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A RE-EXAMINATION OF THE CONFORMATIONAL EQUILIBRIA IN CYCLOHEXYLMERCURIC DERIVATIVES

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The equatorial-axial equilibria in monosubstituted cyclohexanes have been investigated extensively during the past fifteen years and _A_ values (_ΔG°_'s in kcal/mol for the equatorial-to-axial conformational change) for numerous groups have been tabulated.[1] The lowest _A_ values (_ca_ 0.0) reported are for the bromomercuri[2] and the acetoxymercuri groups.[3] A re-investigation of the conformational equilibria of cyclohexylmercuric compounds by high-field (59 Kgauss) ^{1}H and ^{13}C nmr has now revealed that such groups can have distinctly negative _A_ values (Table 1); i.e., these compounds exist preferentially in the axial forms.

The assignments of the axial and equatorial peaks (Table 2) were based on the following: (a) H-1 gives a signal at a higher field when it is axial than when it is equatorial[1], (b) when H-1 is axial a rough 1:2:1 triplet ($J \simeq 12$ Hz) is observed, whereas when H-1 is equatorial, it appears as an unresolved band with a width at half-height of _ca_ 10 Hz,[4] (c) the vicinal $^{199}Hg-^{13}C$ coupling constant is much larger for the equatorial than for the axial conformer (275 _versus_ 70 Hz), in accordance with the Karplus relationship[4] and with experimental data on model compounds.[5] Because of solubility problems, ^{13}C spectra at low temperatures were not obtained for carbon disulfide-pyridine solutions. The _A_ value of the acetoxymercuri group appears to be slightly less negative in the carbon disulfide-pyridine solvent than it is in deuterated chloroform, presumably because pyridine can complex[6] better with an equatorial mercury atom than with an axial one.

Table 1. Conformational A values for Mercury Containing Groups at -90°C

Group	Solvent	K (ax./eq.)	A value
HgOAc	$CDCl_3$	2.3 ± 0.2[a]	-0.30 ± 0.03
HgOAc	$CDCl_3$	2.3 ± 0.3[b]	-0.30 ± 0.05
HgOAc	CS_2-Pyr.[c]	1.6 ± 0.3[b]	-0.17 ± 0.05
HgCl	$CDCl_3$	2.0 ± 0.3[b]	-0.25 ± 0.05

[a] From ^{13}C peak height measurements made on C-1, C-2 (and C-6), and C-4 at 63.1 MHz by the Fourier transform technique with protons noise decoupled

[b] From ^{1}H peak-area measurements on H-1 made at 251 MHz by a digitally controlled frequency-sweep technique. [c] CS_2-Pyridine, 70:30.

Table 2. Chemical Shifts of C-1 and H-1 in Cyclohexylmercuric Compounds at -90°C

Compound	Solvent	Chemical Shifts[a] Axial HgX ^{13}C	 Axial HgX ^{1}H	 Equatorial HgX ^{13}C	 Equatorial HgX ^{1}H
$C_6H_{11}HgOAc$[b]	$CDCl_3$	52.28	3.40	47.80	2.73
$C_6H_{11}HgOAc$	CS_2-Pyr.[c]		3.01		2.34
$C_6H_{11}HgOAc$	CS_2-Pyr.[d]		2.98		2.34
$C_6H_{11}HgCl$[e]	$CDCl_3$		3.28		2.62

[a] In ppm downfield from internal tetramethylsilane. [b] C-1 average chemical shift at +40°C is 50.8; H-1 average chemical shift at 0°C is 3.10. [c] CS_2-Pyridine, 70:30. [d] For CS_2-pyridine-tetramethylsilane, 70:20:10, from reference 3. [e] H-1 average chemical shift at 0°C is 2.99.

Previous ^{1}H nmr work by Jensen et al[3] at the comparatively low frequency of 100 MHz was undoubtedly complicated by the fact that H-1 of the equatorial conformer is not well separated from the ring methylene protons at low temperatures. The presence of ^{199}Hg satellite bands create additional difficulties. Thus, the A value (0.00 ± 0.09) given by these workers for the HgOAc group probably had a too-low error limit.

The reasons given previously for the low A values of mercury groups,[3] namely the presence of a long carbon-mercury bond and the polarizable nature of the mercury atom are also consistent with small negative A values. Other substituents which might have negative A values include the $Tl(OAc)_2$ group, and an investigation of this system is planned.

Vicinal $^{13}C-^{199}Hg$ coupling constants in alkylmercuric chlorides[7] ($R-CH_2-CH_2HgCl$) are as follows: R = Me, 190; R = Et, 183; R = i-Pr, 212; R = t-Bu, 227 Hz, and this indicates the presence of substantial proportions of gauche forms (ca 40%) in propyl- and butylmercuric chloride, since J_{gauche} and J_{trans} should have values similar to those found in cyclohexylmercuric chloride. The population of gauche forms in the aliphatic compounds is perhaps not as great as might have been anticipated from the axial preference of the chloromercuri group on cyclohexane, but there are substantial differences in the two systems.[8]

Although the acetoxy- and chloromercuri groups are the only substituents presently known to have negative A values, axial preferences for substituents on six-membered rings (other than for monosubstituted cyclohexane derivatives) are well documented. In many cases, dipole-dipole interactions are responsible for the axial preferences,[9] but in some compounds at least, attractive interactions of the axial substituent and the ring methylene groups at positions 3 and 5 appear to be dominant.[10]

One interesting aspect of the cmr spectrum of cyclohexylmercuric acetate is the lack of chemical shift difference for C-3 (and C-5) in the axial and equatorial conformers. Axial 1-substituents, such as methyl, cause an upfield shift of about 5 ppm in C-3 and C-5 of a cyclohexane ring (the γ effect) and this has been ascribed to steric compression.[11] The lack of a γ effect from the acetoxymercuri group is of course consistent with the small negative A value of that group, which indicates that there is no steric compression present in the axial conformer.

We wish to point out that cmr spectroscopy provides an excellent means of obtaining equilibrium constants in cyclohexylmercuric acetate in $CDCl_3$ because all the ring carbons are well resolved (except that C-3 and C-5 for the axial and equatorial forms are coincident) and the ^{199}Hg satellites do not cause any interference, at least at the frequency of 63.1 MHz used in the present work. Spin-lattice relaxation times are expected to be relatively short at low temperatures and all ring carbons should give full nuclear Overhauser effects, so that intensity perturbations should be very small in the present system.[12]

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