SHORT PAPER

J. Chem. Research (S),
2002, 25–27

The γ-*cis* effect in the mercury-199 NMR spectroscopy of substituted vinylmercury halides[†]

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The γ-*cis* effect is identified for the first time in the ^{199}Hg NMR data presented here, being proposed as a new criterion for the distinction between *E* and *Z* isomers of substituted vinylmercury compounds.

Keywords: mercury-199 NMR, γ-cis effect

Despite their high toxicity, organomercury compounds[1] have earned their place among the reliable and versatile organometallic intermediates in organic synthesis because of their remarkable stability and tolerance to functionality. Nowadays, when organomercurials are to be employed, the method of choice[1a] is to use organomercury halides because they are fairly high-melting crystalline solids and, thus, the safest form for manipulation. Among them, the most versatile organomercury synthons are the vinylmercury halides, in which case, however, it is of paramount importance to have reliable methods to distinguish between their *E* and *Z* isomers as, usually, only one particular isomer is sought to be used as a synthetic intermediate.

In previous works,[2] we have demonstrated that the shielding due to the γ-*cis* effect can be employed to gauge the stereochemistry of heteroatom substituted olefins and for the straightforward calculation of the *E*/*Z* relationships of such compounds, prepared by various methods. We have also pointed out[2] that the γ-*cis* shielding is observable in the NMR spectra of ^{17}O, as well as in those of spin-$^1/_2$ nuclides of various elements.

On the other hand, previous investigations[3] on dialkylmercury compounds have shown that in ^{199}Hg NMR spectroscopy the γ-*gauche* effect is deshielding (an anomalous behaviour shared only[4] by ^{1}H, among all spin-$^1/_2$ nuclides). In addition, the existence of a deshielding γ-*cis* effect for substituted halomercury olefins is indicated (although the magnitude of the chemical-shift difference (Δδ) is rather small for an element of the 6th periodic row) by the scarce data reported in the literature[3] (Table 1, compounds **1a,b**) concerning the ^{199}Hg chemical shifts of one pair of *E*/*Z* isomers of a substituted vinylmercury chloride.

Our recent interest in organomercury chemistry led us to start a new study, focused on the stereochemical analysis of substituted vinylmercury halides, which we now report We have decided to prepare substituted vinylmercury bromides to be used in the present investigation, in the hopes that the bromo substituent would soften (in Pearson's sense[5]) the mercury and thus lead to larger Δd's, in accordance with our previous reports[2] on other nuclides. Furthermore, we have selected monosubstituted vinylmercury bromides as model compounds because, as they are disubstituted olefins, we could use the olefinic $^3J_{H,H}$ to distinguish *E* from *Z*, in order to be able to test our hypotheses.

Our results (Table 1, compounds **4a,b** and **5a,b**) show that, in fact, the substituted bromomercury olefins present the anticipated much greater Δδ's, confirming unambiguously the existence of the postulated deshielding γ-*cis* effect. Hence, the configuration of substituted halomercury olefins can be determined by the analysis of their ^{199}Hg NMR spectra, a method that is not restricted to disubstituted olefins.

Table 1 ^{199}Hg NMR experimental data for vinylmercury halides

Compd	Formula	Isomer	%[a]	δ^{199}Hg[b]	δ^{199}Hg[c]	Δδ[d]	$^3J_{H,H}$/Hz
1a	ClHC=CHHgCl	*Z*	–	–1168[e]	–1141[f]	19	–
1b	ClHC=CHHgCl	*E*	–	–1187[e]	–1160[f]	–	–
2	H_2C=CHHgCl	–	–	–1172[g]	–1145	–	11.7 (Z) 19.3 (E)
3	H_2C=CHHgBr	–	–	–	–1237	–	11.6 (Z) 19.1 (E)
4a	PhHC=CHHgBr	*Z*	95	–	–1018	182	10.9
4b	PhHC=CHHgBr	*E*	05	–	–1200	–	17.9
5a	MeHC=CHHgBr	*Z*	52	–	–1056	75	11.1
5b	MeHC=CHHgBr	*E*	48	–	–1131	–	19.2
5c	H_2C=CMeHgBr	–	–	–	–1186	–	–

[a] Percent regioisomer ratio (by ^{199}Hg NMR);
[c] This work, in $(CD_3)_2S{=}O$, Ph_2Hg = –750 ppm;
[e] From ref 3a, Me_2Hg = 0 ppm;
[g] This work, in $(CD_3)_2C{=}O$, Ph_2Hg = –750 ppm.

[b] In $(CH_3)_2C{=}O$;
[d] $\Delta\delta = \delta_{Hg}(Z) - \delta_{Hg}(E)$;
[f] Estimated values.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Moreover, since dipolar relaxation is not important[3] for ^{199}Hg, the ratio of the integrated signals of a straightforward proton-broadband-decoupled ^{199}Hg NMR spectrum can be used for the determination of the composition of isomer mixtures: in fact, the ratio values so determined are in the same range (considering experimental errors) than those obtained from the corresponding inverse-gated-decoupling (INVGATE) experiment, run after adding chromium(III) acetylacetonate.[6]

It should be pointed out that, as the results obtained suffice to demonstrate our initial hypotheses, we decided to limit the series of compounds investigated to just two pairs of *E*/*Z* isomers of substituted vinylmercury bromides (Table 1, compounds **4a,b** and **5a,b**) to avoid unnecessary manipulation of organomercury compounds. Furthermore, in view of a recently reported[7a] fatal accident involving dimethylmercury,[7b] we decided to use the far less volatile diphenylmercury[3a] (1 mol/dm^3 in $CDCl_3$) as the reference compound.

The data regarding the two other bromomercury olefins (**3** and **5c**, a by-product in the preparation of **5a,b**) were included for the sake of completeness, for, as far as we know, data on ^{199}Hg NMR of vinylmercury *bromides* is reported here for the first time. Moreover, since Guillemin *et al.*[1c] reported vinylmercury chloride (**2**) in perdeuteroacetone has $\delta(^{199}\text{Hg}) = -1171$, while Wrackmeyer and Contreras[3a] quote $\delta(^{199}\text{Hg}) = -1213.5$ in acetone, we felt we should perform a third measurement (using perdeuteroacetone) to find out which value was the correct one and confirmed the former value (Table 1); on the other hand we measured for **2**, in perdeuterodimethyl sulfoxide, the same value as that quoted (–1144.8 ppm, in dimethyl sulfoxide, from a different source) by Wrackmeyer and Contreras.[3a] We believe that, although ^{199}Hg chemical shifts are known to be sensitive to concentration, this ought not to be a problem in the present case, because the solubilities of the vinylmercury halides either in acetone or in dimethyl sulfoxide are so low that the use of saturated solutions is mandatory. Comparison of the chemical shifts for **2** in deuterated acetone and dimethyl sulfoxide enables one to estimate the corresponding δ's for **1a,b** in the latter solvent (Table 1), and by comparing the results for **2** and **3** in perdeuterodimethyl sulfoxide, one can observe the expected[3] shielding on changing from the chloro- to the bromo-substituent, due to the heavy-atom effect.

In conclusion, we would like to provide a possible explanation to the question of why is the γ-*cis* effect deshielding for ^{1}H and ^{199}Hg.

The Δδ induced by a γ-substituent, while originally thought to be due to a "steric compression",[8] can be better understood if one regards it as an electric field effect,[9] resulting from the repulsion exerted by the electron cloud of the substituent-group over the cloud at the observed nuclide, distorting the latter away from that substituent. This interpretation is the one that best accommodates the experimental finding[2b] that softer nuclides experience a more pronounced γ-*cis* effect.

According to the Ramsey equation, the shielding constant (σ) for any observed nucleus can be expressed as the sum of two components:

$$\sigma = \sigma^d + \sigma^p$$

Local diamagnetic shielding (σ^d) arises from the electrons around the nucleus and, in the case of spherically symmetric electron distribution (free atoms), it is the only component of shielding (*i.e.*, $\sigma^p = 0$). Likewise, it is of decisive importance for hydrogen, which valence-shell is 1s (*i.e.*, $\sigma^p = 0$). All other nuclei have a considerable shielding contribution from the paramagnetic component (σ^p), which is related to their non-spherical distributions of electrons in the valence-shell, due to the use of p, d or f orbitals. Except for hydrogen, σ^d can be seen as related to the effects due to the core electron distribution and, σ^p, to the effects due to the valence-shell electrons; as the magnitude of the latter usually is, at least, 10 times that of the former, σ^p dominates the observable variations of σ and, therefore, the observed variations of δ, which is its experimentally measurable counterpart.

Relativistic *ab-initio* calculations[10] have shown that bonding in organomercury halides is poorly represented by the usual assumption of a sp hybridised mercury atom (because the vacant p orbitals are too high-energy to mix effectively with the filled 6s orbital, due to relativistic contraction[11]), being more realistically described by a 3-atom-3-orbital interaction (among carbon, mercury and halogen) resulting in a linear 3-centre-4-electron bond, having filled both bonding and non-bonding orbitals, and the latter having a node at the mercury atom. In short, this model essentially implies that one can assume that only the 6s orbital of the mercury is involved in the linkage. Hence, for mercury, σ^d might be unusually important to the effects due to the valence-shell electrons, dominating the observable variations of δ. As perturbations on σ^d are usually deshielding, so ought to be the γ-*cis* effect for nuclides having dominant σ^d as is the case of ^{1}H and, per our hypothesis, also ^{199}Hg.

Experimental

The ^{1}H NMR spectra were recorded at 300 MHz in a Varian UNITYINOVA 300, using instrument settings akin to those previously[12] reported, in 5 mm tubes containing a saturated solution of the sample in perdeuterodimethyl sulfoxide or perdeuteroacetone.

The ^{199}Hg NMR spectra were acquired under proton broadband decoupling at 35.7 MHz in a Bruker ARX-200 or AC-200-F with multinuclear probehead, in 5 mm tubes containing the same solution used in for ^{1}H NMR and a sealed 1 mm tube containing, as the standard, 0.5 cm^3 of diphenylmercury (1 mol/dm^3 in $CDCl_3$) as the reference compound, in a co-axial arrangement. Pulse widths were 4.0 μs (45°), the repetition rates were 2 s and the digital resolution was, at least, 2.5 Hz per data point. The reproducibility of the ^{199}Hg chemical shifts, at room temperature (20°C), was 1.0 ppm. For the INVGATE experiments, ca. 10 mg of chromium(III) acetylacetonate[6] were added to the sample solution and the decoupler was gated on just during the acquisition time (set to 0.5 s in all ^{199}Hg NMR experiments). Raw data were zero-filled and Fourier transformed under matched-filter conditions.

The *E*/*Z* mixtures of vinylmercury bromides were prepared according to literature[1] procedures, and were satisfactorily analysed by ^{1}H NMR spectroscopy and elemental analysis.

This work is dedicated to Mr. Luiz Carlos Roque (retired since February 17, 1998).

Thanks are due to FAPESP (Projects 98/10802-5 and 98/10803-1), CNPq and UNIP for financial support. We also gratefully acknowledge Dr. A. G. Ferreira and Mr. A. Magalhães (UFSCar) for the acquisition of the ^{199}Hg NMR data on the ARX-200.

Received 14 May 2001; accepted 16 August 2001
Paper 01/874

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