Journal of Organometallic Chemistry, 301 (1986) 1–13
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

METALLOMETHANES

XII *. VIBRATIONAL SPECTRA AND FORCE FIELDS OF METHYLMERCURIMETHANES

JANOS MINK **,

Institute of Isotopes of the Hungarian Academy of Sciences, POB 77, H-1525 Budapest (Hungary)

DIETRICH K. BREITINGER ** and WOLFRAM KRESS,

Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1,
D-8520 Erlangen (F.R.G.)

(Received July 17th, 1985)

Summary

The vibrational spectra data, the assignments, and the results of normal coordinate calculations for $CH_{4-n}(HgCH_3)_n$ molecules ($2 \leqslant n \leqslant 4$) are reported. The central C–Hg valence force constants are 1.870, 1.653, and 1.582 N cm^{-1}, while the terminal ones are 2.121, 2.101, and 2.160 N cm^{-1} for $n = 2$, 3 and 4, respectively. The latter values are 12, 21, and 27% higher than the central C–Hg force constants, but all of them are substantially lower than those in dimethylmercury (2.379 N cm^{-1}). These findings can be accounted for in terms of increasing shift of electron density towards the periphery of these molecules and increasing non-bonded metal–metal interaction. The nature of the normal modes is discussed.

Introduction

The relative simplicity and high symmetry of methylmercurimethanes of formula $CH_{4-n}(HgCH_3)_n$ ($2 \leqslant n \leqslant 4$) prompted us to study the vibrational spectra of these molecules. It also seemed of interest to compare the vibrational behaviour and force constants of the constituent groups which these compounds have in common with dimethylmercury [2] and methylmercury halides [3,4].

There have been several investigations of the vibrational spectra of mercurimethanes [5–8], and approximate force constants have been obtained in some cases

---

* For contribution XI see ref. 1.

** Authors to whom correspondence should be addressed.

[6,7]. Recently, some selected results of more elaborate force field studies have been published [8], and preliminary assignments of the vibrational spectra of the abovementioned methylmercurimethanes have been made [9]. We present below our interpretations of the infrared and Raman spectra of the $CH_{4-n}(HgCH_3)_n$ molecules ($2 \leq n \leq 4$) and the results of calculations of their force constants.

Experimental

The compounds were prepared by treatment of the appropriate borylmethanes $CH_{4-n}[B(OCH_3)_2]_n$ with methylmercury acetate and lithium methoxide in absolute tetrahydrofuran under dry N_2, and were characterized by elemental analysis (C, H and Hg), and by mass spectrometry [9].

The infrared spectra of solids in KBr and CsI discs and nujol mulls, were recorded on a Perkin-Elmer 621 spectrometer in the range 4000–200 cm^{-1}. The Raman spectra of the pure solids were recorded on a Cary 82 spectrometer with excitation by Spectra Physics 164 (Kr^+) and 165 (Ar^+) lasers.

Results

Vibrational assignments

For $C'H_{4-n}(HgCH_3)_n$ molecules with pseudo-tetrahedral environments of the central carbon atoms (C′) there are the following distributions of internal modes (the spectral activities are given in parentheses):
For $C(HgCH_3)_4$ (I):

$$\Gamma(T_d) = 4a_1(\mathrm{R}) + a_2(ia) + 5e(\mathrm{R}) + 5f_1(\mathrm{ia}) + 9f_2(\mathrm{IR, R}) \quad (1)$$

for $CH(HgCH_3)_3$ (II):

$$\Gamma(C_{3v}) = 5a_1(\mathrm{IR, R}) + a_2(\mathrm{R}) + 6e(\mathrm{IR, R}) \quad (2)$$

for $CH_2(HgCH_3)_2$ (III):

$$\Gamma(C_{2v}) = 11a_1(\mathrm{IR, R}) + 6a_2(\mathrm{R}) + 9b_1(\mathrm{IR, R}) + 7b_2(\mathrm{IR, R}) \quad (3)$$

The complete assignments proposed for solid methylmercurimethanes are given in Tables 1, 2 and 3. These assignments are based on those reported earlier for the compounds $Hg(CH_3)_2$ [2], CH_3HgX (X = F, Cl, Br and I) (11, 3, 4), and other mercurimethanes [5–7]. The assignments of low frequency skeletal deformation modes mainly rely on the results of normal coordinate calculations.

Though obtained with solids the vibrational spectra do not exhibit obvious lattice effects. Thus, there are no clear-cut splittings of degenerate modes either of the CH_3 groups or the entire molecules. Furthermore those bands appearing in both the IR and Raman spectra show no significant differences in frequencies (except for $\nu_{as}(CHg_4)$ of I).

Assuming that the 60 cm^{-1} difference between asymmetric and symmetric CH_3 stretching modes for dimethylmercury [2,10] applies also to methylmercurimethanes, the following pairs of approximate frequencies at 2960/2900 (I), 2960/2900 (II), and 2925/2870 cm^{-1} (III) can be selected as asymmetric and symmetric CH_3 stretching vibrations, respectively.

In the light of the preceding considerations and of the classification of the CH_3

TABLE 1

OBSERVED WAVENUMBERS AND ASSIGNMENTS FOR $C(HgCH_3)_4$ (I)

IR (solid)	Raman (solid)	Assignment [a]
2959 mw	2952 vw, b	CH_3 asym stretch, e, f_2
2899 mw	2898 s	CH_3 sym stretch, a_1, f_2 [b]
2880 sh	2877 sh	
1396 w, b	1380 vw, b	CH_3 asym def, e, f_2
1168 w	1170 m	CH_3 sym def, a_1, f_2
743 s	742 vw, b	CH_3 rock, e, f_2
620 s	583 w, b	CHg_4 asym stretch, f_2
520 sh	514 s	HgMe sym stretch, a_1
510 s	500 sh	HgMe asym stretch, f_2
	137 s	CHg_4 sym stretch, a_1; CHgMe bend, e
	109 s	CHgMe bend, f_2
	91 m	CHg_4 asym def, f_2
	47 s	CHg_4 sym def, e

[a] For spectral activities see representation (1). [b] See text.

valence vibrations ($\Gamma(\mathrm{as}) = e(\mathrm{R}) + f_1(ia) + f_2(\mathrm{IR, R})$; $\Gamma(\mathrm{s}) = a_1(\mathrm{R}) + f_2(\mathrm{IR, R})$), and the near-coincidence of IR and Raman spectra of I in this range, it seems to be reasonable to make the following assignments: 2959 (IR) f_2 mode of ν_{as}, 2899/2880 sh (IR) f_2 species of ν_s with some indication of a lifting of degeneracy; 2952 (R, broad) e and f_2 species of ν_{as}, 2898/2877 sh (R) a_1 and f_2 (split) components of ν_s.

In the CH_3 stretching region of II the highest frequencies at around 2960 cm^{-1} (IR and Raman) can be assigned to three asymmetric modes of a_1, a_2 (only Raman

TABLE 2

OBSERVED WAVENUMBERS AND ASSIGNMENTS FOR $CH(HgCH_3)_3$ (II)

IR (solid)	Raman (solid)	Assignment [a]
2957 m	2929 w, b	CH_3 asym stretch, a_1, a_2, $2e$
2899 m	2900 m	CH sym stretch, a_1
2879 sh	2877 sh	CH_3 sym stretch, a_1, e
1392 w	1400 w, b	CH_3 asym def, a_1, a_2, $2e$
1265 w	1262 vw	515 + 735
1170 w	1173 s	CH_3 sym def, a_1, e
890 w, b	892 w, b	CH bend, e
739 s	732 w, b	CH_3 rock, a_1, a_2, $2e$
615 s	609 w	CHg_3 asym stretch, e
525 sh	526 s	HgMe sym stretch, a_1
515 s	516 s	
	490 sh	HgMe asym stretch, e
450 m	450 m	CHg_3 sym stretch, a_1
	138 m	CHgMe i.p. bend, a_1, e; CHgMe o.o.p. bend, a_2, e
	89 m	CHg_3 sym def. a_1
	64 s	lattice mode

[a] For spectral activities see representation (2).

TABLE 3

OBSERVED WAVENUMBERS AND ASSIGNMENTS FOR $CH_2(HgCH_3)_2$ (III)

IR (solid)	Raman (solid)	Assignment [a]
2958 sh	2960 vw	CH_3 asym stretch, a_1, a_2, b_1, b_2
2923 w	2932 w	CH_2 asym stretch, b_2
	2900 sh	CH_3 sym stretch, a_1, b_1
2870 m	2875 m	CH_2 sym stretch, a_1
1400 vw		CH_3 asym def, a_1, a_2, b_1, b_2
1382 vw		
1330 w	1329 m	CH_2 scissor, a_1
1170 vw	1171 m	CH_3 sym def, a_1, b_1
900 w, b	900 s	CH_2 wag, b_1
740 mw	740 vw, b	CH_3 rock, a_1, a_2, b_1, b_2 CH_2 twist, a_2
610 sh	594 sh	CH_2 rock, b_2
590 s	577 s	CHg_2 asym stretch, b_1
520 m	520 m	HgMe asym stretch, b_1
485 m	487 vs	HgMe sym stretch, a_1
	465 s	CHg_2 sym stretch, a_1
	140 m	CHgMe o.o.p. bend, b_2
	108 m	CHgMe i.p. bend, a_1, b_1; CHgMe o.o.p. bend, a_2
	75 s	CHg_2 scissor, a_1

[a] For spectral activities see representation (3).

active) and e species, with the bands around 2900/2880 cm^{-1} attributed to the symmetric modes (a_1 and e). In the spectra of III the CH_3 valence vibrations are expected at similar frequencies as for I and II, but overlap by the stretching bands of the CH_2 group, with greater relative intensities, renders assignments less certain.

The CH_3 deformation modes of I, II, and III, as assigned in Tables 1–3, agree well with those for other methylmercury derivatives [2,3,4,10–12]. Torsional modes of the CH_3 groups were not observed, possibly due to free rotation around the mercury–carbon bonds.

The methyl group frequencies for some methylmercury derivatives, including the $CH_{4-n}(HgCH_3)_n$ molecules, are summarized in Table 4. It will be seen that the methyl group vibrations for methylmercurimethanes fall in the lower parts of the frequency ranges (Table 4). On the basis of these findings it may be predicted that the corresponding force constants of the CH_3 groups in the $CH_{4-n}(HgCH_3)_n$ molecules will be lower than those of the $Hg(CH_3)_2$ [2] and CH_3HgX [3,12] molecules.

With the methyl groups taken as point masses the skeletal vibrations span the following representations (spectral activities in parentheses):
For $C(HgCH_3)_4$ (I):

$$\Gamma(T_d)_{\text{skeletal}} = 2a_1(\mathrm{R}) + 2e(\mathrm{R}) + f_1(ia) + 4f_2(\mathrm{IR, R}) \qquad (4)$$

for $CH(HgCH_3)_3$ (II):

$$\Gamma(C_{3v})_{\text{skeletal}} = 5a_1(\mathrm{IR, R}) + a_2(\mathrm{R}) + 6e(\mathrm{IR, R}) \qquad (5)$$

TABLE 4

FREQUENCY RANGES (cm^{-1}) FOR METHYL MODES IN METHYL DERIVATIVES OF MERCURY [a]

Mode	Frequency ranges (cm^{-1})
CH_3 asym stretch (e)	3015–2930
CH_3 sym stretch (a_1)	2930–2870
CH_3 asym def (e)	1447–1380
CH_3 sym def (a_1)	1212–1161
CH_3 rock (e)	811– 708

[a] Molecules involved: $(CH_3)_2Hg$ [2,10], CH_3HgX [3,11,12] and $CH_{4-n}(HgCH_3)_n$.

for $CH_2(HgCH_3)_2$ (III):

$$\Gamma(C_{2v})_{\text{skeletal}} = 6a_1(\text{IR, R}) + 2a_2(\text{R}) + 4b_1(\text{IR, R}) + 3b_2(\text{IR, R}) \qquad (6)$$

The differences between appropriate pairs in the representations (1) and (4), (2) and (5), (3) and (6) give the activity of CH_3 vibrations including torsional modes.

It was not possible to observe CH and CH_2 stretching bands unequivocally for II and III, since they overlap with CH_3 stretching vibrations (see above). In the case of III information available for bis(halomercuri)methanes $CH_2(HgX)_2$ favours assignment of the Raman bands at 2930 and 2875 cm^{-1} to the asymmetric and symmetric CH_2 valence vibrations, respectively. However, for the force constant calculations, the CH and CH_2 stretching frequencies for II and III were taken from the $CH(HgI)_3$ and $CH_2(HgI)_2$ molecules [9]. The CH bending mode for II and the CH_2 scissoring, wagging, twisting and rocking modes for III were assigned by analogy to the $CH(HgX)_3$ and $CH_2(HgX)_2$ molecules (X = Cl, Br and I), which are also available in deuterated form [9].

The triply degenerate CHg_4 stretching mode of I shows a strong lattice effect, which is weaker for the HgMe stretching vibrations (Table 1). In the Raman spectra of all three compounds I–III bands around 137 cm^{-1} were observed and these were thus assigned to the C–Hg–Me linear bonding modes. With I Raman bands at 137 and 109 cm^{-1} are possible candidates for the symmetric CHg_4 valence vibration (a_1). The force constant calculation favours assignment of the Raman band at 137 cm^{-1} to the a_1 mode, with the other at 109 cm^{-1} being the f_2 species of the C–Hg–Me linear bending modes.

There are two similarly intense bands at 526 and 516 cm^{-1} in the Raman spectrum of II (Fig. 1). The higher one must be the symmetric and the lower one the asymmetric Hg–Me stretching mode, respectively. Alternatively, the shoulder at 490 cm^{-1} is assigned to the asymmetric mode and the doublet centered at around 520 cm^{-1} to the symmetric vibration. In the force constant calculations both assignments were fitted, and the results will be discussed later. In Table 2 only the second interpretation is taken into account. It should be pointed out that the Hg–Me stretching vibrations of previously known methylmercury compounds fall in the range 570–513 cm^{-1} [2,3,11,12], whereas with methylmercurimethanes these vibrations appear in the range 526–485 cm^{-1} (Tables 1–3). These results indicate that the valence force constants of the mercury to methyl carbon bonds in the molecules I–III are lower than those in other methylmercury compounds.

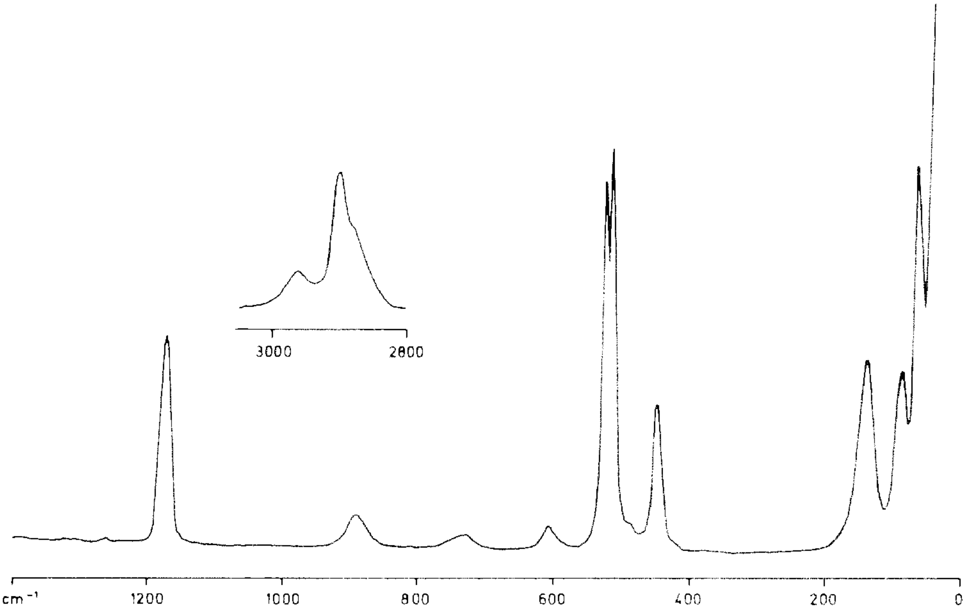


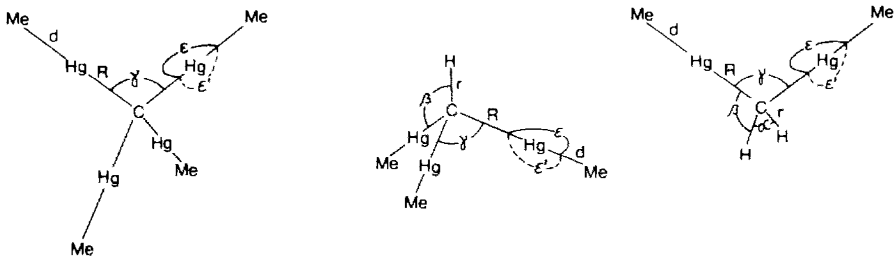
Fig. 1. Raman spectrum of solid $CH(HgCH_3)_3$ (II).

Force constant calculations

Tetrahedral angles about carbon and linear bonding about mercury were assumed for all $CH_{4-n}(HgCH_3)_n$ molecules. The C–Hg, Hg–Me, and C–H bond lengths were taken as 209.6, 209.4 and 109 pm, respectively. Simplified calculations were performed with the assumption of point masses of 15.3 and 19.2 amu for the CH_3 and CD_3 groups, respectively. These mass values are based on comparisons between all-atom [2] and point mass calculations for $Hg(CH_3)_2$ and $Hg(CD_3)_2$ molecules. The Hg–Me bond lengths were corrected for the distance between the centre of mass of the methyl group and the carbon atom, viz. 7.4 and 12.3 pm for the CH_3 and CD_3 groups, respectively. For further simplification a mean Hg–Me bond distance of 219.2 pm was used for both groups.

Mean values of IR and Raman frequencies from solid state spectra were used in the force constant refinements. The types of internal coordinates are shown in Fig. 2. Symmetry coordinates are based on point group T_d, C_{3v}, and C_{2v} for I, II, and III, respectively. A recently developed program [13] was used for calculating the G matrices and for refining the force constants. The initial force constants were taken from previous calculations for $Hg(CH_3)_2$ [2], $Hg(C_2H_5)X$ [14], and $C(HgX)_4$ (X = Cl, Br and I) [6].

There are 8, 12, and 15 observable fundamentals for I, II, and III, respectively, excluding the internal vibrations of the CH_3 groups. We attempted to refine the maximum number of force constants, including all diagonal force constants in symmetry coordinate representation. The other force constants were constrained or assumed to be zero. Tables 5–7 show comparisons of the experimental and calculated wave numbers, and present the potential energy distributions in terms of internal coordinates. The final non-zero force constants are listed in Table 8.



I II III

Fig. 2. Internal coordinates of the molecules $C(HgCH_3)_4$ (I), $CH(HgCH_3)_3$ (II), and $CH_2(HgCH_3)_2$ (III). Coordinate ϵ' refers to the out-of-plane deformation.

The agreement between assigned experimental and calculated wavenumbers is generally very good. The greater discrepancy in C–Hg–Me linear bending modes for I can be attributed to the omission of the bend–bend interaction force constant. Some of the calculated fundamentals below 100 cm^{-1} show poor agreement with the experimental values and this is attributable to the high degree of singularity in the Jacobian matrices. For symmetry species with a singular Jacobian, a damped least-squares procedure with a damping factor around 10^{-3} was used for force constant refinement.

The potential energy distributions in the normal modes show that some of them are more complex than the approximate descriptions suggest. It is noteworthy that

TABLE 5

EXPERIMENTAL AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR $C(HgCH_3)_4$

Assignment and approximate description of mode			(cm^{-1}) obs. (calcd.)	PED × 100
a_1	ν_1	HgMe sym str	517 (517)	99d + 1R
	ν_2	CHg_4 sym str	137 (136.5)	100R
e	ν_3	CHgMe bend	137 (127.5)	$92\epsilon + 11\gamma$
	ν_4	CHg_4 sym def	47 (53.6)	$89\gamma + 8\epsilon$
f_1	ν_5	CHgMe bend	– (122.8)	100ϵ
f_2	ν_6	CHg_4 asym str	620 (620)	$67R + 11\epsilon + 59\gamma$
	ν_7	HgMe asym str	505 (505)	99d
	ν_8	CHgMe bend	109 (124.4)	$61\epsilon + 29R + 6\gamma$
	ν_9	CHg_4 asym def	91 (80.6)	$43\gamma + 29\epsilon + 11R$

TABLE 6

EXPERIMENTAL AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION FOR $CH(HgCH_3)_3$

	Assignments and approximate description of mode	(cm^{-1}) obs. (calcd.)	PED ×100
a_1	CH stretch	2900 (2900)	99r
	HgMe sym str	515.5 (515.5) [a] 520 (520) [b]	99d + 1R
	CHg_3 sym str	450 (450)	$98\gamma\beta^{c} + 31R - 26\epsilon$
	CHgMe i.p. bend	138 (137.3)	$52R + 31\epsilon + 3\gamma\beta$
	CHg_3 sym def	89 (89)	$51\epsilon + 38R + 17\gamma\beta$
a_2	CHgMe o.o.p. bend	138 (138)	$100\epsilon'$
e	CH bend	891 (891)	$105\beta + 4R + 1\gamma$
	CHg_3 asym str	612 (612)	$80R + 28\gamma + 7\epsilon' + 2d$
	HgMe asym str	525.5 (525.5) [a] 490 (490) [b]	$98d + 1R + 1\gamma$
	CHgMe o.o.p. bend	138 (138)	$71\epsilon' + 20R + 1\gamma$
	CHgMe i.p. bend	100 [d] (100)	$101\epsilon + 3R + 1\gamma$
	CHg_3 asym def	80 [d] (80)	$65\gamma + 20\epsilon' + 7R + 2\beta$

[a] Fundamentals for assignments (1). [b] Fundamentals for assignments (2). [c] Combination of two coordinates after redundancy elimination. For explanation of two fundamentals see text. [d] Estimated from experimental data of $CH(HgX)_3$, (X = Cl, Br, I) [9].

the asymmetric CHg_4 stretching mode is strongly coupled with the deformation of the CHg_4 entity in $C(HgCH_3)_4$ (I) (Table 5). For the tris-derivative II, both of the CHg_3 stretching modes (symmetric and asymmetric) are mixed with CHg_3 deformations and C–Hg–Me linear bending vibrations (Table 6). Strong coupling between CHg_2 stretching, scissoring and C–Hg–Me linear bending modes of a_1 species was established for III, whereas all other modes are uncoupled (Table 7).

The stretching and stretch–stretch interaction force constants, e.g. K_r, K_R, and F_R show clear dependence on the extent of mercuration. For comparison, Table 8 also gives the corresponding force constants of dimethylmercury [2].

The C–Hg stretching force constants K_R for $CH_{4-n}(HgCH_3)_n$ decrease with increasing n (Fig. 3, curve 3). The deformation force constants do not vary systematically with the extent of mercuration, and this is not surprising because the

TABLE 7

EXPERIMENTAL AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION FOR $CH_2(HgCH_3)_2$

Assignment and approximate description of mode		(cm^{-1}) obs. (calcd.)	PED × 100
a_1	CH_2 sym str	2872.5 (2870.0)	99r
	CH_2 scissor	1329.5 (1329.5)	$93\beta+1\gamma$
	HgMe sym str	486 (486)	$85d+12R+7\gamma$
	CHg_2 sym str	465 (464.8)	$53R+47\gamma+15d+13\beta$
	CHgMe i.p. bend	108 (117.6)	$51\epsilon+40R+12\gamma+2\beta$
	CHg_2 scissor	75 (80.6)	$58\gamma+42\epsilon+9\beta+1R$
a_2	CH_2 twist	740 (740)	100β
	CHgMe o.o.p. bend	108 (108.2)	$100\epsilon'$
b_1	CH_2 wag	900 (900)	$111\beta+7R$
	CHg_2 asym str	583.5 (583.5)	$98R+4d+2\epsilon$
	HgMe asym str	520 (520)	$96d+4R$
	CHgMe i.p. bend	108 (113.5)	$97\epsilon+3R$
b_2	CH_2 asym str	2927.5 (2927.5)	100r
	CH_2 rock	602 (602)	$99\beta+1\epsilon'$
	CHgMe o.o.p. bend	140 (140)	$99\epsilon'+1\beta$

vibrational forms of the deformation modes change markedly with the number n of metal atoms around the carbon atoms.

Special attention should be paid to the Hg–Me stretching force constants K_d. Using the assignment (1) in Table 6, the refined K_d value for II did not follow the trend observed for other methylmercurimethanes, including dimethylmercury; this dependence of K_d on n is shown in Fig. 3, curve 1. K_d 2.26 N cm^{-1} for II is probably too high (point 2 in Fig. 3). With assignment (2) of Hg–Me stretching modes this discrepancy vanished: Taking the strong Raman and IR bands around 520 cm^{-1} for the symmetric Hg–Me stretching vibration and the weak shoulder at 490 cm^{-1} for the degenerate mode (Fig. 1), as suggested earlier, the refinement gives K_d 2.101 N cm^{-1} and F_d 0.080 N cm^{-1}, in good agreement with the expected trend of Hg–Me stretching force constants (Fig. 3, curve 1). The decrease in the C–Hg force constants K_R and K_d with the extent of mercuration may be explained in terms of increasing non-bonded metal–metal interaction. It is of interest that the

(Continued on p. 12)

TABLE 8

FORCE CONSTANTS FOR $CH_{4-n}(HgCH_3)_n$ MOLECULES (bracketed values were constrained and taken from results of corresponding $CH_{4-n}(HgX)_n$ (X = Cl, Br, I) molecules [8].)

Force constants	Coordinates involved	Common atom(s)	$C(HgCH_3)_4$	$CH(HgCH_3)_3$	$CH_2(HgCH_3)_2$	$(CH_3)_2Hg$	
Stretch							
K_r	CH	–	–	4.600	4.595	4.739	^{a}
K_R	CHg	–	1.582	1.653	1.870	2.379	^{a}
K_d	HgMe	–	2.160	2.290	2.121	2.379	^{a}
				2.101 ^{f}			^{a}
Stretch–stretch							
F_r	CH, CH	C	–	–	−0.025	0.016	^{a}
F_R	CHg, CHg	C	0.255	−0.072	0.194	–	^{a}
F_d	HgMe, HgMe		0.024	−0.036	−0.170		^{a}
				0.080 ^{f}			^{a}
F_{rR}	CH, HgC	C		0	0	−0.075	^{a}
F_{Rd}	CHg, HgMe	Hg	(0.031)	(0.031)	(0.031)	0.031	^{a}
Bend							
H_α	CH_2				0.313	0.433	^{b}
H_β	HCHg	–	–	0.495	0.514	0.538	^{b}
H_γ	HgCHg	–	1.251	1.516	1.243	–	^{b}

H_{ϵ}	CHgMe	–	0.455	0.407	0.422	0.382	[b]
$H_{\epsilon'}$	CHgMe	–	0.455	0.592	0.329	0.382	[b]
Stretch–bend							
$F_{r\alpha}$	CH, CH_2	C–H	–	–	0	0.006	[c]
$F_{r\beta}$	CH, HCHg	C–H	–	0	0	0.179	[c]
$F_{r\beta'}$	CH, HCHg	C	–	–	0	0.124	[c]
$F'_{r\beta}$	CH, HCHg	Hg	–	0 [e]	0 [e]	0.073	[c]
$F_{R\beta}$	CHg, HCHg	C–Hg	–	(0.116)	(0.098)	0.213	[c]
$F_{R\beta'}$	CHg, HCHg	C	–	(–0.116)	(–0.098)	–	[c]
$F_{R\gamma}$	CHg, HgCHg	C–Hg	(0.255)	(0.255)	(0.255)	–	[c]
$F_{R\epsilon}$	CHg, CHgMe	C	0	(–0.126)	(0.051)	–	[c]
Bend–bend							
$F_{\alpha\beta}$	CH_2, HCHg	C–H	-	–	0	–0.041	[b]
F_{β}	HCHg, HCHg	C–H	–	0.142	0.190	–0.110	[b]
$F_{\beta'}$	HCHg, HCHg	C–Hg	–	–	0.246	–	[b]
$F_{\beta''}$	HCHg, HCHg	C	–	–	0.113	–	[b]
F'_{β}	HCHg, HCHg	Hg	–	0 [e]	0 [e]	0.106	[b]
F_{γ}	HgCHg, HgCHg	C–Hg	0.272	(0.130)	–	–	[b]
$F_{\beta\gamma}$	HCHg, HCHg	C–Hg	–	0	(0.048)	–	[b]
F_{ϵ}	CHgMe, CHgMe	C	0	0.084	0	–	[b]
$F_{\epsilon'}$	CHgMe, CHgMe	C	0	0.011	0.057	–	[b]

---

[a] 10^2 Nm^{-1}. [b] 10^{-18} $Nmrad^{-2}$. [c] 10^{-8} Nrad. [d] See ref. 2. [e] Force constants were not introduced in accordance with the point mass model of CH_3 groups. For assignments (2), cf. Table 6.

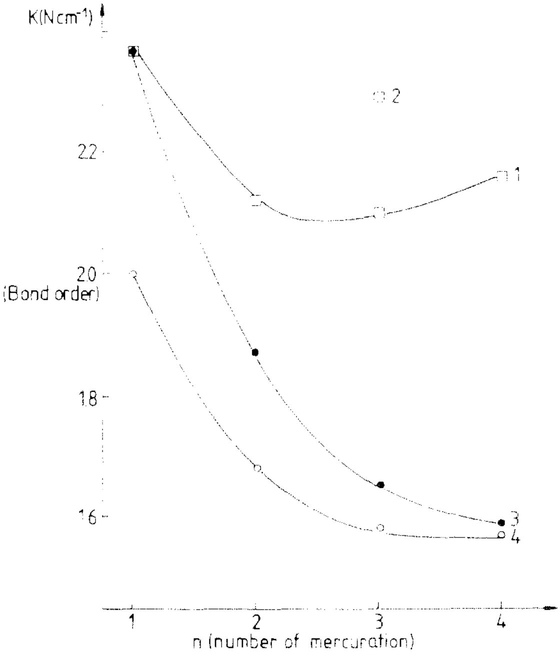


Fig. 3. Relationship of the C–Hg force constants K_d (1) and K_R (3), and of the bond orders of mercury (4) (related to K_d and K_R, cf. [8]) to the number of mercuration n, in methylmercurimethanes $CH_{4-n}(HgCH_3)_n$. For the point 2 see text.

C–Hg force constants K_R (central bonds) are lower than the K_d values (terminal bonds), by 12, 21, and 27% for $n = 2$, 3 and 4, respectively. Similar conclusions may be drawn from the fragmentation patterns in the mass spectra of these compounds [9]. These differences in strengths of bonds of the same kind may be due to increasing shift of electron density towards the periphery of the molecules, leading to decreasing overlap in the central bonds compared with that in the terminal ones.

Acknowledgements

One of the authors (J.M.) thanks the Deutsche Forschungsgemeinschaft and the University of Erlangen-Nürnberg for their hospitality and for the facilities provided during his visiting professorship. D.K.B. thanks the DFG and the Fonds der Chemischen Industrie for support.

References

1 D.K. Breitinger, R. Neufert, and M. Nowak, Z. Naturforsch. B, 39 (1984) 123.
2 J. Mink and B. Gellai, J. Organomet. Chem., 66 (1974) 435.
3 P.L. Goggin, G. Kemény, and J. Mink, J. Chem. Soc. Faraday Trans. II, 72 (1976) 1025.
4 G. Kemény, J. Mink, and P.L. Goggin, J. Mol. Struct., 66 (1980) 227.
5 D.K. Breitinger and W. Morell, Z. Naturforsch. B, 32 (1977) 1022.
6 D.K. Breitinger, W. Morell, and K. Grabetz, Z. Naturforsch. B, 34 (1979) 390.
7 J. Mink, Z. Meić, M. Gál, and B. Korpar-Čolig, J. Organomet. Chem., 256 (1983) 203.
8 J. Mink, D.K. Breitinger, Z. Meić, and M. Gál, J. Mol. Struct., 115 (1984) 435.

9 W. Kress, Ph.D. Thesis, Erlangen, 1983.

10 I.S. Butler and M.L. Newbury, Spectrochim. Acta A, 33 (1977) 669.

11 D.K. Breitinger, A. Zober, and M. Neubauer, J. Organomet. Chem., 30 (1971) C49.

12 Y. Imai and K. Aida, J. Inorg. Nucl. Chem., 41 (1979) 963.

13 J. Mink and L.M. Mink, Computer Program System for Vibrational Analysis of Molecules, Erlangen, 1983.

14 J. Mink and P.L. Goggin, J. Organomet. Chem., 185 (1980) 129.