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VARIABLE TEMPERATURE CARBON-13 AND MERCURY-199 NMR EXAMINATION OF CYCLOHEXYLMERCURY SYSTEMS

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ABSTRACT

The variable temperature carbon-13 and mercury-199 nmr spectra of some cyclohexylmercurials, $C_6H_{11}HgX$ (X = $-OCOCH_3$, $-CN$, $-C_6H_{11}$ and $-C_6H_5$) have been recorded and assigned by consideration of chemical shifts, ^{199}Hg-^{13}C coupling constants and comparisons with the data for 4-methylcyclohexyl derivatives of established constitution. These studies confirm the *axial* preference for the mercury groups (HgX) examined, although X does influence the conformational equilibrium to a minor extent. For dicyclohexylmercury, three arrangements about mercury are possible and anticipated (*a,a; e,e; a,e*), and at low temperatures signals appropriate for the three species are detected in the ^{13}C spectra. Some ^{199}Hg chemical shifts for related miscellaneous compounds are also presented, and *equatorial* mercury groups resonate 80-100 ppm to higher field of the corresponding *axial* groups.

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INTRODUCTION

Much effort has been devoted to the study of the equatorial-axial equilibria in monosubstituted cyclohexanes and tabulations of A-values (A = $-\Delta G^o$ for the equilibrium) for many groups are available.[1] These A-values are often considered to provide a useful measure of "steric sizes" of the groups, although other factors certainly contribute to these conformational free energies.[2] Almost all substituents examined have a definite *equatorial* preference[1,2] and until relatively recently, metal containing groups were generally assumed to follow this pattern. This was because of their large atomic radii, although longer carbon-metal bonds would be expected to relieve 1,3-(axial, axial) and other unfavorable interactions. It was therefore of importance when Jensen and Gale reported[3] that the benzoxymercuri group, compared with methyl, had a relatively small conformational preference. Subsequently, the same authors determined by direct equilibration (in pyridine at 95° using benzoylperoxide) that the bromomercuri group had no conformational preference (A = 0) within the error limits, but there were indications of a slight *axial* preference.[4] The direct ^1H nmr method was applied by Jensen, Bushweller and Beck to cyclohexylmercuricacetate (100 MHz for a pyridine - TMS - CS_2 solvent) and at -79°C, an A-value of 0.00 ± 0.09 was reported.[2]

That -HgOAc and -HgCl can have definitely negative A-values was demonstrated recently by high field (251 MHz) ^1H and ^{13}C (63.1 MHz) nmr spectroscopy, and was the first demonstration that a monosubstituted cyclohexane could prefer the *axial* form.[5] This result indicated that there may be some rather unusual factors determining the conformational preferences of metal- containing groups, and it seemed that a more detailed study of the cyclohexylmercury system would be illuminating. In particular we were interested in the effects that might be associated with changes in X in $C_6H_{11}HgX$, as the "effective" electropositivity and acceptor properties of mercury would be altered. Some measurements of variable temperature ^{199}Hg spectra (16.1 MHz) have also been conducted for these cyclohexyl derivatives.

RESULTS

Compounds of the type $C_6H_{11}HgX$ where X = $-OCOCH_3$,CN, C_6H_5, and C_6H_{11} have been prepared and variable temperature ^{13}C and ^{199}Hg nmr studies have been conducted. The instability of dicyclohexylmercury and to a lesser degree, phenylcyclohexylmercury have prevented satisfactory elemental analyses, but the ^1H, ^{13}C and ^{199}Hg spectra confirm their structures. More detailed measurements of the ^{13}C spectra have been conducted, and will be reported on first. These spectra were obtained as outlined in the Experimental Part.

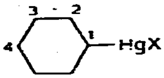
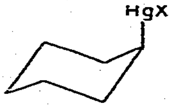
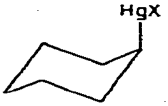
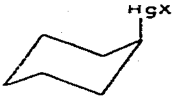
Carbon-13 Spectra:

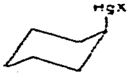
(a) Cyclohexylmercuric acetate:

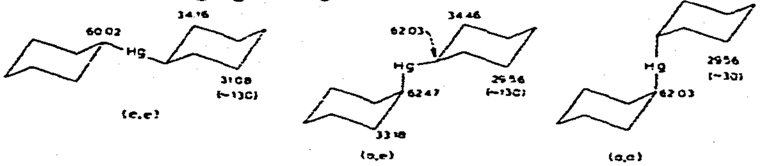
Some preliminary ^{13}C data for this compound have been reported,[5,6] but the complete data will now be discussed in detail, as it nicely illustrates the general features of the variable temperature behaviour of the cyclohexylmercury compounds. The 22.63 MHz spectrum (for CD_2Cl_2-TMS system) exhibits six signals (24.1, 27.0, 29.7, 33.8, 50.3 and 177.3 ppm) as anticipated, with the 24.1 and 177.3 ppm signals being readily assigned to the $\underline{C}H_3$ and $>C=0$ of the acetate moiety. The relatively more intense signals (29.7 and 33.8 ppm) are associated with the $C_{3,5}$ and $C_{2,6}$ pairs, while the signals at 27.0 and 50.3 ppm remain for C_4 and C_1. The latter signal exhibits very strong coupling to ^{199}Hg (I = 1/2; 16.86% natural abundance) (J = 1559 Hz) and must be assigned to C_1, a conclusion also required by the chemical shift. The 27.00 ppm signal (with an unresolvably small coupling to ^{199}Hg) is appropriate for C_4. Distinction between $C_{2,6}$ and $C_{3,5}$ is based upon

(Continued on p. 366)

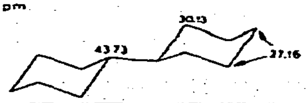
CARBON-13 NMR DATA^{a,b} FOR CYCLOHEXYLMERCURIC SYSTEMS

Compound	Solvent	Temperature(°K)	1	2	3	4	Others	
								
X = OCOCH$_3$	CDCl$_3$	303^d	50.3 (1561.3)	33.6 (58.6)	29.4 (146.5)	26.6 -	24.0; -	177.5 -
	CD$_2$Cl$_2$	303^d	50.3 (1558.8)	33.8 (59.8)	29.7 (148.9)	27.0 -	24.1; -	177.3 -
	CD$_2$Cl$_2$	193^d	51.2 (1491.7)	32.8 (54.9)	29.3 (72.0)	26.4 -	24.5;	177.5
	CD$_2$Cl$_2$	193^d	46.9 (1527.1)	34.5 (63.5)	29.3 (271.0)	27.1 -	24.5; -	177.5 -
	CD$_2$Cl$_2$/py -d$_5$	303^d	49.7 (1595.5)	33.9 (59.8)	29.7 (151.4)	27.0 12.2	24.1; -	177.1 -
	CD$_2$CL$_2$/py -d$_5$	193^d	49.9 (1652.8)	32.9 (56.2)	29.2 (70.8)	26.5 -	24.5; -	177.2 -
	CD$_2$Cl$_2$/py -d$_5$	193^d	45.5 (1718.9)	34.7 (~68)	29.4 (275.9)	27.2 -	24.5; -	177.2 -
— CN	CD$_2$Cl$_2$^{c}	301^e	49.3 (-)	33.2 (46.2)	29.6 (127.6)	26.7	-	
	CD$_2$Cl$_2$^{c}	193^e	50.2 (1387)	32.4	29.4 (48.1)	26.4 -	171.1 -	
	CD$_2$Cl$_2$^{c}	193^e	46.8 (1431)	34.0	29.6 (216.4)	27.0 -	168.1 -	
—CN	CD$_2$Cl$_2$	301^d	49.8 (1389)	33.2 (46.4)	29.8 (127.0)	26.7 -	171.3 -	
—CN	CO$_2$Cl$_2$/py -d$_5$	301^d	48.61 (1601)	33.99 (46.4)	30.10 (133.1)	27.35 -	166.59 -	
	CD$_2$Cl$_2$/py -d$_5$	193^d	47.4 (1592)	33.1 (29.9)	29.3 (58.8)	26.9 -	167.9 -	
	CD$_2$Cl$_2$/py -d$_5$	193^d	44.0 (1624)	34.8 (51.3)	30.0 (220)	27.4 -	166.0 -	
— CN	CD$_2$Cl$_2$/py -d$_5$	301^e	48.9	33.9 (44.3)	30.1 (133.5)	27.3 -	168.3 -	

Compound	Solvent	Temperature(°K)	Carbon Number				
	CD_2Cl_2/py -d_5	193^e	48.1	33.1	29.4	26.9	168.5
	CD_2Cl_2/py -d_5	193^e	44.8	34.7	30.0	27.4	166.3
x = 	CD_2Cl_2	303^e	55.1	33.7	30.1	27.4	181.6;136.9;128.6;127.8 (85s);(81.8)
	CD_2Cl_2/py -d_5	293^e	55.1 (894)	34.1 (19.5)	30.4 (90.3)	27.8	181.9;137.3;129.8; 127.8
	CD_2Cl_2/py -d_5	200^e	54.4	33.2	29.7	27.4	182.5;137.4;128.8; 127.6
	CD_2Cl_2/py -d_5	200^e	53.4	34.6	30.7	27.8	179.9;137.4;128.7; 127.6
	CD_2Cl_2/py -d_5	301^e	55.4 (n.d.)	34.2 (18.5)	30.6 (90.6)	27.9	;137.3;128.8; 127.9 (~85)(~81)
	CD_2Cl_2/py -d_5	193^e	54.7	33.2	29.7 (~50)	27.3	182.2;137.2;128.8; 127.7
	CD_2Cl_2/py -d_5	193^e	53.6	34.6	30.7 (148)	27.8	129.5;137.5;128.7; 127.7
x = 	CD_2Cl_2/py -d_5	301^e	62.52 (~663)	34.0	30.51 (77.7)	28.09	
x = 	CD_2Cl_2/py -d_5	193^e					



C_4 resonances in (e,e) (a,e) and (a,a) at 28.06 (least intense) 27.60 ; 27.05 ppm



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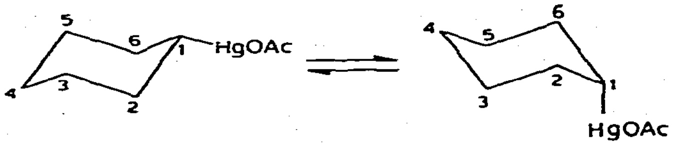
a. Referred to internal TMS (b) Values in parentheses are $^{13}C-^{199}Hg$ couplings (c) Referred to the central peak of CD_2Cl_2. 53.6 at 301°K and 54.5 ppm at 203°K (d) 22.62 MHz (e) 67.89 MHz.

chemical shift considerations and the relative magnitudes of the ^{13}C-^{199}Hg couplings.[6] A coupling of 59.8 Hz (about the 33.8 ppm signal) is expected for a two-bond coupling, while the larger coupling (148.9 Hz) about the 29.7 ppm signal is expected for the average *vicinal* coupling of interconverting (*a,e*) conformers of roughly equal populations. The Karplus-type nature of vicinal ^{199}Hg-^{13}C coupling has been established previously.[6]

The spectral changes with decreasing temperature are fully in accord with these conclusions, and at 193°K, full sets of data for the *axial* and *equatorial* conformers of the cyclohexylmercuric acetate are provided. Assignments



of $C_{3,5}$ in both the (e) and (a) forms are straightforward, being based on the magnitudes (271.0 and 72.0 Hz respectively) of the *vicinal* (^3J) ^{13}C-^{199}Hg couplings. (Previously values of 275 and 72 Hz were reported for $CDCl_3$ solution).[5] Although the chemical shifts of $C_{3,5}$ in both conformers are virtually identical (29.3 ppm) there is clear duplication of the C_1, $C_{2,6}$ and C_4 resonances, with ^{199}Hg coupling to the C_4 signals not being resolved. As noted previously, C_1 in the *axial* form is to lower field (51.2 ppm) than C_1 in the equatorial form (46.9 ppm), while the one-bond ^{199}Hg coupling is greater in the *equatorial* conformer (1527.1 (e) and 1491.7 Hz (a). Based on the relative intensities of the well-separated, duplicated C_1, $C_{2,6}$ and C_4 signals, a value of $K_{193°K}$ $(\frac{axial}{equatorial})$ of 1.93 ± .3 is obtained and compares favorably with that reported (2.3 ± .2) for the acetate in $CDCl_3$ at 183°K.

In view of the relatively strong complexing action of pyridine towards mercury, we anticipated that in a CD_2Cl_2-pyridine-d_5 solvent (*ca* 4:1) significant spectral changes might occur. (K[a/e] for the acetate in CS_2-pyridine does seem slightly smaller than K for $CDCl_3$ solvent).^{5} The ambient, 22.62 MHz ^{13}C spectrum is very similar to that for $CDCl_3$ solvent, except for a minor increase (from 1558.8 to 1595.5 Hz) in the one bond $^{199}Hg-C_1$ coupling, and the resolution of the coupling to C_4 (12.2 Hz). At lower temperatures (193°K) where $a \gtrless e$ interconversion is sufficiently slow, again signal sets for the two conformers are easily identified. The most noteworthy features concern the ^{199}Hg couplings to C_1 (*a* and *e*) and the C_1 chemical shifts. At the lower temperature, both the ^1J's are significantly greater (1652.8(*a*); 1718.8 (*e*)) than the 'averaged' ^1J at ambient temperature (1595.5 Hz). Although the population of the more energetic form (*e*) will be relatively greater at the higher temperature, presumably the chief reason for these enhanced low temperature ^1J's is associated with the more favourable equilibrium constant for pyridine complexation, with a resulting change in nuclear charge at mercury, and a more polar C-Hg bond.

$$\mathrm{RHgOAc} + \mathrm{pyridine} \rightleftharpoons \mathrm{RHgOAc.pyridine}$$

This conclusion seems supported by the generally more shielded nature of the C_1's at the lower temperature, and when compared also with the data obtained for CD_2Cl_2 solvent alone. There appears to be a rather marginal reduction in $K = \frac{[a]}{[e]}$, but the difference may be insignificant considering the intensity ratio differences for the various carbon pairs.

(b) Cyclohexylmercuriccyanide:

Alkylmercuriccyanides RHgCN are rather more covalent than the acetates (RHgOAc) and we considered the less polar Hg-CN system may exhibit a significantly different conformational preference from the acetate. A sample was examined (in CD_2Cl_2; 67.89 MHz) at various temperatures and at 193°K, parameters for the *a* and *e* forms were obtained, with assignments based on the considerations outlined for the acetate. (Fig. 1). At 193°K, distinct resonances (171.1 and 168.1 ppm) for *a* and *e* $\underline{C}N$ are observed, whereas no duplication of $-O\underline{C}O\underline{C}H_3$ resonances occurred. Using intensity data for C_1, $C_{2,6}$, C_4 and $\underline{C}N$, a K value ([a]/[e]) of 1.47 ± .08 is obtained which is measurably less than the value (K = 1.93 ± .3) for the acetate under the same conditions.

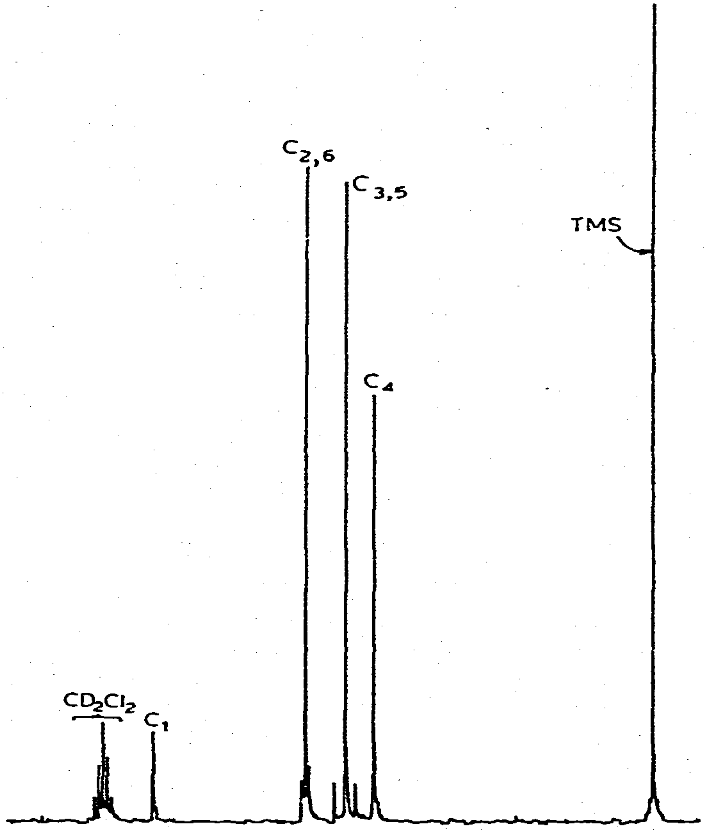


Figure 1(a)

The 67.89 MHz ^{13}C spectrum of cyclohexylmercuric cyanide. (Solvent: CD_2Cl_2: pyridine $-d_5$) obtained at 301°K. The assignments are indicated and the chemical shifts are assembled in Table I. The cyano carbon resonance is not shown.

There is a definite reduction in the values of both one bond (^1J) and *vicinal* (^3J) ^{199}Hg-^{13}C couplings compared with the acetate, as expected for a more covalent mercurial.

The effect of pyridine addition was again explored (CD_2Cl_2:pyridine -d_5 = 4:1) and using the relative intensities of the

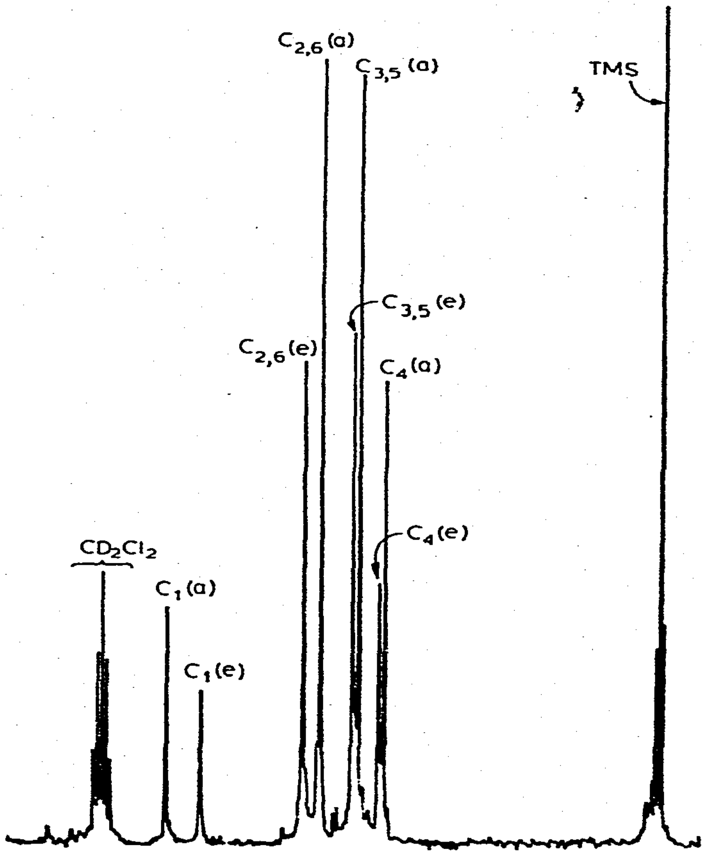


Figure 1(b)

The low temperature (193°K) 67.89 MHz ^{13}C spectrum of cyclohexylmercuric cyanide (Solvent: CD_2Cl_2: pyridine -d_5). The assignments are indicated and note the duplication of carbon signals expected for the slowly interconverting mixture of *axial* and *equatorial* conformers. The cyano carbon signals are not shown, chemical shifts are listed in Table I.

carbon signals, K of 1.63 ± .15 was obtained, indistinguishable, within error of the K-value obtained in the absence of pyridine.

(c) Cyclohexylphenylmercury:

Although the data assembled for both RHgOAc and RHgCN ($R = C_6H_{11}$) in different solvent systems suggested that changes in the X part of RHgX had a rather minor effect on the *a, e* equilibrium, it did seem feasible that changes may result in a bis-organomercurial of the symmetrical (e.g. $(C_6H_{11})_2Hg$) or unsymmetrical (e.g. $C_6H_{11}Hg\ C_6H_5$) types. We therefore prepared phenylcyclohexylmercury, and ^1H and ^{13}C nmr spectra confirmed its unsymmetrical nature. Signals (∿ 300°K) at 55.1 (J=880 Hz), 33.7 (17.1 Hz), 30.10 (90.3 Hz) and 27.4 ppm are assigned to C_1, $C_{2,6}$ $C_{3,5}$ and C_4 of the cyclohexyl residue, while aromatic signals at 181.6 (J not determined), 136.9 (85.0 Hz), 128.6 (81.8 Hz) and 127.8 ppm are assigned to C_{ipso}, C_{ortho}, C_{meta} and C_{para} respectively. On cooling the sample, the anticipated spectral changes occurred, and at 193°K, (67.89 MHz) complete duplication of signals (other than for C_{para}) for the *axial* and *equatorial* conformers occurred. On the basis of chemical shifts and *vic* ^{199}Hg-^{13}C couplings (148 Hz in *equatorial* and ∿50 Hz in *axial*) it is clear the *axial* conformer is favoured, and utilising signal intensities for C_1, C_2, C_3, C_4 (in the cyclohexyl ring) an equilibrium constnat K_{203^oK} (axial/equatorial) of 1.45 ± .1 is obtained.

(d) Dicyclohexylmercury:

This compound was examined (CD_2Cl_2:pyridine d_5; 4:1) in the hope of detecting the three distinct conformational species at the slow interconversion limit *viz. a,a; a,e* and *e,e*. Although it was realised that the general cyclohexyl region in the ^{13}C spectrum may exhibit much signal overlap with indefinite assignments, we felt the downfield $\underline{C}$-Hg region would be sufficiently informative to confirm the presence of the three species.

The 67.89 MHz ^{13}C spectrum (solvent: CD_2Cl_2: pyridine d_5; 4:1) at ambient temperature exhibited the anticipated four signals at 62.52 (J ∿ 663 Hz), 34.00, 30.51 (77.7 Hz) and 28.04 ppm, assignable to C_1, $C_{2,6}$, $C_{3,5}$ and C_4 respectively for the reasons outlined previously. The sample was contamined with some bicyclohexyl, confirmed by matching the extra signals with those (at 43.73, 30.13 and 27.16 ppm) associated with authentic, independently synthesised bicyclohexyl.

The low temperature spectrum (193°K) in the $\underline{C}H_2$ region is complex as expected, but the $>\!\overset{H}{\underline{C}}$-Hg region is well removed (to *ca.* 60 ppm) and permits important deductions. At 213°K, two broad signals are observable, while further cooling (to 193°K) produces a further splitting of the lower field broad signal, so that the slow interconversion situation is characterised by three $>\!\underline{C}$-Hg signals (at 60.02, 62.03 and 62.47) of unequal intensities (Fig. 2). However, as the symmetrical *a*,*a* and *e*,*e* conformers each can exhibit but one $\underline{C}$-Hg signal, the remaining signal must be associated with the unsymmetrical *a*,*e* form, the other $\underline{C}$-Hg signal of which must concide with one of the *a*,*a* or *e*,*e* C_1 resonances. We have established that $\underline{C}$-Hg (axial) resonates at lower field than $\underline{C}$-Hg (equatorial), and the three observed signals (in reality four signals) are assignable as follows: 60.02, *e*,*e*; 62.03 ppm *a*,*a*; 62.03 and 62.47 ppm *e*,*a*. This is in agreement with the prediction that the *a*,*a* form would dominate, and no other analysis of the three $\underline{C}$-Hg signals seems reasonable. Hence the three distinct expected conformers are identifiable at low temperature.

Analysis of the $\underline{C}H_2$ region of the spectrum is more difficult as in principle, twelve resonances should occur in this region. While our assignments must be regarded as somewhat tentative, the spectral features cannot be accommodated even in a general way without the co-existence of the *a*,*a*, *e*,*e* and *a*,*e* forms. The listed assignments are based on the following general considerations (i) when resolved,

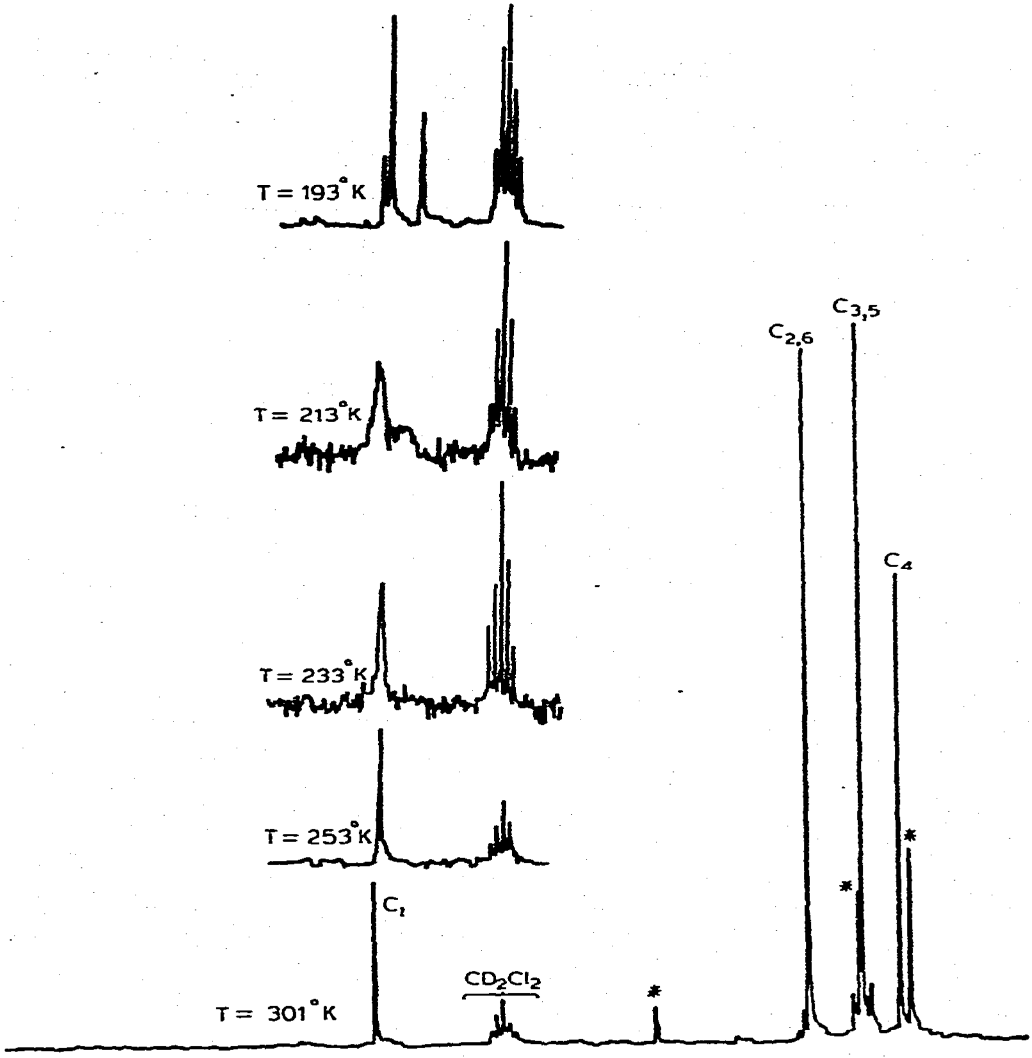
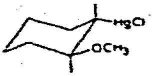
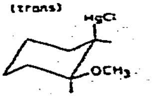


Figure 2

The 67.89 MHz ^{13}C spectra of dicyclohexylmercury obtained at the indicated temperatures. Assignments are indicated, and chemical shifts are listed in Table I. The asterisked signals (*) correspond to dicyclohexyl contaminant. (Solvent: CD_2Cl_2: pyridine -d_5). The temperature dependance of the C_1 signal only is shown.

the $C_{2,6}$, $C_{3,5}$ and C_4 signals are at lower field in the *e* conformer than the *a* form (ii) the dominance of the *a,a* form (iii) the observation of *vic* $^{199}Hg-^{13}C$ couplings of appropriate values in the *a,a* form (∿30 Hz), *e,e* form (130 Hz) and in the *e* component (∿130 Hz) of *a,e* conformer (iv) the general observation that $C_{2,6}$, $C_{3,5}$ and C_4 resonances fall into fairly well defined zones in cyclohexylmercurials being *ca* 34 ± 1 ppm, 30 ± 1 ppm and 27 ± 1 ppm respectively. Three distinct C_4 resonances are resolved, but this region is overlaid by C_4 of the bicyclohexyl contaminant.

Table 2 MERCURY-199 CHEMICAL SHIFTS OF CYCLOHEXYLMERCURIC SYSTEMS

Compound	Solvent	Temperature(°K)	Shift[a]
$C_6H_{11}HgOCOCH_3$	Toluene/pyridine	350	-618
		320	-614
		303	-610
	CH_2Cl_2/pyridine	303	-632
		245	-648(e) -556(a)
		215	-633(e) -556(a)
trans-4-CH_3-$C_6H_{10}HgOCOCH_3$	$CHCl_3$	303	-678(e)
$C_6H_{11}HgCN$	Toluene	350	-222
		320	-217
		303	-216
	CH_2Cl_2/pyridine	303	-209
		230	-249(e); -154(a)
		210	-240(e); -150(a)
$C_6H_{11}HgC_6H_5$	Toluene/pyridine	350	+105
		320	+109
	CH_2Cl_2/pyridine	303	+128
		230	+54(a); +172(a)
		210	+58(e); +172(a)
		200	+61(e); +173(a)
$C_6H_{11})_2Hg$	CH_2Cl_2/pyridine	303	+252
		220^b	+219(e?); +351(a?)
		210^b	+222(e?); +349(a?)
 (trans)	$CHCl_3$	302	-386
 (cis)	$CHCl_3$	302	-365

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a Referenced to diphenylmercury in chloroform. See Experimental Part.

b *a* and *e* assignments not proven.

^{199}Hg Spectra:

Little information is available on ^{199}Hg chemical shifts in organomercurials, and the present state of knowledge has been summarised by Sens *et al*[7] and by Borzo and Maciel.[8] We have obtained the ^{199}Hg spectra of the cyclohexylmercury compounds under FT conditions (16 MHz), at variable temperatures and in different solvents in the hope of providing data of value for understanding the factors regulating such shifts. The full listing of chemical shifts referrred to diphenylmercury in chloroform, is located in Table 2, but the following comments are warranted.

Cyclohexylmercuricacetate:

Under ambient conditions, this compound exhibits a quite broad resonance at -610 ppm (toluene-pyridine solvent), which sharpens considerably on heating (∿350^{o}K). The low temperature spectrum (CD_2Cl_2: pyridine $-d_5$) (215^{o}K) is also broad but two distinct resonances at -556 and -633 ppm are observed, as expected for comparable *a* and *e* populations. An accurate estimate of K was not possible in view of the quite broad resonances. On the assumption that the resonance for *trans*-4-methylcyclohexylmercuric acetate would be a reasonable model for *e*-HgOAc, this compound was examined and exhibited a resonance at -678 ppm ($CHCl_3$), which varied slightly for $CHCl_3$- pyridine mixtures, ranging from -678 ppm (no pyridine) to -654 ppm (∿20% pyridine). This result would indicate that the -633 ppm resonance corresponded to *e*-HgOAc. The effects of incremental pyridine additions to $CHCl_3$ solvent were investigated for cyclohexylmercuric acetate also and increasing pyridine concentration resulted in decreased shielding, as observed for the 4-methyl compound. For example, the shifts ranged from -625 ($CHCl_3$ solvent) to -606 ppm ($CHCl_3$: pyridine::80:20).

Cyclohexylmercuriccyanide:

In contrast to the acetate, relatively narrow spectral lines were observed. In pyridine - CH_2Cl_2 at ambient conditions, a resonance at -209 ppm was observed, which at 210°K was resolved into two signals at -240 and -150 ppm, with the latter most intense, and K (a/e) of ∿1.20 was calculated by the cutting and weighing technique. That the -150 ppm

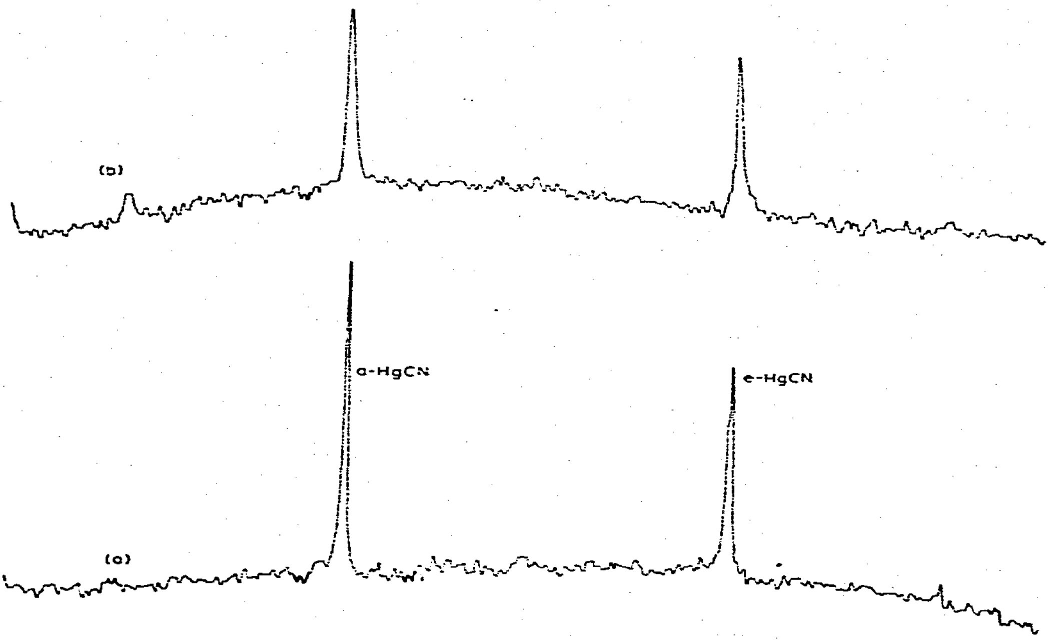


Figure 3(a)

The 16.08 MHz ^{199}Hg spectrum (210°K) of cyclohexylmercuric cyanide (Solvent: CH_2Cl_2: pyridine) showing resonances for the *axial* and *equatorial* HgCN moieties.

Figure 3(b)

The single frequency off-resonance proton decoupled (SFORD) spectra of the system described above in 3(a). Note the preferential broadening of the low-field signal, consistent with its *axial* disposition. This conclusion is consistent with the intensity comparison from Figure 3(a), favouring the *axial* conformer.

resonance was associated with *a*-HgCN was confirmed in the following way. Low temperature single frequency off-resonance decoupled spectra (SFORD) were obtained and it was immediately clear (Fig. 5) that the -150 ppm resonance was substantially broadened, whereas the -240 ppm signal was only very marginally affected, indicating rather minor ^1H couplings. Geminal (^2J) ^{199}Hg-^1H couplings are known[9,10] to be ∿200 Hz in alkylmercuric acetates and cyanides, but *vicinal* (^3J) ^{199}Hg-^1H couplings are as large as ∿600 Hz when the dihedral angle (Θ) is ∿180°, but ∿100 Hz for other values of θ. In fact Kreevoy[11] has demonstrated this definite angular dependence of *vic* ^{199}Hg-^1H coupling for a series of geometrically well-defined systems. Clearly then, the *a*-$^{199}HgCN$ signal should be most broadened (θ=180°), and this conclusion for the cyanide is in harmony with the trend deduced above for the acetate (i.e. *a*-HgX at lower field). Definite location of the ^{13}C couplings in the ^{199}Hg spectra would also be a basis[6] for *a* and *e* assignments, but these are quite difficult to observe under the available conditions.

Phenylcyclohexylmercury:

The single ^{199}Hg resonance (+128 ppm) observed (CH_2Cl_2-pyridine solvent) at ambient temperature (303°K) is resolved into two signals at +58 and +172 ppm at 210°K. While accurate determination of signal intensities was not possible, indications were that the downfield peak corresponded to the more abundant *a* conformer. SFORD spectra, as described for the cyanide associated the lower field signal with the *a*-Hg group. It should be noted that replacement of -OAc with C_6H_5- leads to *ca.* 700 ppm shift to lower field as expected.

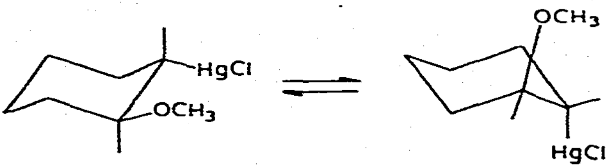
Dicyclohexylmercury:

Although our analysis of the ^{13}C spectrum of this compound indicated quite strongly the co-existence of the three conformers

(*:a,a: e,e; a,e:*) we felt the observation of three distinct ^{199}Hg signals at low temperatures would be absolute confirmation. Unfortunately our careful examination of the system in the 210°-230°K range, identified only two signals at +351 and +220 ppm. The signals were relatively broad, but solubility problems prevented examination at lower temperatures. The substantial movement to low field on introduction of the cyclohexyl group for the phenyl group for example, is consistent with other observations.[7,8]

Trans and *cis*-2-Methoxy Cyclohexylmercuric Chlorides:

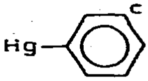
Examination of these compounds at ambient temperatures provided shifts of -386 and -365 ppm respectively. These values are some 250 ppm to lower field of the signals for the acetates, in line with other reports[7] that the change $RHgOCOCH_3 \rightarrow RHgCl$ results in low field shifts of the order of 200 ppm. The ($\delta_{axial} - \delta_{equatorial}$) figure is small when compared with $\Delta\delta$ for the cyclohexylmercuric acetates (78 ppm), but conformer populations in these 2-substituted cyclohexyl systems would need to be taken into account. Considering that the A-value for -HgCl is slightly negative (∿ -0.2 kcal/mole) and the A-value for $-OCH_3$ is +0.60 kcal/mole[2,12] the *trans* compound would exist at ∿300°K with a significant contribution from the *a*-HgCl conformer.



DISCUSSION

The ^{13}C data establish that for a wide range of cyclohexylmercuric compounds, the *axial* conformer is preferred. The

Table 3 CONFORMATIONAL A-VALUES[a] FOR MERCURY CONTAINING GROUPS

Group	Solvent	Temp.(°K)	K(ax/eq)	Measurement	A-Value	
$HgOCOCH_3$[b]	CD_2Cl_2	193	1.84	C_1	-.235	
			1.70	$C_{2,6}$	-.204	-.25±.06
			2.25	C_4	-.312	
$HgOCOCH_3$[b]	CO_2Cl_2/py $-d_5$	193	1.99	C_1	-.265	
			1.53	$C_{2,6}$	-.164	-.24±.08
			2.14	C_4	-.293	
HgCN[c]	CD_2Cl_2	193	1.38	C_1	-.124	
			1.40	$C_{2,6}$	-.129	
			1.50	C_4	-.156	-.14±.02
			1.54	CN	-.166	
HgCN[c]	CD_2Cl_2/py $-d_5$	193	1.58	C_1	-1.76	
			1.64	$C_{2,6}$	-.191	
			1.51	$C_{4,5}$	-.159	-.19±.04
			1.81	C_4	-.229	
	CD_2Cl_2/py $-d_5$	193	1.52	C_1	-.161	
			1.38	$C_{2,6}$	-.124	-.14±.03
			1.35	$C_{3,5}$	-.115	
			1.54	C_4	-.166	

For $C_6H_{11})_2Hg$ (CD_2Cl_2:py $-d_5$) C_1 intensities indicate (a,a) is ∿40-45%; with (e,e) and (a,e) each about 25-30%. See Fig. 2

a. $A = -\Delta F° = RT\ln K$ b. 22.62 MHz. c. 67.89 MHz.

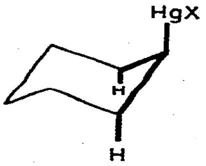
K-values are small ($1 < K \leq 2$) providing negative A-values (Table 3) but nevertheless real in favour of the *axial* form, and these compounds represent the first cases in which the *axial* conformer is the preferred one in a monosubstituted cyclohexane. In energy terms, the differences are small, but some factor is presumably significantly favouring the *a* form. Changes in X in $C_6H_{11}HgX$ have a very minor influence on the K-values but this result is not unreasonable on steric grounds, as X is quite remote from the cyclohexyl ring. Addition of the strongly co-ordinating solvent, pyridine, has very minor effects on the A-values.

It did seem possible that changes in the charge distribution in the C-Hg-X system would be important but this does not appear to be the case, despite wide fluctuation in the ^{199}Hg shifts as a function of X. The very small differences between the $C_{3,5}$ resonances in *a*,*e* pairs suggest that non-bonded or proximity effects are not important either, and this is associated with the large C-Hg bond length ($\sim$ 2.07Å).

A useful approach to conformational analysis was recently discussed by Eilers and Liberles,[13] and consideration is given to the energy components T (kinetic energy of electrons), V_{ne} (attraction of electrons for nuclei) V_{ee} (interelectronic term) and V_{nn} (internuclear repulsion), so that for a conformational change,

$$\Delta E = \Delta T + \Delta V_{ne} + \Delta V_{ee} + \Delta V_{nn}$$

When $\Delta V_{ee} + \Delta V_{nn} > \Delta V_{ne}$, the classical "steric" approach qualitatively succeeds, but the reverse ($|\Delta V_{ne}| > \Delta V_{ee} + \Delta V_{nn}$) situation describes an "attractive steric effect". It therefore seems this latter circumstance describes the *a*-HgX case, and the electron-nuclear attraction is promoted in the *a* conformer more than in the *e*.



This favourable interaction may depend on a proper (anti) alignment of the neighbouring C-H bonds as present in the *a* conformer, and certain similarities to n-σ^* interactions may exist. These considerations suggest that other electropositive elements with long bonds to carbon may behave similarly and other systems of this sort are being studied.

The ^{199}Hg chemical shifts have a range of *ca.* 1000 ppm from -633 ppm in *e*-cyclohexylmercuric acetate to +351 ppm in (low temperature) dicyclohexylmercury. In the low temperature spectra *a* and *e* ^{199}Hg signals are observed for X = CN, OAc and C_6H_5 and Δδ are of the order of 80-100 ppm. It seems generally true that *e* mercury groups resonate at higher field, a result apparently true also for ^{207}Pb and ^{119}Sn resonances in cyclohexyl systems.[14] As pointed out previously, some of the ^{199}Hg signals (e.g. in the acetate) are broad ($W_{1/2}$ ∿ 70 Hz) (broader at lower temperatures) and the reasons are not fully understood. Relaxation measurements indicate operation of efficient processes $(T_1 = 0.81\ \text{sec.})_{302^oK}$ ($CHCl_3$, degassed, vac. sealed) at least for methylmercuriccyanide.[15] It is possible that molecular aggregation and deaggregation, perhaps involving acetate bridges and other processes may be implicated, but of course these suggestions cannot apply for dicyclohexylmercury. A major disappointment was our inability to observe three ^{199}Hg signals for the *a,a; e,e* and *a,e* conformers of dicyclohexylmercury, the co-existence of which was indicated by the ^{13}C spectrum.

Attempts to understand the chemical shifts observed must be very preliminary and it is known that solvent and concentration effects are significant.[7,8] The shielding sequence $C_6H_{11}HgOAc > C_6H_{11}HgCN > C_6H_{11}HgC_6H_5 > (C_6H_{11})_2Hg$ is in line with the general observation that "dissociated" mercury derivatives are the most shielded, a trend not unexpected for nuclei for which paramagnetic contributions to the shielding constant are dominant.[7,8]

Our study of solvent effects was very limited, but we did observe that incremental addition of pyridine to both cyclohexylmercuric acetate and the *trans*-4-methylcyclohexyl compound, (in $CHCl_3$) resulted in significant moves to *lower* field. This is opposite to the general pattern observed for dimethylmercury in a range of solvents,[7] and such changes might have been anticipated to result in increased shielding. However, R_2Hg and RHgOAc are difficult to compare, as in the latter case, dissociation, strong complexation, bonding changes etc. will be more severe and several species presumably co-exist. From the results of Maciel and Borzo,[8] CH_3HgCl is *less* shielded in pyridine than in the poorer co-ordinating solvent THF, by some 70 ppm. More detailed studies of these substantial solvent effects are required.

EXPERIMENTAL

Compounds

Cyclohexylmercuric cyanide was prepared by stirring cyclohexylmercuric bromide with silver cyanide in methanol for 2 hours. Separation of the insoluble silver bromide and solvent removal left white crystals (89%) which recrystallized from chloroform/hexane, m.p. 139-140°C, ν_{max} (KBr) 2160. (Found: C, 27.14; H, 3.61. $C_7H_{11}HgN$ requires C, 27.14; H, 3.58). Cyclohexylmercuric acetate was prepared in a similar manner from cyclohexylmercuric bromide and silver acetate, and provided appropriate ^1H and ^{13}C spectra. Cyclohexylphenylmercury and dicyclohexylmercury were prepared by a standard Grignard procedure, using cyclohexylmagnesium bromide with phenylmercuric chloride and cyclohexylmercuric bromide respectively. The instability of dicyclohexylmercury and to a lesser degree cyclohexylphenylmercury, have prevented satisfactory elemental analyses being obtained. As reported, dicyclohexylmercury decomposed rapidly at room temperature, but could be stored for long periods at -40°C with the exclusion of light and oxygen. NMR comparison with authentic bicyclohexyl confirmed this to be the decomposition product.

^{13}C Spectra

The ^{13}C spectra were obtained at either 67.89 MHz on a Bruker HX-270 or 22.63 MHz on a Bruker HX-90 nmr spectrometer, both using the Bruker Variable Temperature Accessory and the PFT technique. Chemical shifts are referred to internal TMS and are accurate to ±0.1 ppm. J values are considered accurate to ±0.5 Hz on small couplings and ±1 Hz on the larger one bond couplings. Spectra were obtained for

$CDCl_3$, CD_2Cl_2 on CD_2Cl_2/pyridine -d_5 (4:1) solutions in 10 mm tubes. Samples for variable temperature examination were saturated solutions at acetone/dry ice bath temperature (-78°C). For example, variable temperature spectra in CD_2Cl_2/pyridine -d_5 (4:1) solution for cyclohexylmercuric cyanide were obtained for -0.5M solution, cyclohexylmercuric acetate -0.8M, cyclohexylphenylmercury -0.45M and dicyclohexylmercury -0.5M.

^{199}Hg Spectra

The ^{199}Hg spectra were obtained at 16.08 MHz, on a Bruker HX-90 modified for multi-nuclear operation, using the PFT technique. Modifications consisted of the addition of the Bruker Multi-nuclear Accessory combined with a Schomandl frequency synthesizer type ND 100M (300 Hz-100 MHz). An external D_2O lock was used and all spectra were proton noise decoupled or single frequency off resonance decoupled. Spectra were recorded using a 90° pulse (*ca.* 18 μsec), 5000 Hz sweep width, 2.4 or 8K data points giving pulse repeat times of *ca* 2, 4 or 8 secs respectively. Chemical shifts are referred, for convenience, to external diphenylmercury in $CHCl_3$. Samples were prepared as for ^{13}C nmr examination using spectroscopic grade $CHCl_3$, CH_2Cl_2, pyridine and toluene. Concentration effects on shifts, although noticable, have been ignored as these are not significant compared with the large range of shifts between compounds.

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