $J(^1H—C—^{199}Hg)$ constant in comparison with the $J(^1H—C—C—^{199}Hg)$ constant, it was assumed that there is a dipole contribution of the opposite sign to the former constant. Turning now to the experimental fact that $J(^1H—C—^{199}Hg)$

TABLE 7

SPECTRAL PARAMETERS [a] FOR SOLUTIONS OF EtHgX IN PYRIDINE [41]

Compound	$\delta(^1H)CH_3$ [b]	$\delta(^1H)CH_2$ [b]	Δ [c]	$J(^1H—C—^{199}Hg)$	$J(^1H—C—C—^{199}Hg)$
Et_2Hg	0.06	+0.37	0.31	100.1	127.5
EtHgCN	0.02	—0.26	0.28	186.0	222.0
EtHgBr	0.06	—0.52	0.58	213.8	301.0
EtHgCl [d]	0.10	—0.47	0.57	216.0	296.0
$EtHgNO_3$	0	—0.65	0.65	233.0	311.0
EtHgI [e]	0.02	—0.65	0.67		
$EtHgClO_4$ [f]	0.14	—0.84	0.98		

[a] δ in ppm, J in Hz. [b] With respect to internal cyclohexane. [c] $\Delta = \delta(^1H)CH_3—\delta(^1H)CH_2$. [d] For DMSO solution $J(^1H—C—^{199}Hg)$ is —222 and $J(^1H—C—C—^{199}Hg)$ is 300Hz [5]. [e] CH_2Cl_2 solution [29]. [f] D_2O solution [29].

TABLE 8

MERCURY—PROTON COUPLING CONSTANTS (Hz) FOR CH_3CH_2HgX IN VARIOUS SOLVENTS [41]

Compound		Solvent		
		Benzene	Pyridine	D_2O
C_2H_5HgCN	$J(^1H—C—^{199}Hg)$	182.0	186.0	
	$J(^1H—C—C—^{199}Hg)$	222.0	222.0	
$C_2H_5HgNO_3$	$J(^1H—C—^{199}Hg)$	236.6	233.0	250.0
	$J(^1H—C—C—^{199}Hg)$	348.0	311.0	369.0

is negative and $J(^1H—C—C—^{199}Hg)$ positive (see above), one can see from Tables 6—8 that the difference between the $J(^1H—C—^{199}Hg)$ and $J(^1H—C—C—^{199}Hg)$ constants is much greater than the difference between the absolute values of these constants.

The effect of solvents upon the magnitudes of both the coupling constants is also appreciable (see Table 8). The data in Table 8 show that for the covalent ethylmercuric cyanide the behavior of the $J(^1H—C—^{199}Hg)$ and $J(^1H—C—C—^{199}Hg)$ constants is analogous to that of the respective constants for Et_2Hg (see Table 6). This behavior differs from that observed for ethylmercuric nitrate. It was concluded that this compound resembles CH_3HgNO_3 (see above) and exists in pyridine or D_2O solutions as $C_2H_5HgPy^+$ or $C_2H_5HgOD_2^+$ ions. For the ethylmercuric bromide and iodide the broadening of the satellites due to mercury—proton coupling was also erroneously explained in terms of exchange of ethyl groups, as it was done in the case of methyl compounds [41]. We believe that the reasons for this broadening are the same as those for the CH_3HgX molecules [38, 40, 138] (see above).

3. *Bis(perfluoroethyl)mercury.* This and related compounds were firstly studied in 1960 [66] by means of ^1H and ^{19}F NMR spectroscopy. The spectral parameters are given in Table 9.

Recently [34] the solvent effect upon the mercury coupling constants with proton and fluorine nuclei in $(R_f)_2$ Hg compounds has been studied. The data are given in Table 10. These two Tables show that changes in $J(^{19}F—C—C—^{199}Hg)$ constants can be easily explained in terms of *s*-electron densities on the coupled nuclei. However, it is impossible to explain in the same way the changes in $J(^1H—C—^{199}Hg)$ and $J(^{19}F—C—^{199}Hg)$ constants. Therefore it was proposed [34] that there is an intramolecular interaction between the *p*-electrons of fluorine atoms, bonded to α-carbons, with the vacant orbitals of mercury, the interaction decreasing the *s*-character of the mercury *sp*-hybridized orbitals and, accordingly, the values of $J(^1H—C—^{199}Hg)$ constants. As for $J(^{19}F—C—^{199}Hg)$ constants, the authors [34] believe that the changes in these constants are "anomalous" and also due to the presence of F atoms in the α-position. From the viewpoint of these authors, this assumption is supported by the observation of the solvent effect upon these constants (see Table 10). On going from inert solvents to the strongly solvating ones, the $J(^1H—C—^{199}Hg)$ and $J(^{19}F—C—C—^{199}Hg)$ constants increase, whereas $J(^{19}F—C—^{199}Hg)$ constants decrease. It was shown, however, in our laboratory [113] in a study of solvent effects upon the $J(^1H—C—^{199}Hg)$

TABLE 9

^{1}H AND ^{19}F NMR SPECTRAL PARAMETERS[a] FOR SOLUTIONS OF FLUOROETHYLMERCURIC COMPOUNDS IN CCl_4 AT 40 MHz [66]

Compound	$\delta(^{19}F)CF_3$[b, c]	$\delta(^{19}F)CF_2$[b, c]	$\delta(^1H)$[c, d]	$J(^{19}F{-}C{-}^{199}Hg)$	$J(^{19}F{-}C{-}C{-}^{199}Hg)$	$J(^1H{-}C{-}^{199}Hg)$
$(C_2F_5)_2Hg$	240	1275		770	71	
$(CF_3CFH)_2Hg$[e]	− 25	5850	− 52	480	161	
$(CF_3CH_2)_2Hg$[f]	−1154		112		224	130

[a] δ in ppm, J in Hz. [b] In Hz with respect to external CF_3COOH. [c] Resonances at magnetic fields lower than the zero points are considered negative. [d] In Hz with respect to external H_2O. [e] $J(^1H{-}C{-}C{-}^{19}F)$ 13, $J(^1H{-}C{-}^{19}F)$ 48, $J(^{19}F{-}C{-}C{-}^{19}F)$ 17 Hz. [f] $J(^1H{-}C{-}C{-}^{19}F)$ 15 Hz.

TABLE 10

SPIN–SPIN COUPLING CONSTANTS (Hz) FOR $(R_f)_2Hg$ COMPOUNDS IN VARIOUS SOLVENTS [41]

R_f	$J(^1H{-}C{-}^{199}Hg)$				$J(^{19}F{-}C{-}^{199}Hg)$				$J(^{19}F{-}C{-}C{-}^{199}Hg)$			
	CCl_4	CH_2Cl_2	DMF	Pyridine	CCl_4	CH_2Cl_2	DMF	Pyridine	CCl_4	CH_2Cl_2	DMF	Pyridine
CF_3CF_2					793	787	745	684	61.4	60.8	78.1 102.8	86.6 112.1
CF_3CFCl					689	680	585	533	80.7	81.4	104.0	112.4
$(CF_3)_2CF$					535	507	387	338	115.2	116.4	135.6	132.5
CF_3CFH	54.8	66.4	93.6	99.2	511	510	494 496	443 450	144.7 145.8	149.9	172.4 175.0	188.7 190.8
CF_3CH_2	125.4	130.7	142.1	145.4					219.5	229.2	251.4	261.5
$(CF_3)_2CH$	161.9	170.1		200.4					174.5	178.2	199.2	206.0

and $J(^{19}F—C—^{199}Hg)$ constants for $PhCH_2HgCF_3$ that the interaction of p-electrons of fluorine atoms bonded to α-carbons with the vacant orbitals of mercury has an anomalous influence on $J(^{19}F—C—^{199}Hg)$ only. At the same time, the $J(^1H—C—^{199}Hg)$ constants change analogously to the respective constants for Me_2Hg, Et_2Hg and $(PhCH_2)_2Hg$. Therefore, there are no reasons to use any additional assumptions on the mechanisms of their changes discussed above for Et_2Hg.

4. *Other ethyl derivatives of mercury.* The first paper concerned with NMR spectra of an organomercury compound was published in 1958 [18] and dealt with the hydroxy- and methoxy-ethylmercury derivatives. The same and related systems were studied later by other authors [11, 154, 129, 56, 48], in particular in order to try to demonstrate the existence of mercurinium ions in systems such as ethylene—HgX_2—water (see Section VIII.C.).

C. Miscellaneous alkylmercury compounds

The ^1H, ^{13}C and ^{199}Hg NMR spectral parameters for various propyl and butyl derivatives of mercury are given in Table 11.

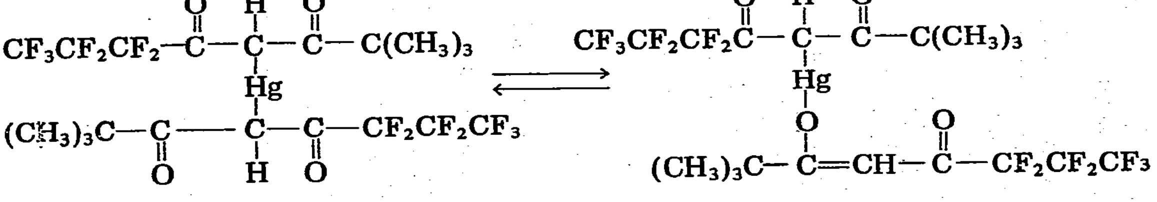
^1H and ^{19}F NMR parameters of $CF_3CH_2CH_2HgX$ are given in Table 12.

The neopentyl derivatives of mercury have been thoroughly studied by means of ^1H and ^{13}C NMR spectroscopy [139, 140]. For compounds such as $(CH_3)_3CCH_2HgR$ (or X), where R is a covalently bonded Me, Et, t-Bu, Me_3CCH_2 or $CH_2{=}CH$ group, and X is an easily-ionizable, CN, Br, Cl, $OCOCH_3$ or ONO_2 group, there are linear relationships of the methylene $J(^1H—^{13}C)$ vs $J(^1H—C—^{199}Hg)$ or vs. $J(^1H—C—C—C—^{199}Hg)$, and $J(^{13}C—C—^{199}Hg)$ vs. $J(^{13}C—C—C—^{199}Hg)$. However, deviations from linearity occur for the chloride, the bromide, the acetate, and the nitrate in the relationships between $J(^1H—C—^{199}Hg)$ and $J(^1H—C—C—^{199}Hg)$ or $J(^1H—C—^{199}Hg)$ and $J(^{13}C—C—^{199}Hg)$. These deviations are discussed in terms of hyperconjugative $p_\pi—d_\pi$ bonding between the methylene C—H bonds and mercury.

Some interesting model alkylmercury compounds have been studied with ^1H NMR spectroscopy by Kiefer and coworkers [148, 53—55], in particular for investigation of secondary valence forces operating in the intramolecular coordination of various electron-donor atoms with mercury. It should be emphasized that the authors [53] have shown for the first time that in many methoxyalkyl derivatives of mercury, methylene protons are sometimes coupled non-equivalently with the mercury bonded to the same carbon atom.

The mercury derivatives of acetoacetic ester also have been studied [52] in various solvents and it was shown that the $J(^1H—C—^{199}Hg)$ constant is the most sensitive to the nature of the solvent ^1H NMR spectral parameters.

It was shown with NMR recently [37] that there is a keto—enol tautomerism in bis (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadione-5-yl) mercury:



K *E*

TABLE 11

NMR SPECTRAL PARAMETERS[a] FOR PROPYL AND BUTYL DERIVATIVES OF MERCURY

Compound	Solvent	$\delta(^{199}Hg)$	$J(^{13}C-^{199}Hg)$	$J(^{13}C-C-^{199}Hg)$	$J(^{13}C-C-C-^{199}Hg)$	$J(^{1}H-C-^{199}Hg)$	$J(^{1}H-C-C-^{199}Hg)$
$(n-C_3H_7)_2Hg$	neat	240[b]				90[b]	
	CCl_4	210[c]	659[d]	−25[d]	102[d]	95[e]	108[b]
$(i-C_3H_7)_2Hg$	neat	640[b]					
	CCl_4	597[c]	633[d]	32[d]		78[b]	126[b]
$(n-C_4H_9)_2Hg$	CCl_4	205[c]	656[d, f]	26[d, f]	100[d, f]		
$(t-C_4H_9)_2Hg$	CCl_4	$\tau(CH_3)$:8.8[g]					103.6[g]
$t-C_4H_9HgCl$	CCl_4	$\tau(CH_3)$:8.85[h]					124.0[h]

[a] δ values are given in ppm, J values in Hz. [b] Ref. 23. [c] Ref. 145. [d] Ref. 153. [e] Ref. 62. [f] Ref. 152. [g] Ref. 94. [h] Ref. 115.

TABLE 12

^{1}H AND ^{19}F NMR SPECTRAL PARAMETERS[a] FOR $CF_3CH_2CH_2HgX$ COMPOUNDS IN CCl_4 [116]

X in $CF_3CH_2CH_2HgX$	$\delta(^{1}H)$[b]		$\delta(^{19}F)$[c]	$J(^{1}H-C-C-^{1}H)$	$J(^{1}H-C-C-^{19}F)$	$J(^{1}H-C-^{199}Hg)$	$J(^{1}H-C-C-^{199}Hg)$
	$\alpha-CH_2$	$\beta-CH_2$					
$CF_3CH_2CH_2$	1.15	2.48	10.1	7.9	10.5	110.0	109.5
I	2.09	2.55	11.0	6.8	10.1	198.0	217.5
Cl	1.99	3.06	10.6	7.9	10.1	223.0	226.0

[a] δ values in ppm, J values in Hz. [b] With respect to internal hexamethyldisiloxane. [c] From external CF_3COOH.

The *K* and *E* isomers have in acetone solutions at —75° different $J(^1H—C—^{199}Hg)$ constants: 257 (*K*) and 273 Hz (*E*).

^{19}F NMR spectroscopy has been used by Knunyantz and his coworkers in a study of some perfluoroalkyl derivatives of mercury [26] and various esters of mercurated perfluorocarboxylic acids [117].

It is interesting also that it was impossible to observe proton—mercury coupling for an industrially important organomercury compound, chloromerodrin, $H_2NCONHCH_2CH(OCH_3)CH_2HgCl$, in D_2O [21].

III. Aralkylmercury compounds

A. *Benzylic derivatives*

1. Dibenzylmercury. This compound has been widely studied by means of ^1H [8, 111], ^{13}C [35] and ^{199}Hg [145] NMR spectroscopy. The most important NMR parameters of dibenzylmercury are given below:

$\delta(^1H)CH_2$ —2.39 (from internal TMS in CH_2Cl_2) [8]; $\delta(^{13}C)CH_2$ 46.5 (from internal CS_2 in $CHCl_3$) [35]; $\delta(^{199}Hg)$ 700 ppm (from external Me_2Hg) [145]; $J(^1H—C—^{199}Hg)$ 130.0 (in CCl_4) [111], $J(^{13}C—^{199}Hg)$ 631.0 Hz (in $CHCl_3$) [35].

Comparison with the respective parameters for dimethylmercury (see Section II.A.1) shows that in compliance with the electron-withdrawing properties of the phenyl group there is a decrease of $\delta(^1H)$ and $\delta(^{13}C)$ and an increase of $J(^1H—C—^{199}Hg)$ on going from Me_2Hg to $(PhCH_2)_2Hg$. Nevertheless, an increase of $\delta(^{199}Hg)$ and a decrease of $J(^{13}C—^{199}Hg)$ are observed at the same time, which can be rationalized only if we assume that not only electronic factors but also other contributions are important. It was shown [8, 111] that $\delta(^1H)$ and $J(^1H—C—^{199}Hg)$ parameters for dibenzylmercury are markedly dependent on the nature of solvent and that there is a good correlation between the changes in these parameters in polar or non-polar solvents. The study of concentration- and temperature-dependences of $J(^1H—C—^{199}Hg)$ for $(PhCH_2)_2Hg$ in various solvents showed [111] that dibenzylmercury when dissolved in monodentate electron-donor solvents forms 1/1 complexes predominantly, whereas 1/2 complexes exist only at low temperatures. The data suggest that the 1/1 complexes are very weak and have planar T-structures, whereas the 1/2 ones are probably tetragonal pyramids. On the basis of experimental facts it was concluded that in the 1/1 complexes the relative content of s-electrons in the H—C—Hg site is higher than it is in the 1/2 complexes.

2. $PhCH_2HgX$ compounds. These compounds were intensively studied in our laboratory [104, 107, 113]. It was shown [104, 113] that for $PhCH_2HgX$ molecules the $J(^1H—C—^{199}Hg)$ constant increases with the electronegativity of X (Table 13).

The linear correlations between chemical shifts of methylene protons in $PhCH_2HgX$ molecules and methyl protons in CH_3CH_2X [143] suggests that the magnetic anisotropy of the C—Hg—X site influences predominantly the screening constants of protons in $PhCH_2HgX$ molecules.

On the basis of chemical shifts of aromatic protons in $PhCH_2HgX$ molecules (7.15—7.17 ppm) it was assumed [104] that CH_2HgX groups possess weak electron-donor properties, in good accordance with ^{19}F NMR data [103] show-

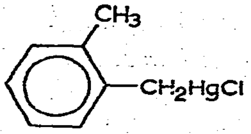
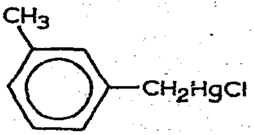
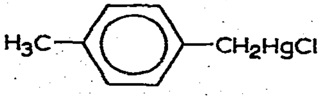
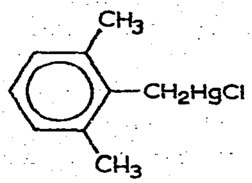
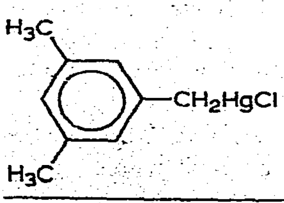
TABLE 13

^{1}H NMR SPECTRAL PARAMETERS FOR PhCH$_2$HgX COMPOUNDS [104, 113]

X in PhCH$_2$HgX	δ(^{1}H)CH$_2$ (ppm)		J(^{1}H—C—^{199}Hg) (Hz)
	dioxane	DMF	(in DMF)
OAc	3.05	3.12	287.5
Cl	3.07	3.14	285.0
Br	3.10	3.20	282.0
I	3.13		
CF$_3$		2.75	198.0

TABLE 14

^{1}H—^{199}Hg COUPLING CONSTANTS THROUGH 5,6 and 7 BONDS [107]

Compound	Number of bonds	J(^{1}H—^{199}Hg) (Hz)
	5	26.0
	6	14.0
	7	38.0
	5	28.0
	6	15.0

ing that for the CH_2HgCl group solvated by dioxane molecules σ_i is -0.02 and σ_R is -0.14. It was assumed also [103] that the enhancement of solvating power of solvents increases the weak electron-donor features of the CH_2HgCl group. This assumption is borne out by the experimental data of other authors [1, 57, 63] who studied ^{19}F chemical shifts for *m*- and *p*-fluorine-substituted dibenzylmercury and $FC_6H_4CH_2HgX$ (X = Cl, CH_3COO) molecules in various solvents. The study of a large series of substituted benzylmercuric chlorides showed that the screening constants of methylene protons in these molecules increase in the series *o*-NO_2 < *p*-NO_2 < H < *m*-F, *p*-F, < *m*-Cl, *p*-CH_3 < *p*-Cl, *m*-Br, *p*-Br, *m*-CH_3 < 3,5-di-CH_3 < *o*-Cl < *o*-F, *o*-CH_3, 2,6-di-CH_3 < 2,4,6-tri-CH_3. It was shown in this case that there is a linear correlation between the chemical shifts of the methylene and methyl protons in monomethylbenzylmercuric chlorides. These molecules are very interesting because they allowed observation for the first time of proton—mercury spin—spin coupling through five, six, and seven bonds (Table 14) [107]. The most interesting feature of the data obtained is the fact that $|{}^6J({}^1H{-}{}^{199}Hg)| < |{}^5J({}^1H{-}{}^{199}Hg)|$ and $|{}^7J({}^1H{-}{}^{199}Hg)|$ is higher than the respective constants through five and six bonds. Bearing in mind that proton—mercury coupling constants through two and three bonds have opposite signs [83] (see Section II.B.1), it was assumed [107] that the respective constants through 5, 6, and 7 bonds have also signs opposite to one another.

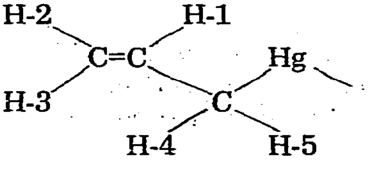
B. *Other aralkyl derivatives*

It was shown by Kiefer and his co-workers [54] that there is a substantial magnetic non-equivalence for protons of $ArCH_2$ and CH_2Hg groups in $ArCH_2C(CH_3)(OCH_3)CH_2HgX$ compounds, whereas in $ArCH_2C(CH_3)(OCH_3)CH_2Br$ this non-equivalence is greatly diminished. Bearing in mind that HgCl and $PhCH_2$ substituents are very nearly of the same effective size, the authors [58] concluded that there is an intramolecular mercury—arene coordination and that the mercury atoms should be situated above the edge of the ring rather than over the center.

IV. Allylmercury compounds

A. *Diallylmercury*

This compound was studied in detail by Zieger and Roberts [162] by means of 60, 100, and 220 MHz PMR spectroscopy. The PMR parameters obtained for a THF-d_8 solution of $(CH_2{=}CHCH_2)_2Hg$ at 37° are given below.



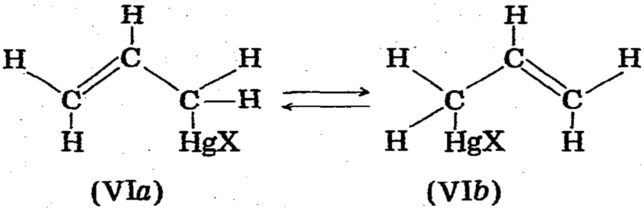
(V)

$\delta({}^1H\text{-}1)$ 6.04; $\delta({}^1H\text{-}2)$ 4.56; $\delta({}^1H\text{-}3)$ 4.68; $\delta({}^1H\text{-}4)$ and $({}^1H\text{-}5)$ 1.88 ppm. J_{12} 9.43; J_{13} 17.09; J_{14} and J_{15} 8.81; J_{23} 2.21; J_{24} and J_{25} -0.63; J_{34} and J_{35} -0.98; $J({}^1H\text{-}1{-}{}^{199}Hg)$ 45.85; $J({}^1H\text{-}2{-}{}^{199}Hg)$ 48.82; $J({}^1H\text{-}3{-}{}^{199}Hg)$ 49.96; $J({}^1H\text{-}4{-}{}^{199}Hg)$ 144.30 Hz.

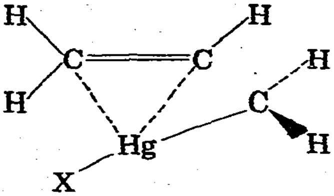
It was also shown that the broad, poorly resolved, lines in the spectrum of neat diallylmercury sharpen noticeably upon cooling or on dissolving in solvents such as tetrahydrofuran or carbon tetrachloride. The same observation was made earlier by West [157] and was rationalized in terms of concomitant allylic rearrangement and intermolecular exchange. The authors [162] believe that "the argument for intermolecular exchange is that degradation of the $ABCD_2X$ spectrum in the direction of an $ABCD_2$ spectrum seems qualitatively faster than the degradation of the $ABCD_2$ spectrum in the direction of an AB_4 spectrum".

B. $CH_2{=}CHCH_2HgX$ compounds

It was shown in 1963 [119] that pure $CH_2{=}CHCH_2HgX$ derivatives in a solvent such as $CDCl_3$ or DMSO display PMR spectra associated with ordinary "frozen" π-allyl structures (VI). However, addition of catalysts such as HgX_2 salts produces PMR spectra with the AX_4 proton pattern associated with rapidly equilibrating π-allyl species *a* and *b*. In more recent work [60] allylmercuric halides and acetate were studied in detail. It was shown, in particular, that in $CH_2{=}CHCH_2HgOAc$ $J(^1H\text{-}4{,}5{-}^{199}Hg)$ is 286, $J(^1H\text{-}1{-}^{199}Hg)$ 104 and $J(^1H\text{-}2{,}3{-}^{199}Hg)$ 95 Hz*. The fact that $J(^1H\text{-}2{,}3{-}^{199}Hg)$ values are only marginally smaller than $J(^1H\text{-}1{-}^{199}Hg)$ was rationalized by the authors [60] to be due to a substantial contribution from a conformation in which the mercury atom is located quite near the region of the double bond (VII). The authors believe, however, that the strong coupling may in part be due to a π-component in the C-1—C-2 bond as a result of extensive polarisation of the C-1—Hg bond, permitting "σ—π conjugation." The conformation VIII would then be most favored for the allylmercury system.



(VI*a*) (VI*b*)



(VII)

It was concluded also on the basis of PMR spectral parameters, that in allylmercuric perchlorate the interaction of the mercury atom with the double bond would be strongly favored and may lead to structure IX. The authors [60] be-

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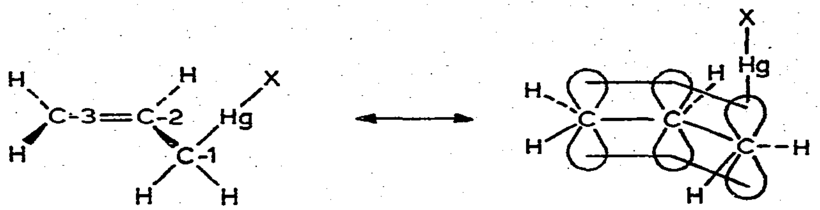
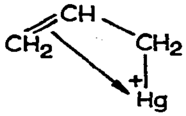
* The notation is the same as for diallylmercury (see above).



(VIIIa) (VIIIb)



(IX)

lieve that Hg—ene interaction in σ-allylic derivatives of mercury is a quite significant factor determining spectroscopic and reactivity properties.

C. Other allylic derivatives

The PMR spectra of β-methallyl, crotyl and cinnamyl-mercuric halides and acetates were comprehensively studied recently [60]. A very broad spectrum was observed for β-methallylmercuric chloride in $CHCl_3$ and it was sharpened by the addition of $HgCl_2$. Salts other than Hg^{II} were also examined, but only halides affected the spectra in a similar way. As for crotyl- and cinnamyl-mercuric bromides, they yielded well resolved spectra in DMSO-d_6. The addition of $HgBr_2$ or NaBr in trace, equimolar or excess amounts caused no discernible change in the NMR spectra in either DMSO-d_6 or $CHCl_3$. These data show that there is no doubt that the σ-allyl description for crotyl- and cinnamyl-mercuric bromides is appropriate. As for β-methallylmercuric chloride, the data suggest the operation of an equilibrating process even in the absence of HgX_2. Gubin and his coworkers [127] have studied recently the PMR spectra of some *m*- and *p*-fluorophenyl substituted allylmercuric chlorides in $CDCl_3$.

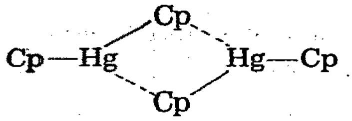
V. Cyclopentadienylmercury compounds

A. Dicyclopentadienylmercury

This molecule was assigned by Wilkinson and Piper [159] in 1956 to the σ-type with a localized mercury—carbon bond on the basis of IR and UV data and some chemical properties. It was also shown by the same authors [116] that in a PMR spectrum of this compound there is only one peak for all cyclopentadienyl protons. It was postulated that "the mercury atom is executing a 1,2-rearrangement at a rate greater than the expected chemical shift; the σ-cyclopentadienyl ring may thus be regarded as rotating, and with respect to NMR measurements all of the protons thus become equivalent".

On the other hand, it was concluded by Nesmeyanov and his coworkers [86, 25, 89] on the basis of PMR spectra of dicyclopentadienyl mercury in $CDCl_3$, acetone-d_6 or THF, that the π (or "sandwich") structure is most favorable for this molecule, particularly since no splitting of the cyclopentadienylic proton signal was observed even at —70°. The observation [74] of such a splitting for solution of Cp_2Hg in SO_2 at —70° was shown [90] to be incorrect. Nevertheless, it was shown later [158] that below —100° in Me_2O—THF the main peak in the 100 MHz spectrum of Cp_2Hg [$\delta(^1H)$ 6.35 ppm; $J(^1H—C—^{199}Hg)$ 71.0 Hz] rapidly broadens. This observation was rationalized in terms of a decrease in the fluxional character of Cp_2Hg at these very low temperatures. It was concluded in two papers independently by different authors [19, 75] that infrared spectra of Cp_2Hg demonstrate unequivocally that this molecule contains C—Hg σ-bonds and does not contain π-cyclopentadienyl rings.

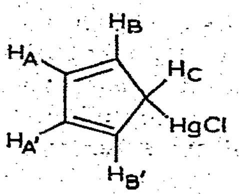
It was concluded also on the basis of the PMR spectra of Cp_2Hg in various solvents [76, 158] that intermolecular exchange of cyclopentadienyl groups takes place in the solutions under investigation. Bearing in mind that Cp_2Hg does not dissociate in solution [91], the authors [76] proposed the associative mechanism of the exchange shown below (X), and showed that the rate of this exchange increases in the solvent series $C_6H_6 < CCl_4 < CDCl_3 <$ ROR $< C_5H_5N$ $<$ DMF $<$ DMSO. This observation was rationalized in terms of specific solvation of Cp_2Hg and additional polarization of Cp—Hg bonds.



(X)

B. CpHgX molecules

The study of these molecules by means of NMR spectroscopy was carried out in parallel with the study of dicyclopentadienylmercury. PMR spectra of the compounds in THF or acetone-d_6 in the temperature range —73° to +25° [25, 89] involved single peaks with the satellites due to $^1H—C—^{199}Hg$ coupling. Therefore these spectra were rationalized in terms of π-bonded compounds. However, it was shown in 1969 [158] that for a solution of CpHgCl in THF-d_8 there are two signals in the PMR spectrum below —100°, with the chemical shifts $\delta_{av} = 1/4\,(2\delta_{AA'} + 2\delta_{BB'}) = 6.61$ and $\delta_C = 4.14$ ppm and with the relative intensities of 4/1 (XI). This spectrum is similar to those reported for other σ-Cp organometallic compounds and consistent with an assumption that CpHgCl is a fluxional molecule with the nuclear configuration of the lowest free energy, the cyclopentadienyl moiety being σ-bonded to mercury atom.

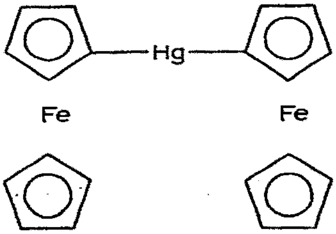


(XI)

In an analogous fashion fluxional character associated with a predominance of σ-Cp—Hg bonding in THF solutions of CpHgBr and CpHgI was observed [158]. It was concluded also that the rate of intramolecular "ring-whizzing" of the mercury atom about the cyclopentadienyl ring increases in the series CpHgCl < CpHgBr < CpHgI < Cp_2Hg. On the other hand, the extent to which intermolecular exchange of cyclopentadienyl groups takes place increases in a different order: Cp_2Hg < CpHgCl < CpHgBr < CpHgI.

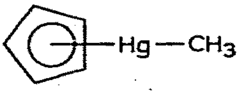
C. Other cyclopentadienyl derivatives

In 1963 Rausch [120] studied the PMR spectra of some ferrocenylmercury compounds. The spectral parameters obtained were in agreement with the structure proposed for diferrocenylmercury (XII). Several attempts to observe spin—spin coupling constants between the α-hydrogens and ^{199}Hg in this compound were unsuccessful. This unusual observation was rationalized in terms of rigid geometry of cyclopentadienyl ring, permitting no spin—spin coupling of this sort to occur.

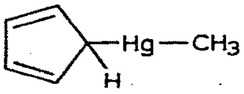


(XII)

The ^{1}H [89, 69] and ^{13}C [39] NMR spectra were studied for methylcyclopentadienylmercury. It was concluded [89] that the high shielding of methyl protons in MeHgCp [$\delta(^1H) = -0.35$ ppm] favours π-structure of this compound (XIII), whereas with the σ-structure (XIV) one would expect a shift to the low field. The ^{13}C NMR spectrum of MeHgCp at room temperature displays just one narrow signal responsible for the cyclopentadienyl ligand with $\delta(^{13}C_{Me})$ 15.6 and $\delta(^{13}C_{Cp})$ 117.7 ppm (from TMS reference) [39]. No ^{13}C—^{199}Hg satellites have been found for this molecule although the ^1H—^{199}Hg spin—spin coupling was observed [69] for benzene solutions of methyl- and ethyl-mercuric cyclopentadienyls:



(XIII)



(XIV)

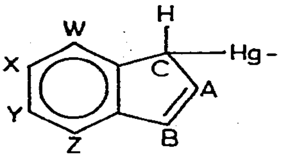
MeHgCp: $\delta(^1H_{Me})$ 0.16; $\delta(^1H_{Cp})$ 6.00 ppm.
$J(^1H_{Me}$—$^{199}Hg)$ 140; $J(^1H_{Cp}$—$^{199}Hg)$ 48 Hz.
EtHgCp: $\delta(^1H_{Et})$ 0.97; $\delta(^1H_{Cp})$ 6.00 ppm. $J(^1H$—C—$^{199}Hg)$ 140;
$J(^1H$—C—C—$^{199}Hg)$ 204; $J(^1H_{Cp}$—$^{199}Hg)$ 41 Hz.

It was concluded on the basis of a ^{13}C NMR spectrum of MeHgCp [39], that this molecule has the σ-structure. From the fact that satellites due to the mercury—proton coupling were observed [69] it was also assumed [39] that there is an intramolecular migration of mercury in MeHgCp, although it was noted that an intermolecular exchange could also occur.

VI. Indenylmercury compounds

A. Bis(indenyl)mercury

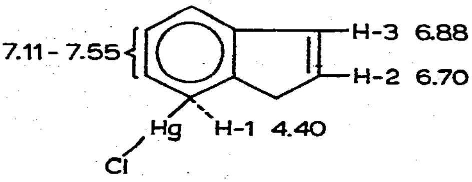
The PMR spectrum of this molecule was studied as a function of temperature at —41° to + 68° [19]. It was shown that the spectrum observed for the $CDCl_3$ solution at —41° (C proton singlet of relative intensity 1 with δ 3.81 ppm, WXYZ proton multiplet of relative intensity 4 lying at δ 7.1 to 7.8, and an AB proton pattern centered at δ 6.76 ppm with a relative intensity of 2 and $J_{AB} \approx 5.7$ Hz) is in excellent accord with the structure XV. With an increase in temperature this spectrum changes in a manner rationalized by the authors [19] in terms of 1,3 intramolecular migration of mercury. An intermolecular exchange was ruled out on basis of the concentration independence of the spectrum in the temperature range of intermediate exchange rates. It was suggested also that in the activated state (or in the very short-lived intermediate) the mercury atom lies over the face of the five-membered ring forming a kind of delocalized bond to three or more of the carbon atoms. The authors [19] believe that the mercury atom uses in this activated state two additional 6*p*-orbitals, although it was noted that the participation of 5*d*-orbitals cannot be ruled out.



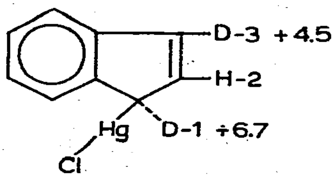
(XV)

B. Indenyl-HgX molecules

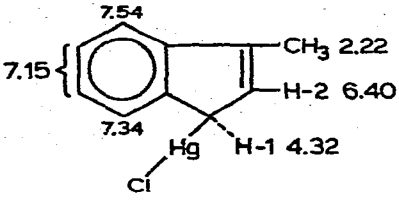
The ^1H and ^2D NMR spectra of indenylmercury chloride (XVI), (1,3-dideuteroindenyl)mercury chloride (XVII) and (3-methylindenyl)mercury chloride (XVIII) were studied carefully [58, 59]. The spectral parameters (chemical shifts in δ units) are given below together with structures of the compounds under investigation.



(XVI)



(XVII)



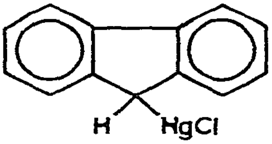
(XVIII)

(XVI). $J(^1H\text{-}1—^{199}Hg) \pm 476$; $J(^1H\text{-}2—^{199}Hg) \pm 50$; $J(^1H\text{-}3—^{199}Hg) \pm 76$ Hz.
(XVII). $J(^2D\text{-}1—^{199}Hg)$ 72.8; $J(^2D\text{-}3—^{199}Hg)$ 11.6 Hz. (^2D chemical shifts from external D_2SO_4)
(XVIII). $J(^1H\text{-}1—^{199}Hg)$ 466; $J(^1H\text{-}2—^{199}Hg)$ 50; $J(^1H_{Me}—^{199}Hg)$ 86 Hz.

The authors [59] concluded that there are no structures other than XVI-XVIII which would account for the spectral features. They assumed also that the 1,3-migration is the most favorable process in which bond formation is significant at early stages on the reaction coordinate (competing with the bond rupture).

VII. Fluorenylmercury compounds

A new method for the preparation of fluorenylmercuric chloride (XIX), which utilizes the reaction of $HgCl_2$ with bis(π-fluorenyl)zirconium dichloride, has been described recently [130].



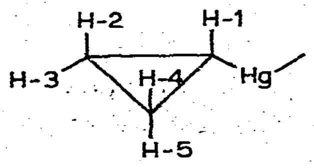
(XIX)

The PMR spectrum of this compound in DMSO-d_6 consists of an aromatic proton absorption at δ 7.2 to 8.0 and a sharp singlet resonance with δ 4.82 ppm and $J(^1H—C—^{199}Hg)$ 490 Hz due to the methine proton at C-9. The relative intensities of these absorptions are approximately 8/1. Bearing in mind that the methine proton in Indenyl-HgCl (δ 4.4 in DMSO, δ 4.32 ppm in THF [59]) is deshielded compared to the methine proton in the limiting structure of CpHgCl (δ 4.14 ppm in THF [158]), the authors [130] concluded that the diamagnetic anisotropic deshielding effects imposed by the second aromatic ring evidently result in a further lowering of the methine proton resonance in fluorenylmercuric chloride. It was concluded also [130] that this spectrum is consistent with the localized carbon-to-metal σ-bonding (XIX) and both fluorenylmercuric chloride and difluorenylmercury would be expected to be stereochemically rigid, since intramolecular rearrangements within the five-membered rings would not be possible.

VIII. Cycloalkylmercury compounds

A. Dicyclopropylmercury

The PMR spectrum of this molecule (XX) was studied in detail by Scherr and Oliver [131, 132]. The spectral parameters are given below (for benzene solution):



(XX)

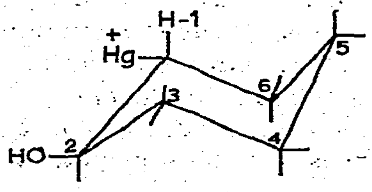
$\delta(^1H\text{-}1)$ -0.001; $\delta(^1H\text{-}2)$, $\delta(^1H\text{-}4)$ 0.746; $\delta(^1H\text{-}3)$, $\delta(^1H\text{-}5)$ 0.467 ppm.
J_{12}, J_{14} 9.60; J_{13}, J_{15} 6.90; J_{23}, J_{45} -3.71; J_{24} 8.53; J_{35} 7.88; J_{25}, J_{34} 4.82 Hz.
$J(^1H\text{-}1\text{—}C\text{—}^{199}Hg)$ +17.97; $J(^1H\text{-}2\text{—}C\text{—}^{199}Hg)$, $J(^1H\text{-}4\text{—}C\text{—}^{199}Hg)$ 71.51;
$J(^1H\text{-}3\text{—}C\text{—}^{199}Hg)$, $J(^1H\text{-}5\text{—}C\text{—}^{199}Hg)$ 120.38 Hz.

The comparison of these data with the relative spectral parameters for other monosubstituted cyclopropyl compounds showed that there are linear correlations between the chemical shifts or spin—spin coupling constants with the electronegativity of the substituents.

It was shown also by comparison of the respective $J(^1H\text{—}C\text{—}X)$ spin—spin coupling constants ($X = {}^{199}Hg$, ^{207}Pb, ^{119}Sn, ^1H and ^{19}F), that a simple empirical equation of the form $J(^1H\text{—}C\text{—}X) = A\,J(^1H\text{—}C\text{—}Y) + B$ can be used to predict and correlate coupling constants in monosubstituted ethanes, cyclopropanes, and ethylenes. The authors [132] believe that the equation may be quite general for indirect coupling. However, one must be careful to keep the molecular systems very similar in order to obtain good predictions.

B. Cyclohexyl derivatives

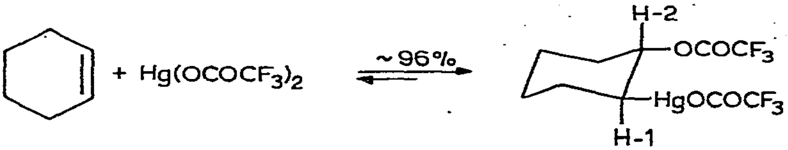
The PMR spectra of various cyclohexylmercury compounds have been intensively studied by various authors [4, 160, 65, 10, 99] in connection with a study of mechanisms of electrophilic additions to cyclohexane. As early as 1961 Anderson and Henry [4] showed that in a PMR spectrum of the oxymercuration product of cyclohexene (XXI) the proton H-1 has two coupling constants of 10 Hz and one of about 3.5 Hz. It was concluded that $J_{16} = 3.5$ Hz is reasonable for the axial—equatorial coupling and the product (XXI) is therefore *trans*.



(XXI)

Wolf and Campbell [160] showed the usefulness of working with cyclohexene-3,3, 6, 6-d_4 instead of unlabelled cyclohexene. The PMR spectra of some partially deuterated cyclohexylmercuric compounds have been studied by Kreevoy and Schaefer [65]. They suggested the existence of a systematic relation between dihedral angle, φ, defined by the C, C, H plane and the C, C, Hg plane, and the coupling constant for proton and mercury on vicinal carbons, $J(^1H—C—C—^{199}Hg)$. It was concluded that HgX groups attached to a cyclohexane ring have little or no preference for equatorial or axial positions. On the basis of the new relation it was also assumed that there is no preference for a *trans* as opposed to a *gauche* relation between oxygen functions and XHg groups on adjacent carbon atoms. All the data were rationalized [65] with the aid of two hypotheses: (*i*) values of $J(^1H—C—C—^{199}Hg)$ are generally around 100 Hz except when φ is close to 180°; for the angles 120—180° the constant rises to about 600 Hz, and (*ii*) in its lateral interactions with small vicinal atoms and groups, the ClHg group behaves approximately like a hydrogen atom.

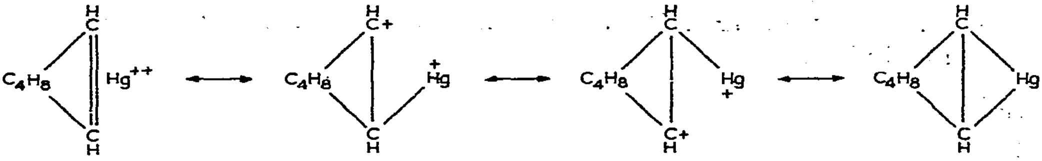
Brown and his coworkers [10] have shown by means of PMR spectroscopy that in benzene at room temperature the reaction of mercuric trifluoroacetate with cyclohexene attains the equilibrium position very rapidly in the course of about 1 min.



The PMR spectrum shows that the product is clearly a *trans* 1,2-addition compound because $J(^1H—C—C—^1H\text{-}2)$ is 8.5 and $J(^1H—C—C—^{199}Hg)$ 100 Hz, while the *cis* isomer exhibits a $J(^1H—C—C—^{199}Hg)$ value of 425 Hz [65].

C. NMR and mercurinium ions

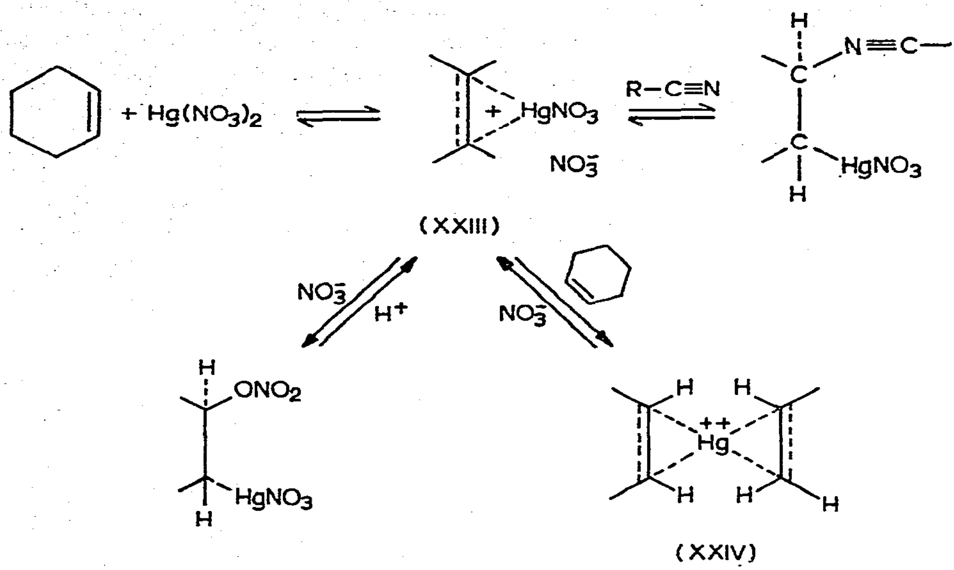
As early as 1939 it was proposed [71] that the process of mercuration of an olefin (such as XXII) proceeds through a coordination complex of mercuric ion with olefin, and the resonating forms for the cyclohexenemercurinium ion were represented as shown below:



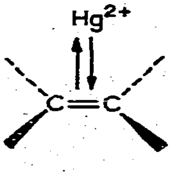
(XXII)

As has been noted above (see Section II.B.4.), Cotton and Leto [18] have concluded on the basis of the PMR spectra of $CH_3OCH_2CH_2HgOCOCH_3$ and $HOCH_2CH_2HgOH$ that addition of HgX_2 across the double bond gives σ-bonded organomercury compounds rather than π-complexes of mercury salts with olefins. These conclusions were verified in the subsequent papers [11, 154, 53] by observing proton—mercury spin—spin coupling in the molecules mentioned above and related compounds. It was claimed in 1967 [129] that the NMR spectra of the reaction solution of the oxymercuration of ethylene could be interpreted as indicating the presence of mercurinium ions in solution. However, it was shown very soon [58, 59] that the resonances attributed [129] to mercurinium ions were actually due to impurities formed in oxymercuration side reactions.

It was shown also in 1967 [142] that the addition of equimolar amounts of mercuric nitrate to the solution of cyclohexene in acetonitrile makes the cyclohexene olefinic proton reasonance (δ 5.36 ppm) disappear immediately. At the same time a broad singlet at δ 7.85 and a broad doublet at δ 7.5 ppm appear, which were attributed to olefinic protons of mercurinium ions (XXIII) and (XXIV), respectively.



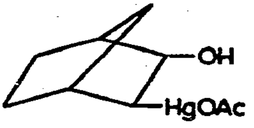
In a subsequent molecular orbital calculation it was shown [6] that the bonding strength between ethylene and Hg^{2+} is intermediate between the well-known chloronium ion and a silver complex, the existence of which was proved by NMR [96] and X-ray spectrometry [44], respectively. It was also concluded [6] that the ethylene transferred 0.764 electron to mercury, developing a sufficient positive charge on carbon, therefore a mercurinium ion more closely resembles the π complex (XXV) than the three-membered ring structures (XXIII) and (XXIV).



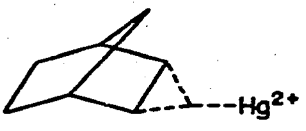
(XXV)

Stable, long-lived mercurinium ions have been observed very recently [97]. It was shown that the PMR spectrum of 2-methoxyethylmercuric chloride in $FSO_3H—SbF_5—SO_2$ at —30° consists of a triplet with δ 4.80, a singlet [δ 7.68,

$J(^1\text{H—C—}^{199}\text{Hg})$ 190 Hz], and a quartet with δ 9.77 ppm. The triplet and quartet are due to protonated methanol, whereas the singlet was assigned to the ethylene mercurinium ion. The PMR spectrum of *exo-cis*-3-hydroxy-2-norbornylmercuric acetate (XXVI) in the same superacid solvent system was rationalized in terms of norbornylenemercurinium ion (XXVII).



(XXVI)



(XXVII)

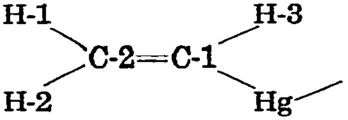
It should be emphasized that the direct observation of mercurinium ions in solution is possible only under suitable experimental conditions. As for convenient conditions in which mercuration reactions proceed, it was shown [98] that there are only resonances in ^{13}C NMR spectra of methanolic solutions of equimolar amounts of cyclopentene or cyclohexene and $Hg(OCOCH_3)_2$, which can be assigned to σ-bonded organomercurials.

The stereochemistry of the mercuration of simple and strained olefins was studied with NMR by various authors [18, 11, 154, 48, 53, 148, 4, 160, 65, 10, 99, 98, 149, 70, 125, 45, 150].

IX. Vinylmercury derivatives

A. Divinylmercury

This molecule (XXVIII) has been intensively studied by means of ^{1}H [80, 15, 43, 147], ^{13}C [35, 153] and ^{199}Hg [145] NMR spectroscopy.



(XXVIII)

All the spectral parameters obtained are given below:

δ(H-1) 5.314; δ(H-2) 5.881; δ(H-3) 6.637 (relative to internal TMS in cyclopentane) [147]; $\delta(^{13}\text{C-1})$ 168.2; $\delta(^{13}\text{C-2})$ 133.7 (relative to internal TMS in $CHCl_3$) [35]; $\delta(^{199}\text{Hg})$ 648 ppm (relative to Me_2Hg in CH_2Cl_2) [145].
J(H-1—H-2) 3.28; J(H-1—H-3) 13.83; J(H-2—H-3) 20.72 (in cyclopentane [147]; $J(\text{H-1—}^{199}\text{Hg})$ 296.4; $J(\text{H-2—}^{199}\text{Hg})$ 159.5; $J(\text{H-3—}^{199}\text{Hg})$ 128.3 (neat) [15, 43]; $J(^{13}\text{C-1—}^{199}\text{Hg})$ 1133; $J(^{13}\text{C-2—}^{199}\text{Hg})$ 134.3 Hz (in $CHCl_3$) [35].

The large internal chemical shift of the vinylic protons for $(CH_2{=}CH)_2Hg$ was rationalized [80] in terms of a general relationship between the magnitude of the internal chemical shift and the atomic number of the central element of the vinyl compound, the shift being attributed [16] to the diamagnetic anistropy of the metal—carbon bond. The proton—proton, as well as mercury—proton, coupling constants for $(CH_2{=}CH)_2Hg$ obey well the known rule: $J_{\text{trans}} > J_{\text{cis}} > J_{\text{gem}}$. Never-

TABLE 15

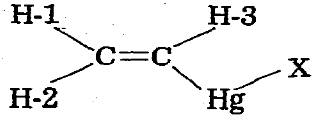
^{13}C NMR SPECTRAL PARAMETERS FOR $(CH_2{=}CH)_2Hg$ IN VARIOUS SOLVENTS [35]

Solvent	$\delta(^{13}C\text{-}1)$ (ppm)	$\delta(^{13}C\text{-}2)$ (ppm)	$J(^{13}C\text{-}1—^{199}Hg)$ (Hz)	$J(^{13}C\text{-}2—^{199}Hg)$ (Hz)
$CHCl_3$	168.2	134.3	1133	38
DME	168.6	133.4	1162	41
Pyridine	168.9	133.7	1200	42
DMSO	169.2	133.5	1202	42

theless, the authors [80, 15] believe that $J(^1H—C—^{199}Hg)$ is relatively large and it was assumed [15] that an additional contribution to this constant results from direct coupling "through space", analogous to the mechanisms proposed for unusually large vicinal coupling in metal alkyls [62] and in CF_3HgX molecules [34, 112, 113]. It should be emphasized also that ^{13}C chemical shifts for $(CH_2{=}CH)_2Hg$ do not depend on the nature of the solvent used, whereas carbon—mercury coupling constants change very markedly on going from inert to strongly solvating solvents (Table 15). These facts were interpreted [35] in terms of enhancement of solvent polarity and solvating power.

B. $CH_2{=}CHHgX$ molecules

The PMR spectra of unsubstituted vinyl mercurials of the type $CH_2{=}CHHgX$ (XXIX) were first described by Wells and his coworkers [156]. Other molecules of this type were studied by means of ^1H [146, 140] and ^{13}C [140] NMR spectroscopy more recently. The PMR spectral parameters for these molecules are given in Table 16.



(XXIX)

As for $MeHgCH{=}CH_2$, it was only noted [146] that replacing a vinyl group in $(CH_2{=}CH)_2Hg$ by a more electron-donating methyl group causes a downfield shift or a deshielding effect on the vinyl protons. The authors [146] assumed that this observation may be rationalized in terms of anisotropy effects.

It was concluded [156] on the basis of $J(^1H\text{-}1—^1H\text{-}2)$ values for $CH_2{=}CHHgX$ molecules that they have a larger H—C—H angle than have vinyl-lithium or -magnesium compounds ($J \sim 7$Hz). The absence of a pattern due to $^{199}Hg—^1H$ coupling in $CH_2{=}CHHgBr$ was interpreted in terms of vinyl group exchange. As we know now, an alternative explanation of such effects exists (see Section II.A.2).

The ^{13}C NMR spectral parameters for the $(CH_3)_3CCH_2HgCH{=}CH_2$ molecule were published recently [140].

C. Dipropenylmercury

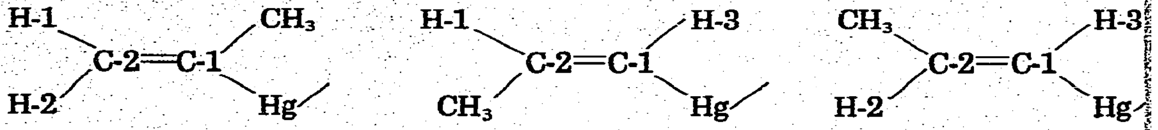
All the three geometrical isomers of this compound (XXX) were studied with PMR spectroscopy by Oliver and his coworkers [81]. The spectral param-

TABLE 16

PMR SPECTRAL PARAMETERS[a] FOR CH_2=CHHgX COMPOUNDS IN DIOXANE [156]

X in CH_2=CHHgX	δ(H-1)	δ(H-2)	δ(H-3)	J(H-1—H-2)	J(H-1—H-3)	J(H-2—H-3)	J(H-1—^{199}Hg)	J(H-2—^{199}Hg)	J(H-3—^{199}Hg)
$CH_2C(CH_3)_3$				4.5[b]	14.0[b]	20.0[b]			
Br	5.92	5.52	6.45	3.1	11.9	18.7			
$OCOCH_3$	5.90	5.50	6.42	3.0	12.0	18.0	658	331	291

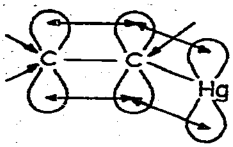
[a] δ values are in ppm, J values in Hz. [b] For $CDCl_3$ solutions [140].



a *b* *c*

(XXX)

eters are given in Table 17. The comparison of these data with the spectral parameters for $(CH_2{=}CH)_2Hg$ (see Section IX.A) shows that introduction of the methyl group in various positions of $(CH_2{=}CH)_2Hg$ leads to a substantial decrease in all of the proton—mercury spin—spin couplings. Keeping in mind that these constants, similarly to others, are mainly due to *s*-electron density on the nuclei coupled [41, 42], we can assume that on going from $(CH_2{=}CH)_2Hg$ to dipropenylmercury there is a further enhancement of overlap between the π-orbital of the double bond and the lowest vacant orbital of mercury according to the scheme, shown below:



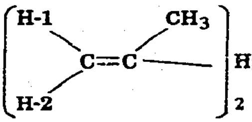
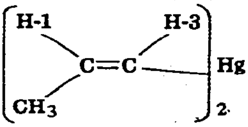
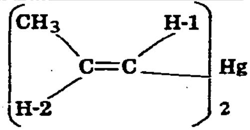
As for other spectral parameters of dipropenylmercury there are no general trends on going from $(CH_2{=}CH)_2Hg$ to this molecule.

D. β-Chlorovinylmercury compounds

These compounds (XXXI and XXXII) have been intensively used [85] in a

TABLE 17

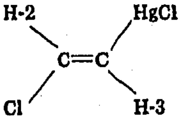
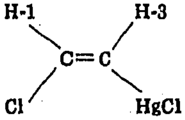
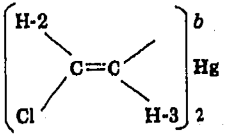
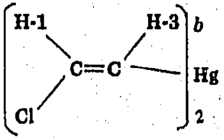
PMR SPECTRAL PARAMETERS FOR DIPROPENYLMERCURY [82]

Parameter[a]			
δ(H-1)	5.532	6.932	
δ(H-2)	4.807		5.592
δ(H-3)		6.183	6.183
δ(CH₃)	1.999	1.933	1.933
J(H-1—H-2)	4.1		
J(H-1—H-3)		11.1	
J(H-2—H-3)			19.2
J(H-1—HCH₃)	1.4	6.5	
J(H-2—HCH₃)	1.4		5.0
J(H-3—HCH₃)		1.3	1.3
$J(H\text{-}1—^{199}Hg)$	256.5	244.0	
$J(H\text{-}2—^{199}Hg)$	127.8		140.0
$J(H\text{-}3—^{199}Hg)$		134.0	125.0
$J(HCH_3—^{199}Hg)$	88.2	12.0	5.0

[a] δ in ppm, *J* in Hz.

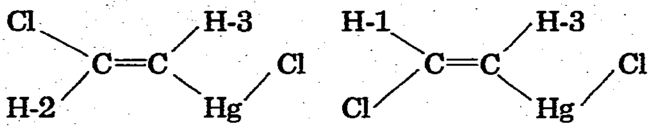
TABLE 18

^{1}H AND ^{13}C NMR SPECTRAL PARAMETERS FOR β-CHLOROVINYLMERCURY COMPOUNDS IN ACETONE [155, 87, 88, 35]

Parameter[a]			 [b]	 [b]
δ(H-1)		6.85		6.95
δ(H-2)	6.28		6.45	
δ(H-3)	6.22	6.30	6.13	6.28
δ(^{13}C-1)[c]			156.3	156.6
δ(^{13}C-2)[c]			130.7	132.0
J(H-1—H-3)		7		7
J(H-2—H-3)	15		15.5	
J(H-1—^{199}Hg)		±474.5		214.0
J(H-2—^{199}Hg)	±155, 160.5[d]		92.8	
J(H-3—^{199}Hg)	±124, 115[d]	±110	60.4	63.0
J(^{13}C-1—^{199}Hg)[c]			1256	1330
J(^{13}C-2—^{199}Hg)[c]			191	53

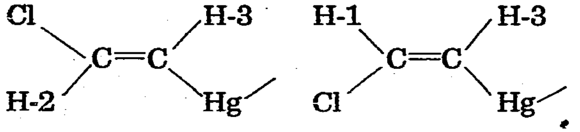
[a] δ in ppm, J in Hz. [b] Neat liquids. [c] For $CHCl_3$ solutions. [d] For DMSO solutions [5].

study of stereochemistry of metal exchange reactions in various systems. The PMR spectra of these molecules were studied first by Wells and Kitching [155] and then by the present writers in collaboration with Nesmeyanov and his coworkers [87]. The use of PMR spectroscopy in this case met with success in determination of stereochemical purity and helped strongly in the confirmation of the regularities [88] observed previously. ^{13}C NMR spectra of these molecules were studied recently [35]. All the spectral parameters for these molecules are given in Table 18.



a *b*

(XXXI)



a *b*

(XXXII)

It was concluded [155] on the basis of comparison of the PMR spectral parameters for vinyl chloride, vinylmercury, and β-chlorovinylmercury compounds that the mercury atom has essentially the same electronegativity as hydrogen. On the basis of the deviation of $J(^{13}C\text{-}1\text{—}^{199}Hg)$ for XXXII*b* from the linear dependence between $J(^{1}H\text{—}^{13}C)$ and $J(^{13}C\text{-}1\text{—}^{199}Hg)$ for various organomercury compounds it was concluded again [35] (see also [51]) that a weak intramolecular interaction between the chlorine lone pairs of electrons and unfilled 6*p*-orbitals of mercury is occurring.

E. β-Ketovinylmercury derivatives

These molecules were studied recently with PMR spectroscopy by Nesmeyanov and his coworkers [128]. The spectral parameters are given in Table 19. It should be noted that for the *trans*-isomers studied there is only one signal for vinylic protons in the molecules containing no ^{199}Hg isotope, as was observed earlier for *trans*-ClCH=CHHgCl (see preceeding Section). At the same time, for the molecules with a ^{199}Hg isotope one observes a doublet of quartets due to proton—proton and proton—mercury spin—spin coupling. This has made it possible to obtain $J(H_\alpha\text{—}H_\beta)$ values and the chemical shifts for the α- and β-protons. The absence of patterns due to mercury—proton spin—spin coupling in β-keto-vinylmercuric iodides was rationalized in terms of intermolecular anion exchange, previously observed for methyl, ethyl and other derivatives of mercury (see above). It was assumed [128], that there is an intramolecular coordination between the oxygen and mercury atoms in the *cis*-compounds studied, providing for higher stability of the *cis*-isomers, compared to the *trans*-isomers.

TABLE 19

PMR SPECTRAL PARAMETERS[a] FOR RCOCH=CHHgX MOLECULES IN ACETONE [128]

Compound	$\delta(H_\alpha)$	$\delta(H_\beta)$	$J(H_\alpha—H_\beta)$	$J(H_\alpha—{}^{199}Hg)$	$J(H_\beta—{}^{199}Hg)$
(*cis*-$C_6H_5COCH{=}CH)_2Hg$	8.43	7.68	12.0	256	142
(*cis*-*p*-$CH_3C_6H_4COCH{=}CH)_2Hg$	8.31	7.67	12.0	258	143
cis-$CH_3COCH{=}CHHgI$	7.43	7.14	10.5		
cis-$C_6H_5COCH{=}CHHgI$	8.26	7.43	10.3		
cis-*p*-$CH_3C_6H_4COCH{=}CHHgI$	8.25	7.43	10.4		
cis-*p*-$ClC_6H_4COCH{=}CHHgI$	8.26	7.47	10.2		
cis-$C_6H_5COCH{=}CHHgCl$	8.17	7.26	10.5	526	255
cis-*p*-$CH_3C_6H_4COCH{=}CHHgCl$	8.13	7.17	10.4	526	254
trans-$C_6H_5COCH{=}CHHgCl$	7.50	7.50	18.6	278	238
trans-*p*-$CH_3C_6H_4COCH{=}CHHgCl$	7.53	7.53	18.4	278	240

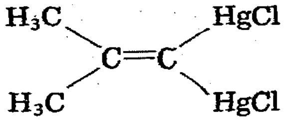
[a] δ in ppm, J in Hz.

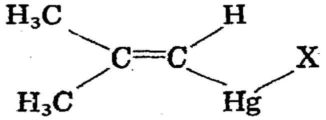
F. Miscellaneous vinylmercury compounds

It was shown recently [77] that 2-methylpropene-1,1-dimercuric chloride (XXXIII), m.p. 250°, exists and its PMR spectrum in DMSO-d_6 consists of a single resonance with δ 2.02 ppm and a spectral pattern due to mercury—proton spin—spin coupling with $J(^1H—^{199}Hg)$ 36 Hz.

The PMR spectral parameters for some β-alkyl-, cycloalkyl- and aryl-substituted vinylmercuric chlorides were published by Larock and Brown [68].

Zakharkin and his coworkers [50] have published recently the $J(^1H—C—^{199}Hg)$ coupling constants for isobutenylmercuric derivatives of carboranes (XXXIV) in various solvents in comparison with the respective constants for isobutenylmercuric bromide. It was shown, first of all, that $J(^1H—C—^{199}Hg)$ constants for these compounds decrease in the series Br > o-$CB_{10}H_{10}CC_6H_5$ > o-$CB_{10}H_{10}CCH_3$ > m-$CB_{10}H_{10}CCH_3$. As for the solvent effect upon the values of $J(^1H—C—^{199}Hg)$ constants, it was shown that these coupling constants increase on going from CCl_4 to CH_2Cl_2 and $CHCl_3$ and decrease in the series CCl_4 > benzene > dioxane > diethyl ether > CH_3CN > THF > DME > pyridine. These observations were rationalized in terms of changes in C—Hg bond polarity and interaction between π-electrons of the double bond and the vacant mercury orbitals.


(XXXIII)


(XXXIV)

PMR spectroscopy was used recently in our laboratory [92] for assignment of geometrical structures for XXXV and XXXVI. obtained from the respective phosphorus ylides.

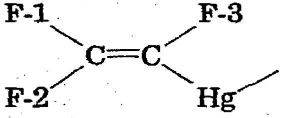
$(CH_3CH{=}CCOOCH_3)_2Hg$ (XXXV) [in CCl_4] $J(^1H—^{199}Hg)_{cis}$ 228, $J(^1H—^{199}Hg)_{trans}$ 313 Hz.

$(C_6H_5CH{=}CCOOCH_3)_2Hg$ (XXXVI) [in HMPT] $J(^1H—^{199}Hg)_{cis}$ 180, $J(^1H—^{199}Hg)_{trans}$ 256 Hz.

The only isolated isomer of $(CCl_3CH{=}CCN)_2Hg$ in HMPT has the $J(^1H—C—^{199}Hg)$ constant of about 280 Hz [93].

G. Bis(perfluorovinyl)mercury

The ^{19}F NMR spectrum of this compound (XXXVII) was studied by Stone and his coworkers [20] in 1961.


(XXXVII)

The spectral parameters are given below:
$\delta(^{19}F\text{-}1)$ 89.9; $\delta(^{19}F\text{-}2)$ 124.5; $\delta(^{19}F\text{-}3)$ 185.0 (in ppm relative to CCl_3F internal reference).

TABLE 20

PMR SPECTRAL PARAMETERS[a] FOR ALLENIC DERIVATIVES OF MERCURY [47]

Compound	Solvent	$\delta(H_\alpha)$	$\delta(H_\gamma)$	$J(H_\alpha—H_\gamma)$
$CH_2=C=CHHgCl$	$CHCl_3$	5.10	4.70	~7
$(CH_2=C=CH)_2Hg$	acetone	5.05	4.34	7.1

[a] δ in ppm, *J* in Hz.

$J(^{19}F\text{-}1—^{19}F\text{-}2)$ 75; $J(^{19}F\text{-}1—^{19}F\text{-}3)$ 37; $J(^{19}F\text{-}2—^{19}F\text{-}3)$ 109; $J(^{19}F\text{-}1—^{199}Hg)$ 223; $J(^{19}F\text{-}2—^{199}Hg)$ 17; $J(^{19}F\text{-}3—^{199}Hg)$ 820 Hz.

It was shown [20] that in $(CF_2=CF)_2Hg$, as in other perfluorovinyl compounds, the absorptions due to the individual fluorine atoms are more complex than what is predicted by the first-order theory. The authors [20] believe that a possible explanation of this observation is a long-range spin-coupling between the fluorine atoms in the different perfluorovinyl groups. If such coupling does occur, the corresponding fluorine atoms on the two groups will no longer be magnetically equivalent, even if their chemical shifts are identical and the system is of the $A_2M_2X_2$ type.

X. Allenic derivatives of mercury

It was shown recently [47] that one can obtain allenylmercury compounds by a reaction of allenic derivatives of tin with mercuric chloride in ether or acetone. The PMR spectral parameters [47] are given in Table 20.

Unfortunately, nothing was reported on the mercury—proton spin—spin coupling in these compounds.

XI. Alkynylmercury compounds

There are only two mercury-substituted acetylenes whose NMR spectra have been studied. The first, ethynylmethylmercury was studied by various authors [41, 155, 5] with PMR spectroscopy, whereas bis(phenylethynyl) mercury was studied only by means of ^{13}C NMR spectroscopy [35]. The data obtained are given in Table 21.

TABLE 21

NMR SPECTRAL PARAMETERS[a] FOR ALKYNYLMERCURY COMPOUNDS [155, 5, 35]

Compound	Solvent	δ(H-1)	$\delta(^{13}C_\alpha)$	$\delta(^{13}C_\beta)$	$J(H\text{-}1—^{199}Hg)$	$J(^{13}C_\alpha—^{199}Hg)$
$(H\text{-}1)C\equiv CHgCH_3$[b]	CCl_4	1.5			69	
	$CDCl_3$	1.8			67	
$(C_6H_5C\equiv C)_2Hg$	$CHCl_3$		121.5	108.7		2584
	Pyridine		122.2	106.5		2694

[a] δ in ppm, *J* in Hz. [b] The $\delta(^1H_{CH_3})$ and $J(^1H—C—^{199}Hg)$ values are given in Table 2.

TABLE 22

PMR SPECTRAL PARAMETERS FOR Ph_2Hg IN VARIOUS SOLVENTS [100, 102]

Solvent	$\delta(^1H)$ (ppm)	$J(^1H_{ortho}—^{199}Hg)$ (Hz)
C_6H_{12}	7.20	102.5
CCl_4	7.24	102.5
Dioxane	7.32	102.5
THF	7.40	102.5
CH_2Cl_2	7.43	102.5
CH_3CN	7.45	102.5
Acetone	7.48	102.5
DMF	7.59	105.0
DMSO	7.73	105.0
HMPT	7.90	105.0

XII. Phenylmercury compounds

A. Diphenylmercury

We have shown in 1967 [102] that the PMR spectra of Ph_2Hg in the molten state or in various solvents show broad unresolved resonances due to *o*-, *m*- and *p*-protons in the molecules containing no ^{199}Hg isotopes, and satellite doublets due to spin—spin coupling of *ortho*-protons with the ^{199}Hg in molecules of the type $Ph_2\,^{199}Hg$. It was shown also (Table 22) that the screening constants of *ortho*-protons in the melt are larger than those of *meta*- and *para*-protons. At the same time, these screening constants decrease substantially on going from non-polar to polar and solvating solvents.

It was assumed [100] that mainly the magnetic anistropy of the carbon—mercury bond affects the shielding of *ortho*-protons in Ph_2Hg. This assumption is strongly supported by experimental data of Ladd [67], who has shown that for solutions of phenyl compounds of lithium, beryllium, magnesium, zinc, and cadmium in diethyl ether the shielding of *ortho*-protons decreases substantially with an increase in carbon—metal bond ionicity. Our calculations [100] have

TABLE 23

PMR SPECTRAL PARAMETERS FOR $(p\text{-}YC_6H_4)_2Hg$ MOLECULES [105]

Y in $(p\text{-}YC_6H_4)_2Hg$	$\delta(H_{ortho})$ (ppm)		$\delta(H_{meta})$ (ppm)	
	Dioxane	DMSO	Dioxane	DMSO
H[a]	7.32	7.73		
CH_3O	7.30	7.61	6.90	7.11
CH_3CONH		7.76		7.53
C_2H_5OOC[b]		7.73		7.94
Cl	7.37	7.78	7.37	7.57
Br	7.29	7.69	7.53	7.69
I	7.06	7.41	7.67	7.75

[a] For $CDCl_3$ solution of Ph_2 Hg $J(^1H_{meta}—^{199}Hg)$ is 26 Hz [31].
[b] For DMSO solutions of this compound $J(^1H_{ortho}—^{199}Hg)$ is 104 Hz [31].

TABLE 24

^{13}C NMR SPECTRAL PARAMETERS[a] FOR DIPHENYLMERCURY [152, 153, 35]

Solvent	$\delta(C_\alpha)$	$\delta(C_{ortho})$	$J(^{13}C\text{—}^{199}Hg)$	$J(^{13}C_{ortho}\text{—}^{199}Hg)$	$J(^{13}C_{meta}\text{—}^{199}Hg)$	$J(^{13}C_{para}\text{—}^{199}Hg)$
$CHCl_3$[b]	170.5	137.5	1176	87		
CH_3OH[c]			1186	88	101.6	17.8
Pyridine[b]	171.5	138.6	1254	85		

[a] δ in ppm, *J* in Hz. [b] Ref. 35. [c] Refs. 152 and 153.

shown that the effect of magnetic anisotropy of the second benzene ring upon the screening constants of *ortho*-protons in the most reliable configurations of Ph_2Hg (with the C—Hg—C angles of 180 to 110°) is small and varies from + 0.09 to −0.11 ppm.

As for $J(^1H_{ortho}—^{199}Hg)$, it was concluded [100] that these vicinal spin—spin coupling constants are not very sensitive to the solvation and increase only on going to strongly solvated solvents (see Table 22). It should be noted that McFarlane [78] showed somewhat later that the spin—spin coupling constants of Ph_2Hg *ortho*-protons and ^{199}Hg are positive. The PMR spectra of *p*-substituted derivatives of Ph_2Hg were studied [105] in dioxane and DMSO solution at 40° and 50°, respectively, owing to the very limited solubilities of these compounds. The spectral parameters are given in Table 23. Some ^{13}C NMR spectral parameters for Ph_2Hg are given in Table 24.

B. ArHgX molecules

We have studied various PhHgX compounds by means of 100 MHz PMR spectroscopy [105]. It was shown, first of all (see Table 25), that the chemical shifts of *ortho*-protons in these molecules do not depend on the nature of X, whereas the $J(^1H_{ortho}—^{199}Hg)$ constants do.

McFarlane [78] studied independently the signs of proton—mercury coupling constants by means of heteronuclear magnetic double resonance and showed that for a DMSO solution of PhHgOAc $J(^1H_{ortho}—^{199}Hg)$ is +204 Hz and $J(^1H_{meta}—^{199}Hg)$ is +54 Hz. We believe that the changes in $J(^1H_{ortho}—^{199}Hg)$, analogous to the respective variations in $J(^1H—C—^{199}Hg)$ for CH_3HgX compounds (see Section II.A.2), are due to changes in relative content of *s*-electrons in the H—C—C—Hg site in phenylmercury compounds.

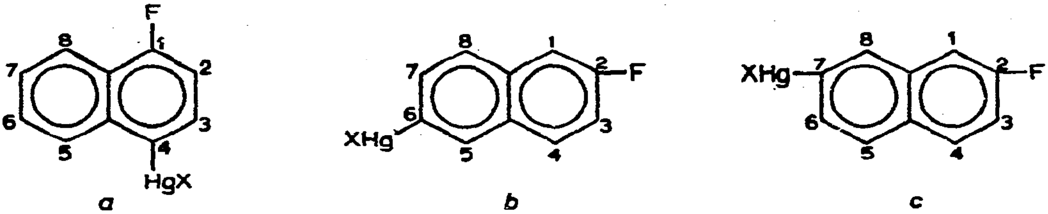
It was important to know also the PMR spectral parameters for *meta*-protons in PhHgX molecules. We therefore synthesized [105] 2, 4, 6-trideuteriophenylmercuric chloride and obtained the values of $\delta(^1H_{meta})$ of 7.45 ppm and $J(^1H_{meta}—^{199}Hg)$ of 55 Hz in DMSO. On the basis of $\delta(H_{ortho})$ and $\delta(H_{meta})$ values we assumed [105] that the ClHg group in phenylmercuric chloride is an electron-acceptor group. At the same time we have obtained [103], on the basis of measurements of fluorine chemical shifts in *p*- and *m*-fluorine-substituted phenylmercuric chlorides, the values of σ_i 0.17 and σ_r, 0.01, for the ClHg group, solvated by dioxane molecules. It was assumed also [103] that enhancement of the solvating power will decrease the electron-acceptor power of ClHg group. This assumption is borne out by the experimental data of other authors [1, 57, 63, 64] who studied ^{19}F chemical shifts for *m*- and *p*-fluorine-substituted diphenylmercury and PhHgX molecules with different X substituents, in $CHCl_3$, THF and

TABLE 25

PMR SPECTRAL PARAMETERS FOR PhHgX MOLECULES IN DMSO [105, 13]

X in C_6H_5HgX	Cl	Br	I	CH_3COO	NO_3	ClO_4
$\delta(H_{ortho})$ (ppm)	7.63	7.63	7.63	7.63	7.63	7.63
$J(H_{ortho}—^{199}Hg)$ (Hz)	202.5	202.5		205	211	238

DMSO. Recently these studies were expanded [2] by investigation of ^{19}F NMR spectra of a number of substituted α (1)- and β(2)-fluoronaphthalenes with HgX (X = halogen or aryl) substituents in the 4, 6 and 7 positions (XXXVIII *a-c*). It was concluded on the basis of these data that there is little net movement of π-charge either in or out of both ring systems, and it was shown that the aryl—mercury bond, at least in *a* and *b* has a π-component of unknown magnitude.



a *b* *c*

(XXXVIII)

It was demonstrated in our laboratory [105] that the chemical shifts of phenyl protons and the spin—spin coupling constants of these protons with mercury in *para*- and *meta*-substituted YC_6H_4HgX molecules depend strongly on the nature of Y. Some data illustrating this conclusion are given in Tables 26-28.

The two most interesting features of these data should be emphasized. First of all, it is strange enough that both electron-donor and electron-acceptor substituents decrease strongly the $J(H_{ortho}—^{199}Hg)$ and $J(H_{meta}—^{199}Hg)$ constants. The results obtained proved to be similar to those reported for *p*-substituted benzene fluorides [141], but it is difficult to understand both these observations.

C. PhHg⁺ cation

We found [13] that phenylmercuric perchlorate on dissolution in various electron-donor solvents dissociates and forms complexes, as shown below.

$$C_6H_5HgClO_4 \overset{S:}{\rightarrow} [C_6H_5Hg—S]^+ ClO_4^-$$

Keeping in mind that in PhHgX molecules $J(H_{ortho}—^{199}Hg)$ spin—spin coupling constants change strongly depending on the nature of X (see Table 25), we have measured the values of these constants for solutions of $PhHgClO_4$ in various solvents. The experimental data are given in Table 29.

It should be noted that the correlation between the $J(H_{ortho}—^{199}Hg)$ and

TABLE 26

PMR SPECTRAL PARAMETERS[a] FOR p-YC_6H_4HgCl MOLECULES IN DMSO [105]

Y in p-YC_6H_4HgCl	$\delta(H_{ortho})$	$\delta(H_{meta})$	$J(H_{ortho}—^{199}Hg)$	$J(H_{meta}—^{199}Hg)$
H	7.63	7.45	202.5	55.0
CH_3	7.48	7.25	200.0	47.0
C_2H_5COO	7.80	8.05	197.5	52.5
F[b]	7.65	7.28	195.0	47.0
NO_2	7.96	8.35	192.5	40.0

[a] δ in ppm, *J* in Hz. [b] $J(H_{ortho}—^{19}F)$ 9.8 Hz; $J(H_{meta}—^{19}F)$ 11.3 Hz.

TABLE 27

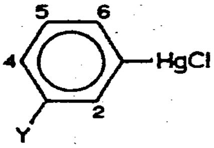
PMR SPECTRAL PARAMETERS[a] FOR p-YC_6H_4HgBr MOLECULES IN DMSO [105]

Y in p-YC_6H_4HgBr	$\delta(H_{ortho})$	$\delta(H_{meta})$	$J(H_{ortho}—^{199}Hg)$	$J(H_{meta}—^{199}Hg)$
H	7.63		202.5	
CH_3	7.50	7.28	198.5	46.0
CH_3O	7.56	7.09	195.0	40.0
$(CH_3)_2N$	7.41	6.86		
CH_3CONH	7.55	7.70	195.0	50.0
Br	7.65	7.67	195.0	50.0
I	7.45	7.82	195.0	50.0
$COOC_2H_5$	7.81	8.05	195.0	50.0

[a] δ in ppm, J in Hz.

TABLE 28

PMR SPECTRAL PARAMETERS[a] FOR m-YC_6H_4HgCl MOLECULES IN DMSO [105]

Y in 	δ(H-2)	δ(H-4)	δ(H-5)	δ(H-6)	$J(H\text{-}2—^{199}Hg)$	$J(H\text{-}6—^{199}Hg)$
$COOC_2H_5$	8.31	8.00	7.62	7.92	207.5	197.5
NO_2	8.57	8.21	7.74	8.07	217.5	192.5

[a] J in Hz, δ in ppm.

TABLE 29

$J(H_{ortho}—^{199}Hg)$ (Hz) CONSTANTS FOR $C_6H_5HgClO_4$ IN VARIOUS SOLVENTS [13]

Solvents	Coordinating group	$J(H_{ortho}—^{199}Hg)$	$\lg K_1$[a]
THT[b]	>S	208	10.0
HMPT	P=O	226	6.2
TMU[c]	C=O	235	3.8
DMSO	S=O	238	3.3
THF	>O	241	0.6

[a] Calculated from electrochemical data. [b] Tetrahydrothiophene. [c] Tetramethylurea.

TABLE 30

^{19}F NMR SPECTRAL PARAMETERS[a] FOR C_6F_5HgX MOLECULES [78]

Compound	$\delta(^{19}F_{ortho})$	$\delta(^{19}F_{meta})$	$\delta(^{19}F_{para})$	$J(^{19}F_{ortho}—^{19}F_{meta})$	$J(^{19}F_{ortho}—^{19}F_{para})$
$(C_6F_5)_2Hg$	—45.6	—2.4	—9.4	—26.0	10.3
C_6F_5HgOAc	—45.7	—2.3	—6.3	—25.9	9.7
	$J(^{19}F_{ortho'}—^{19}F_{ortho})$	$J(^{19}F_{ortho}—^{19}F_{para})$	$J(^{19}F_{meta'}—^{19}F_{meta})$	$J(^{19}F_{meta}—^{19}F_{para})$	
$(C_6F_5)_2Hg$	—7.2	1.4	—1.7	—18.9	
C_6F_5HgOAc	—7.3	1.0	—1.7	—19.5	

[a] δ in ppm with respect to internal C_6F_6. J in Hz.

TABLE 31

^{199}Hg NMR SPECTRAL PARAMETERS[a] FOR C_6F_5HgX MOLECULES

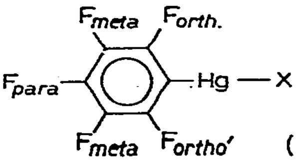
Compound	$\delta(^{199}Hg)$	$J(^{19}F_{ortho}—^{199}Hg)$	$J(^{19}F_{meta}—^{199}Hg)$	$J(^{19}F_{para}—^{199}Hg)$
$(C_6F_5)_2Hg$	17.894	443.0	116.0	14.4
C_6F_5HgOAc	17.885	597.0	215.0	29.0

[a] $\delta(^{199}Hg)$ values in relative units (see [78]), $J(^{19}F—^{199}Hg)$ values in Hz.

lgK_1 is linear. A similar correlation for the complexes of CH_3Hg^+ was observed independently by Scheffold [137].

D. Pentafluorophenyl derivatives

These molecules (XXXIX) were studied by various authors in 1964 [121, 26, 9] and most carefully by McFarlane [78]. The ^{19}F and ^{199}Hg spectral parameters obtained are given in Tables 30 and 31.



(XXXIX)

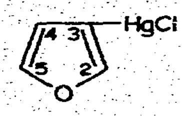
It was concluded [78] on the basis of the comparison of ^{19}F chemical shifts for various monosubstituted perfluorobenzenes [9] that a mercury atom is similar in its effect to iodine for all the three kinds of fluorine, and the effect on the chemical shifts is not sensitive to the nature of the other group attached to mercury. The high-field shift of ^{199}Hg resonance in going from $(C_6F_5)_2Hg$ to C_6F_5HgOAc is consistent with the electronegative group making a large contribution to the paramagnetic shielding term [133]. The author [78] believes that large values of $J(^{19}F_{ortho}—^{19}F_{meta})$ for these compounds are also due to high polarizability of the mercury atom. As for $J(^{19}F—^{199}Hg)$ spin—spin coupling, it appears [78] that the Fermi contact contribution dominates and leads to positive couplings in all cases listed above.

The ^{19}F NMR spectral parameters were published also for $C_6F_5HgCH_3$ [9] and $C_6F_5HgCF_3$ [121] molecules.

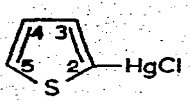
XIII. Heterocyclic derivatives of mercury

A. Furyl- and thienyl-mercury compounds

The PMR spectra of 3-chlormercurifuran (XL) and 2-chlormercurithiophene (XLI) have been studied carefully in 1963 [17] and 1969 [12] respectively. The PMR spectra and the ^{199}Hg satellite bonds of two symmetrical isomers of difuryl- and dithienyl-mercury have been fully analyzed recently [72]. All the spectral parameters obtained are given in Table 32.



(XL)

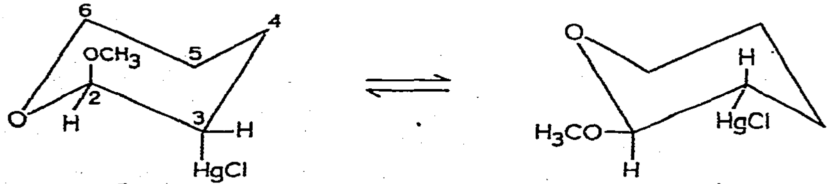


(XLI)

It should be noted, first of all, that double resonance experiments [17] and the comparison of experimental and simulated spectra [72] have shown that all $J(^1H—^1H)$ and $J(^1H—^{199}Hg)$ constants have the same relative sign, but the relative sign of $J(^1H—^{199}Hg)$ with respect to $J(^1H—^1H)$ could not be ascertained. It was shown also, by comparison of $J(^1H—^{199}Hg)$ for furyl and thienyl derivatives of mercury and $J(^1H—^1H)$ for furan and thiophene that a linear correlation between these parameters exists. It was assumed on the basis of this linear plot, which has no appreciable intercept (~ 0.4 Hz) that the mechanism of long-range mercury—proton coupling should be very similar to that of proton—proton coupling. Since the Fermi contact term gives the main contribution to the proton—proton coupling, it seems likely that the same term is also mainly responsible for the mercury—proton couplings in the compounds under investigation.

B. 2-Methoxy-3-chloromercuritetrahydropyran (XLII)

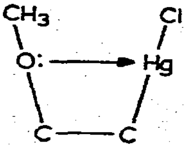
It was shown in 1967 [161] that in the PMR spectrum of (XLII) in CH_3CN the resonance of a proton at C-2 is a doublet with δ 4.45 ppm and J 7.6 Hz. The authors [161] concluded therefore that it has a *trans*-configuration. Calculation



a *b*

(XLII)

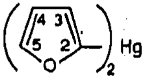
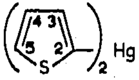
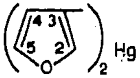
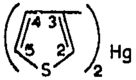
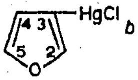
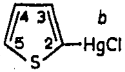
revealed 56% of *ee*-conformation (*b*) and ΔG —0.14 Kcal/mole for the equilibrium. Keeping in mind that for the HgX-group the ΔG value is equal or, at least, very near to zero [27], the authors [161] concluded that there is an intramolecular coordination of oxygen and mercury atoms, which stabilizes the *ee*-conformation, as shown below:

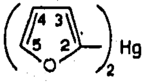
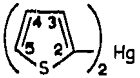
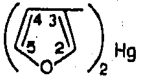
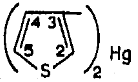
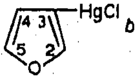
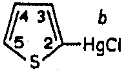


It was concluded that this coordinational stabilization effect should be ~ 1 kcal/mole.

TABLE 32

PMR SPECTRAL PARAMETERS[a] FOR FURYL AND THIENYL DERIVATIVES OF MERCURY IN DMSO [17, 12, 72]

Compound	$\delta(^1H\text{-}2)$	$\delta(^1H\text{-}3)$	$\delta(^1H\text{-}4)$	$\delta(^1H\text{-}5)$	J(H-2—H-3)	J(H-2—H-4)	J(H-2—H-5)	J(H-3—H-4)
		6.56	6.61	7.89				2.95
		7.24	7.38	7.72				3.28
	7.31		6.48	7.67		1.03	1.15	
	7.48		7.31	7.68		0.75	2.46	
	7.33		6.40	7.67		0.6	1.3	
		7.08	7.29	7.57				3.41

Compound	J(H-3—H-5)	J(H-4—H-5)	$J(H\text{-}2\text{—}^{199}Hg)$	$J(H\text{-}3\text{—}^{199}Hg)$	$J(H\text{-}4\text{—}^{199}Hg)$	$J(H\text{-}5\text{—}^{199}Hg)$
	0.52	1.69		22.6	14.7	20.7
	0.72	4.66		70.7	14.4	35.8
		1.49	26.7		46.1	12.7
		5.01	68.7		45.3	14.5
		1.7	40.4		74.9	27.9
	0.65	4.98		118.0	32.4	71.0

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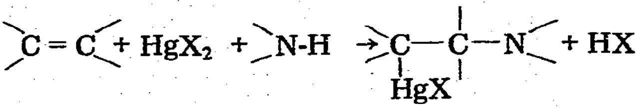
[a] δ in ppm, J in Hz. [b] Dioxan solutions.

C. Heterocyclic products of aminomercuration reactions

These reactions have been extensively studied by Lattes and his coworkers [126]. The PMR spectra of the products of these reactions are very complicated,



$$>C=C< + HgX_2 + >N\text{-}H \rightarrow >\underset{HgX}{\overset{|}{C}}-\overset{|}{\underset{|}{C}}-N< + HX$$

but the careful analysis of the spectra allowed the assignment of the conformations of the molecules studied.

XIV. Conclusions

It is evident from the data considered that organomercury compounds have been extensively studied by NMR spectroscopy during the last fifteen years by various workers in different countries. Unfortunately, in many cases these studies were not systematic. Nevertheless, the big success of NMR application for assignment of electronic and spatial structures of various organomercury compounds is clear.

A deeper understanding of the nature of the spectral parameters, such as screening constants and heteronuclear spin—spin couplings of mercury, will allow investigators to use this valuable tool even more fruitfully for a study of structure and complexation of organomercury compounds.

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