

## METALLOMETHANES

### XIII \*. VIBRATIONAL SPECTRA AND FORCE FIELDS OF CYANOMERCURIOMETHANES

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#### Summary

Vibrational spectra with assignments and results of normal coordinate calculations for cyanomercuriomethanes  $\text{CH}_{4-n}(\text{HgCN})_n$  ( $2 \leq n \leq 4$ ) are discussed. The valence force constants of the central C–Hg bonds are 2.149, 1.944, and 1.798  $\text{N cm}^{-1}$ , while those of the Hg–CN bonds are 2.204, 2.123, and 2.162  $\text{N cm}^{-1}$ , for  $n = 2, 3$  and 4, respectively. All these force constants are lower than the corresponding constants for methylmercury cyanide (2.445 and 2.379  $\text{N cm}^{-1}$ ). The overall behaviour of these force constants as a function of the degree of mercuration  $n$  is quite similar in both the cyanomercuriomethanes  $\text{CH}_{4-n}(\text{HgCN})_n$  and methylmercuriomethanes  $\text{CH}_{4-n}(\text{HgCH}_3)_n$  series with the difference that there are variations in the constants at higher values in the former series. The potential energy distributions indicate that the valence vibrations of the C–H,  $\text{C}\equiv\text{N}$ , and Hg–CN bonds are almost independent of all other vibrations, which in turn are more or less strongly coupled.

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#### Introduction

Vibrational spectra of cyanomercuriomethanes have been studied previously [1–4], and a few approximate force constants were obtained from a simplified

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calculation for  $C(HgCN)_4 \cdot H_2O$  [3]. An X-ray structural study of  $C(HgCN)_4 \cdot H_2O$  [6] revealed a nearly tetrahedral arrangement of four mercury atoms around the carbon atom, with the  $CHgCN$  fragments close to linearity. We present here our interpretations of the infrared and Raman spectra of  $CH_{4-n}(HgCN)_n$  molecules ( $2 \leq n \leq 4$ ), together with the results of calculations of the force constants.

## Experimental

The compounds were prepared by metatheses between potassium cyanide and the appropriate acetoxymercuriomethanes  $CH_{4-n}(HgOAc)_n$  [5]. The IR spectra of the solids in KBr and CsI discs, and in Nujol mulls, were recorded with a Perkin-Elmer 621 spectrometer in the range  $4000-200\text{ cm}^{-1}$ ; the far infrared spectra of the compounds in polyethylene pellets were recorded with a Fourier-transform spectrometer Polytec FIR 30. The Raman spectra of the pure compounds, and of some solutions in dimethylsulfoxide, were recorded with a Cary 82 spectrometer with excitation by Spectra Physics 164 ( $Kr^+$ ) and 165 ( $Ar^+$ ) lasers.

## Force constant calculations

Geometrical parameters used in the calculations (Table 3) were taken from X-ray [6] and neutron diffraction studies [7]. Averaged X-ray data [6] are used for  $C \equiv N$  bond lengths, and estimated C-Hg and Hg-CN interatomic distances for  $CH(HgCN)_3$  and  $CH_2(HgCN)_2$  molecules. The bond angles around the central carbon atoms are taken as tetrahedral, and linear C-Hg-C=N arrangements are assumed.

A FORTRAN program was used for calculating the  $G$  matrices and for refining the force constants [8]. The initial force constants were taken from earlier calculations for  $CH_3HgCN$  [9] and  $CH_{4-n}(HgCH_3)_n$  [10].

Since solution data are not available in most cases, mean values of the infrared and Raman frequencies from spectra of the solids were used as the basis for the force constant refinements. Raman solution data were available only for  $C(HgCN)_4$  [2], and three fundamentals belonging to  $a_1$  symmetry species were used for the refinement. The types of internal coordinates are shown in Fig. 1. The construction

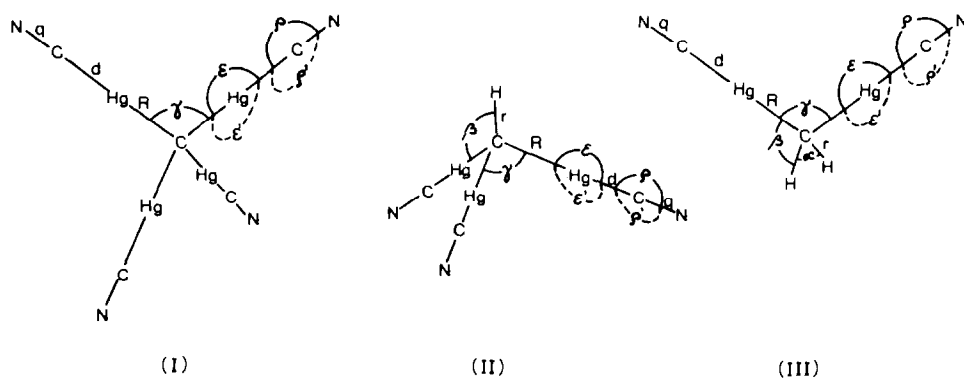


Fig. 1. Internal coordinates of the molecules  $C(HgCN)_4$  (I),  $CH(HgCN)_3$  (II), and  $CH_2(HgCN)_2$  (III). Coordinates  $\epsilon'$  and  $\rho'$  refer to the  $CHgC'$  and  $HgCN$  out-of-plane deformations, respectively.

of symmetry coordinates is based on  $T_d$ ,  $C_{3v}$ , and  $C_{2v}$  symmetries for  $C(HgCN)_4$  (I),  $CH(HgCN)_3$  (II), and  $CH_2(HgCN)_2$  (III), respectively.

We attempted to refine the maximum number of force constants, including all diagonal elements in the  $F$  matrices in symmetry coordinate representation. Most of the off-diagonal force constants were constrained or were assumed to be zero. The experimental and calculated wavenumbers for the normal modes, together with the potential energy distribution (PED) of the symmetry coordinates between the normal modes are listed in Tables 4, 5, and 6 for  $C(HgCN)_4$ ,  $CH(HgCN)_3$  and  $CH_2(HgCN)_2$ , respectively.

The agreement between the experimental and calculated wavenumbers (Tables 4–6) is generally very good. In a few cases, especially for the  $C(HgCN)_4$  molecule, the calculated fundamentals below  $100\text{ cm}^{-1}$  show poorer agreement with the experimental values; this is attributable to the high degree of singularity of the Jacobian matrices. A damped least-squares procedure was used for the force constant refinement to avoid convergence problems. The refined non-zero force constants in terms of internal coordinates are listed in Table 7.

TABLE 1  
INFRARED AND RAMAN FREQUENCIES OF  $CH(HgCN)_3$  ( $\text{cm}^{-1}$ )

IR (solid)	Raman (solid)	Assignment
<sup>a</sup>	2949vw	$a_1$ CH stretch
2190vw	2183w	$e$ CN stretch
2170vw	2167s	$a_1$ CN stretch
1020vw		373 + 646 ( $e$ )
985vw	964vw, b)	$e$ CH bend
960vw	946vw, b)	
675vs	676vw)	$e$ $CH_3$ <i>asym</i> stretch
646vs	646vw)	
	600vw, b	$2 \times 303$ ( $a_1$ )
498s	505m	$a_1$ $CH_3$ <i>sym</i> stretch
400vs, b	393s, b	$e$ $HgC'$ <i>asym</i> stretch <sup>b</sup>
373sh		$a_1$ $HgC'$ <i>sym</i> stretch
	303s	$a_2$ $HgCN$ o.o.p. <i>sym</i> bend
293s		$e$ and $a_1$ $HgCN$ i.p. bend
	289s	$e$ $HgCN$ o.o.p. bend
120s	120s	$a_1$ $CH_3C'$ i.p. bend
95vs	95s)	$e$ $CH_3C'$ i.p. bend
90sh		
68s	67vs	$a_1$ $CH_3$ <i>sym</i> def, $a_2$ $CH_3C'$ o.o.p. <i>sym</i> bend
50vw	56vs	$e$ $CH_3$ <i>asym</i> def
43vw	46vs)	lattice
34w	35vs)	
	26vs)	

<sup>a</sup> Very weak and broad band in the IR spectrum. <sup>b</sup>  $C'$  refers to the carbon atom of the CN group. Assignments of bands in the range  $400\text{--}289\text{ cm}^{-1}$  based on results of calculations.

## Discussion

On the basis of earlier experience with  $C(HgCN)_4 \cdot H_2O$  [3], we assumed that there is practically no coupling between the CN stretching vibrations in the  $C(HgCN)_4$  molecule. The calculated potential energy distribution also showed that

TABLE 2  
INFRARED AND RAMAN FREQUENCIES OF  $CH_2(HgCN)_2$  ( $cm^{-1}$ )

IR (solid)	Raman (solid)	Assignments
	2992m	$b_2$ $CH_2$ <i>asym</i> stretch
2955vw	2932s	$a_1$ $CH_2$ <i>sym</i> stretch
2175vw		$b_1$ CN <i>asym</i> stretch
	2165vs	$a_1$ $^{12}CN$ <i>sym</i> stretch
	2117vw	$a_1$ $^{13}CN$ <i>sym</i> stretch
1370vw, b	1362w	$a_1$ $CH_2$ scissoring
1180vw		540 + 636 ( $b_1$ )
1020vw		
995w	985m	$b_1$ $CH_2$ wagging
960vw	966w	
810vw		$a_2$ $CH_2$ twisting
660s		$b_2$ $CH_2$ rocking
636s	639m	$b_1$ $CHg_2$ <i>asym</i> stretch
600sh	605vw, b	$2 \times 304$ ( $a_1$ )
540s	542s	$a_1$ $CHg_2$ <i>sym</i> stretch
450sh	460w, b	
410sh	407sh	$b_1$ $HgC'$ <i>asym</i> stretch
382vs, b	380s	$a_1$ $HgC'$ <i>sym</i> stretch
311w, sh	304s	$a_1, a_2, b_1, b_2$ $HgCN$ linear bend
(148m)	(165vw, b)	$b_2$ $CHgC'$ o.o.p. bend
114sh	102w	$a_1$ $CHgC'$ i.p. bend
96s	88m	$b_1$ $CHgC'$ i.p. bend
77sh		$a_2$ $CHgC'$ o.o.p. bend
68sh	70vs	$a_2$ $CHg_2$ scissoring
46m	41s	lattice modes
38sh	37s	

TABLE 3  
GEOMETRICAL PARAMETERS FOR CYANOMERCURIOMETHANES (bond lengths in pm, bond angles in  $^\circ$ )

	$C(HgCN)_4$ <sup>a</sup>	$CH(HgCN)_3$	$CH_2(HgCN)_2$	$CH_3HgCN$ <sup>b</sup>
$R(CHg)$	205.5	206.3	206.3	208
$d(HgC')$	203.5	203	203	205
$q(CN)$	115.5	115.5	115.5	114
$r(CH)$	-	109	109	110
$\alpha(HCH)$	-	-	109.45	110.7
$\beta(HgCH)$	-	109.45	109.45	108.2
$\gamma(HgCHg)$	109.45	109.45	109.45	-

<sup>a</sup> Mean values from X-ray study [6]. <sup>b</sup> Neutron diffraction study [7].

TABLE 4

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

Assignment and approximate description of mode	Wavenumber ( $cm^{-1}$ )		PED ( $\times 100$ )	
	obs. <sup>a</sup>	calcd.		
$a_1$	C'N <i>sym</i> str	2168	2167.8	$96q + 4d$
	HgC' <i>sym</i> str	407	408.3	$89d + 4q + 3R$
	CHg <sub>4</sub> <i>sym</i> str	127	139	$99R + 10d$
$e$	HgC'N bend	310	306	$80\rho + 20\epsilon$
	CHgC' linear bend	86.5	94	$58\epsilon + 29\gamma + 16\rho$
	CHg <sub>4</sub> <i>sym</i> def	52	43	$71\gamma + 22\epsilon + 5\rho$
$f_1$	HgC'N bend	291	297.7	$81\rho + 19\epsilon$
	CHgC' linear bend	146	147.1	$81\epsilon + 19\rho$
$f_2$	C'N <i>asym</i> str	2168	2168.2	$96q + 4d$
	CHg <sub>4</sub> <i>asym</i> str	655	655.1	$69R + 45\gamma + 13\epsilon$
	HgC' <i>asym</i> str	392	390.6	$94d + 6\gamma + 3q + 3R + 3\epsilon$
	HgC'N bend	297	300.4	$82\rho + 13\epsilon + 4R$
	CHgC' linear bend	102.5	106.5	$37R + 23\epsilon + 22\gamma + 6\rho$
	CHg <sub>4</sub> <i>asym</i> def	64.5	57.2	$49\epsilon + 34\gamma + 11\rho$

<sup>a</sup> Observed frequencies from refs. 1–3.

the symmetric and asymmetric CN stretching modes are not mixed with other vibrational modes (Tables 1 and 2). The other stretching modes have also very characteristic vibrational forms, except the CHg<sub>4</sub> asymmetric stretching, which involves strong deformation of the CHg<sub>4</sub> entity. The CHgC and HgCN linear bending modes are strongly coupled motions, but the most complicated forms appear for the two low-frequency vibrations of  $f_2$  species, viz for the CHgC linear bending and CHg<sub>4</sub> asymmetric deformation modes.

The strongest vibrational coupling in CN stretching modes was observed with  $CH(HgCN)_3$ . The CHg<sub>3</sub> symmetric stretching mode is strongly mixed with CHgC linear bendings and CHg<sub>3</sub> deformation modes, while the CHg<sub>3</sub> asymmetric stretching vibration is involved in the strong coupling with HgCN linear bendings (Table 5).

For the  $CH_2(HgCN)_2$  molecule the potential energy distribution (see Table 4) shows that all stretching modes are relatively pure vibrational motions, except for the CHg<sub>2</sub> symmetric stretching which couples strongly with the CHg<sub>2</sub> scissoring mode. As in the foregoing cases the two types of linear bending modes are much more mixed than the approximate descriptions suggest (Table 6). Table 7 also includes the force constants for  $CH_3HgCN$  [9]. Some of the stretching force constants, e.g.  $K_R$  and  $K_d$ , and stretch–stretch interaction force constants ( $F_R$ ,  $F_d$ ) show clear dependence upon the extent of mercuration.

It is of interest to compare the vibrational frequencies and force constants of cyanomercuriomethanes and methylmercuriomethanes [10]. All the CH and CH<sub>2</sub> stretching and deformation modes are considerably higher for II and III than for the corresponding methyl derivatives [10]. Consequently the CH stretching force constants  $K_r$  are 3–5% higher for cyano derivatives. The central carbon–mercury stretching fundamentals are 50–70  $cm^{-1}$  lower for methylmercuriomethanes except

TABLE 5

EXPERIMENTAL AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR CH(HgCN)<sub>3</sub> (II)

Assignment and approximate description of mode		Wavenumber (cm <sup>-1</sup> )		PED (×100)
		obs.	calcd.	
<i>a</i> <sub>1</sub>	CH str	2949	2949	99 $r$
	CN <i>sym</i> str	2168.5	2168.5	97 $q$ + 3 $d$
	CHg <sub>3</sub> <i>sym</i> str	501.5	501.2	78 $\gamma\beta$ + 35 $\epsilon$ + 27 $R$ + 1 $\rho$
	HgC' <i>sym</i> str	373	373	95 $d$ + 3 $q$ + 1 $R$
	HgCN i.p. bend	293	293.4	74 $\rho$ + 11 $\epsilon$ + 10 $\gamma\beta$ + 5 $R$
	CHgC' i.p. bend	120	120.7	78 $R$ + 7 $\rho$ + 3 $\epsilon$
	CHg <sub>3</sub> <i>sym</i> def	67.5	67.7	56 $\epsilon$ + 17 $\rho$ + 22 $\gamma\beta$ + 5 $R$
<i>a</i> <sub>2</sub>	HgCN o.o.p. <i>sym</i> bend	303	303	86 $\rho'$ + 11 $\epsilon'$
	CHgC' o.o.p. <i>sym</i> bend	67.5	67.5	88 $\epsilon'$ + 11 $\rho'$
<i>e</i>	CN <i>asym</i> str	2186.5	2186.5	96 $q$ + 4 $d$
	CH bend	964	964	104 $\beta$ + 5 $R$
	CHg <sub>3</sub> <i>asym</i> str	661	661	82 $R$ + 24 $\gamma$ + 32 $\rho$ + 5 $\epsilon'$
	HgC' <i>asym</i> str	396.5	397	95 $d$ + 4 $q$
	HgCN i.p. bend	293	294	67 $\rho$ + 33 $\epsilon$
	HgCN o.o.p. bend	289	289	83 $\rho'$ + 16 $\epsilon'$
	CHgC' o.o.p. bend	113	110.3	45 $\gamma$ + 19 $\epsilon'$ + 20 $R$
	CHgC' i.p. bend	93.3	92.2	65 $\epsilon$ + 2 $\epsilon'$
CHg <sub>3</sub> <i>asym</i> def	53	53	57 $\epsilon'$ + 30 $\gamma$ + 11 $\rho$	

TABLE 6

EXPERIMENTAL AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR CH<sub>2</sub>(HgCN)<sub>2</sub> (III)

Assignment and approximate description of mode		Wavenumber (cm <sup>-1</sup> )		PED (×100)
		obs.	calcd.	
<i>a</i> <sub>1</sub>	CH <sub>2</sub> <i>sym</i> str	2943.5	2943.5	99.7 $r$
	CN <i>sym</i> str	2165	2165	96.5 $q$ + 4 $d$
	CH <sub>2</sub> scissor	1366	1366	93.1 $\beta$ + 1 $R$ + 1 $r$
	CHg <sub>2</sub> <i>sym</i> str	541	540.9	53 $R$ + 52 $\gamma$ + 13 $\epsilon$
	HgC' <i>sym</i> str	381	381.2	95 $d$ + 3 $q$ + 1 $\gamma$
	HgCN i.p. bend	307.5 <sup>a</sup>	307.5	79 $\rho$ + 15 $\epsilon$ + 6 $R$
	CHgC' i.p. bend	108	118.7	45 $R$ + 26 $\gamma$ + 17 $\epsilon$ + 5 $\rho$
	CHg <sub>2</sub> scissor	69	64.2	54 $\epsilon$ + 34 $\gamma$ + 14 $\rho$
<i>a</i> <sub>2</sub>	CH <sub>2</sub> twist	810	810	100 $\beta$
	HgCN o.o.p. bend	307.5	307.5	83 $\rho'$ + 17 $\epsilon'$
	CHgC' o.o.p. bend	77	79.3	83 $\epsilon'$ + 17 $\rho'$
<i>b</i> <sub>1</sub>	CN <i>asym</i> str	2175	2175	95.9 $q$ + 4 $d$
	CH <sub>2</sub> wag	990.5	990.5	108 $\beta$ + 10 $R$
	CHg <sub>2</sub> <i>asym</i> str	637.5	637.5	95 $R$ + 3 $\epsilon$ + 1 $d$
	HgC' <i>asym</i> str	408.5	408.4	95 $d$ + 4 $q$
	HgCN i.p. bend	307.5	307.5	79 $\rho$ + 20 $\epsilon$
	CHgC' i.p. bend	92	87.6	77 $\epsilon$ + 21 $\rho$ + 3 $R$
<i>b</i> <sub>2</sub>	CH <sub>2</sub> <i>asym</i> str	2992	2992	99.8 $r$
	CH <sub>2</sub> rock	660	660	97 $\beta$ + 3 $\epsilon'$
	HgCN o.o.p. bend	310	310	69 $\rho'$ + 30 $\epsilon'$ + 1 $\beta$
	CHgC' o.o.p. bend	156.5	156.5	67 $\epsilon'$ + 31 $\rho'$ + 2 $\beta$

<sup>a</sup> For HgCN linear bending modes only two experimental frequencies at 311 and 304 cm<sup>-1</sup> were found.

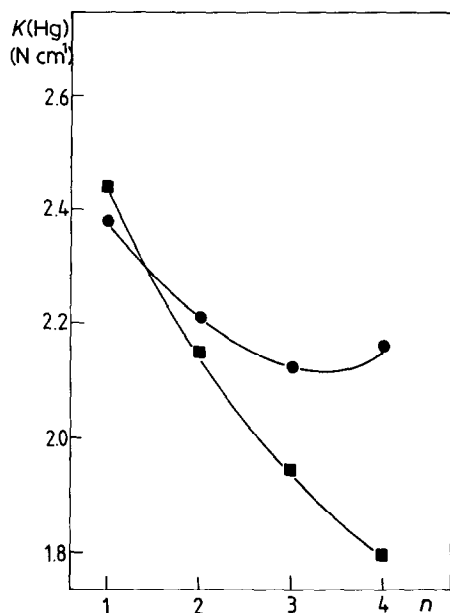


Fig. 2. Relationships of the C-Hg valence force constants  $K_R$  (■) and  $K_d$  (●) to the number of mercuration  $n$  in cyanomercuriomethanes  $\text{CH}_{4-n}(\text{HgCN})_n$ .

for the symmetric stretching mode of  $\text{C}(\text{HgCH}_3)_4$  [10]; that is why the central carbon-metal stretching force constants  $K_R$  are about 13% higher for the cyano derivatives. The higher stretching force constants around the central carbon atom suggest that the electron density in the bonds around this carbon atom is considerably higher for cyanomercuriomethanes than for methylmercuriomethanes.

It should be pointed out that the carbon-mercury force constants  $K_R$  and  $K_d$  are almost the same for  $\text{Hg}(\text{CH}_3)_2$  [13] and  $\text{CH}_3\text{HgCN}$  [9]. The mean value of the CN stretching modes is highest for  $\text{CH}(\text{HgCN})_3$  in this series, leading to the highest  $K_q$  stretching force constant. Consequently the lowest  $K_d$  stretching force constant for the Hg-CN bond is obtained for this molecule.

The dependence on  $n$  of the force constants  $K_R$  and  $K_d$  for  $\text{CH}_{4-n}(\text{HgCN})_n$  is shown in Fig. 2. It is of interest that  $K_d$  shows a minimum at  $n = 3$ , and the same is true for the  $\text{CH}_{4-n}(\text{HgCH}_3)_n$  series [10]. The C-Hg stretching force constants  $K_R$  decrease with increasing  $n$ . The sums of the two stretching force constants  $K_R + K_d$  also decrease with increasing mercuration, which means the non-bonded metal-metal interaction should increase with increased mercuration. This finding applies to all the mercuriomethanes investigated so far.

In the  $\text{CH}_{4-n}(\text{HgCN})_n$  series the chemical shifts in the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{199}\text{Hg}$  NMR spectra, and all observable coupling constants vary progressively with increasing  $n$  [5,14]. The same behaviour is found for the force constants  $K_R$ ; therefore an almost linear correlation is obtained between  $\delta(^{13}\text{C})$ ,  $\delta(^{199}\text{Hg})$ , or  $^1J(^{199}\text{Hg}-^{13}\text{C})$ , and the central carbon-metal stretching force constants. Since the stretching force constants  $K_d$  for the Hg-CN bonds pass through a minimum as a function of  $n$  (Fig. 2), the relationships of  $K_d$  to the corresponding NMR data, viz.  $\delta(^{13}\text{CN})$ ,  $^1J(^{199}\text{Hg}-^{13}\text{CN})$ , and  $^3J(^{199}\text{Hg}-^{13}\text{CN})$ , show also a minimum near  $n = 3$ . It is difficult to explain why

(Continued on p. 282)

TABLE 7  
 FORCE CONSTANTS FOR  $\text{CH}_{4-n}(\text{HgCN})_n$  MOLECULES (bracketed values were constrained and taken from results of the corresponding  $\text{CH}_{4-n}(\text{HgX})_n$  ( $\text{X} = \text{Cl}$ ,  
 Br, I) molecules [11])

Force constant	Coordinates involved	Common atom(s)	$\text{C}(\text{HgCN})_4$ (I)	$\text{CH}(\text{HgCN})_3$ (II)	$\text{CH}_2(\text{HgCN})_2$ (II)	$\text{CH}_3\text{HgCN}^d$
<i>Stretch</i>						
$K_r$	CH	-	-	4.753	4.815	4.770 <sup>a</sup>
$K_R$	CHg	-	1.798	1.944	2.149	2.445 <sup>a</sup>
$K_d$	HgC'	-	2.162	2.123	2.204	2.379 <sup>a</sup>
$K_q$	CN	-	17.246	17.477	17.277	17.273 <sup>a</sup>
<i>Stretch-stretch</i>						
$F_r$	CH, CH	C	-	-	0.043	0.001 <sup>a</sup>
$F_R$	CHg, CHg	C	0.171	-0.146	-0.292	-
$F_d$	HgC', HgC'	-	-0.006	-0.099	-0.171	-
$F_{Rd}$	CHg, HgC'	Hg	(0.025)	(0.025)	(0.025)	-0.372 <sup>a</sup>
$F_q$	CN, CN	-	-0.012	-0.069	-0.030	-
<i>Bend</i>						
$H_\alpha$	$\text{CH}_2$	-	-	-	(0.313)	0.509 <sup>b</sup>
$H_\beta$	HCHg	-	-	0.569	0.589	0.460 <sup>b</sup>
$H_\gamma$	HgCHg	-	1.179	1.513	1.681	-



$H_e$	-	0.577	0.806	0.675	0.505 <sup>b</sup>
$CH_2C'$	-	0.577	0.430	0.529	0.505 <sup>b</sup>
$H_p$	-	0.216	0.180	0.223	0.199 <sup>b</sup>
$H_p'$	-	0.216	0.210	0.219	0.199 <sup>b</sup>
<i>Stretch-bend</i>					
$F_{\beta}$	C-H	-	0	0	0.174 <sup>c</sup>
$F_{\beta\beta'}$	C	-	-	0	0.174 <sup>c</sup>
$F_{R\beta}$	C-Hg	-	(0.116)	(0.098)	0.074 <sup>c</sup>
$F_{R\beta'}$	C	-	(-0.116)	(-0.098)	-
$F_{R\gamma}$	C-Hg	(0.255)	(0.255)	(0.255)	-
$F_{R\epsilon}$	C	0	(-0.126)	(0.051)	0
<i>Bend-Bend</i>					
$F_{\beta}$	HCHg, HCHg	-	0.162	0.211	-
$F_{\beta'}$	HCHg, HCHg	-	-	0.233	0.014 <sup>b</sup>
$F_{\gamma}$	HgCHg, HgCHg	0.162	(0.130)	-	-
$F_{\beta\gamma}$	HCHg, HgCHg	-	(0.048)	(0.048)	-
$F_{\epsilon}$	CHgC', CHgC'	0	0.007	0.051	-
$F_{\epsilon'}$	C	0	-0.043	-0.043	-0.028 <sup>b</sup>
$F_{\epsilon''}$	HgCHg, CHgC'	0.014	0	0	-
$F_{\rho}$	HgCN, HgCN	0	0.008	0.003	-
$F_{\rho'}$	HgCN, HgCN	0	0.011	0.010	-
$F_{\beta''}$	HCHg, HCHg	-	-	0.162	-

<sup>a</sup>  $10^2$  N m<sup>-1</sup>, <sup>b</sup>  $10^{-18}$  N m rad, <sup>c</sup>  $10^{-8}$  N rad<sup>-1</sup>, <sup>d</sup> See ref. 9.

the NMR parameters for the atoms involved in the Hg–CN bonds vary progressively with increasing  $n$ , and the force constants  $K_d$  show a minimum for the metallomethanes so far studied [10].

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### References

- 1 W. Morell, Ph.D. Thesis, Erlangen (1976).
- 2 R. Sendelbeck, Diploma Work, Erlangen (1979).
- 3 J. Mink, Z. Meić, M. Gál and B. Korpar-Čolig, *J. Organomet. Chem.*, 256 (1983) 203.
- 4 W. Kress, Ph.D. Thesis, Erlangen (1983).
- 5 D.K. Breitingner, W. Kress, R. Sendelbeck and K. Ishiwada, *J. Organomet. Chem.*, 243 (1983) 245.
- 6 D. Grdenić, M. Sikirica and B. Korpar-Čolig, *J. Organomet. Chem.*, 153 (1978) 1.
- 7 J.C. Mills, H.S. Preston and C.H.L. Kennard, *J. Organomet. Chem.*, 14 (1968) 33.
- 8 J. Mink and L.M. Mink, "Computer Program System for Vibrational Analysis of Molecules", Erlangen (1983).
- 9 Y. Imai and K. Aida, *J. Inorg. Nucl. Chem.*, 41 (1979) 963.
- 10 J. Mink, D.K. Breitingner and W. Kress, *J. Organomet. Chem.*, 301 (1986) 1.
- 11 J. Mink, D.K. Breitingner, Z. Meić and M. Gál, *J. Mol. Struct.*, 115 (1984) 435.
- 12 D.K. Breitingner, R. Neufert and M. Nowak, *Z. Naturforsch. B*, 39 (1984) 123.
- 13 J. Mink and B. Gellai, *J. Organomet. Chem.*, 66 (1974) 435.
- 14 W. Kress, D.K. Breitingner and R. Sendelbeck, *J. Organomet. Chem.*, 246 (1983) 1.