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σ,π-CONJUGATION AND ^{199}Hg SHIELDING CONSTANTS IN BENZYL DERIVATIVES OF MERCURY

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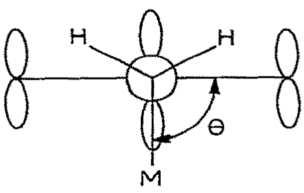
Summary

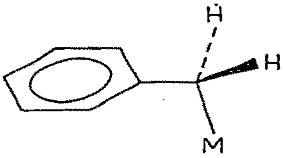
The ^{199}Hg chemical shifts in a number of benzylmercuric chlorides containing methyl substituents in various positions of the benzene nucleus are studied by the heteronuclear ^{1}H-{^{199}Hg} double resonance technique. *Meta*- and *para*-methyl substituents are shown to have no pronounced action on the shielding whereas *ortho*-methyl groups each shift the signal by 30 ppm downfield. The observed effect is due to an increase in the population of conformers with the C—Hg bond lying out of the aromatic cycle plane. The departure from planarity favours conjugation between the electrons of the C—Hg bond and the π-electronic system of the ring. The $J(^1H—^{199}Hg)$ and $J(^{13}C—^{199}Hg)$ coupling constant values obtained in this work confirm the latter conclusion.

Hyperconjugative interaction of the σ-electrons of the easily polarizable metal—carbon bonds with adjacent unsaturated groups (σ,π-conjugation), which was first put forward by Nesmeyanov in the late forties [1], has been postulated to be responsible for the peculiarities in the chemical reactivity, physical properties and structure of α-metallated carbonyl compounds [2], allyl [3], cyclopentadienyl [4], indenyl [5] and indanyl [5] metal derivatives. Reutov, Bundel' et al. have reported the reaction center transfer to the aromatic ring occurring with mercury—carbon bond cleavage in benzylmercury derivatives under the action of electrophiles. Almost exclusive deuterium incorporation to the *ortho*-position of the benzene ring had taken place when benzylmercuric chloride was treated with DCl in dioxane [6]. The dual reactivity of α-metallated carbonyl compounds and their metallotropic rearrangements were studied extensively [7].

Hyperconjugation of the metal—carbon bond with adjacent unsaturated bond systems in metal allyl [3] and benzyl [8,9] derivatives favours conformations in which the metal—carbon bond lies in the plane parallel to π-orbitals of double bonds (Ia, b). According to the electron diffraction and X-ray data, such conformations are preferable in both gas and crystal phases.



(Ia)



(Ib)

Bach et al. [10] have reported the value of 87° for the dihedral angle in $C_6H_5CH_2HgSC(C_6H_5)_3$ which is near to the theoretical preferred value of 90°. The angle between the metal—carbon bond and the cyclopentadienyl ring plane in cyclopentadienyl derivatives of Si, Ge and Sn in the gas phase has been found to be larger than half the tetrahedral angle by 8 to 14° [11].

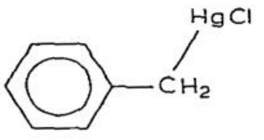
Partial delocalization of an electron from the metal—carbon bond over the π-bond system of the unsaturated moiety causes essential destabilization of the highest filled π-orbital and lowering of the ionization potential, as follows from the VIS-spectra of the charge transfer complexes [12], photoelectron spectroscopy [8] and mass spectrometry data [5,13]. The MO LCAO SCF calculations have been carried out using the CNDO/2 and extended Hückel approaches [14] to show that hyperconjugation invariably stabilizes the conformations described above with $\theta = 90°$, increasing the positive charge on the metal atoms involved in the adjacent unsaturated bond system.

The NMR parameters are highly sensitive to electron density distribution and molecular geometry. The ^{13}C chemical shift deviations and values of the metal—carbon coupling constants in α-metallated ketones [2] and some indenyl compounds [22] were attributed to the σ,π-conjugation. Shielding constants of metal magnetic isotopes should be especially sensitive towards the hyperconjugation as was shown for the ^{119}Sn nuclei [15]. The study of shielding constants of the ^{199}Hg nuclei in mercury allyl, benzyl and related compounds as well as in α-metallated carbonyl compounds, thus appears to be of considerable interest. A number of factors influence mercury chemical shifts, such as the nature of the radicals and the substituents X in R_2Hg and RHgX, and intermolecular interactions of organomercury compounds with solvents [16—20].

As the ^{199}Hg chemical shifts vary within the range of 3500 ppm, even the slightest changes in the electronic environment of this nucleus cause significant changes in the positions of signals in the spectrum. In the present work, we report the results of our study of methyl substituted benzylmercuric chlorides with ^{13}C NMR and INDOR ^1H-$\{^{199}Hg\}$ techniques.

Experimental

The synthetic routes to the compounds studied (I—V) have been reported elsewhere [21]. All the samples were solutions in purified chloroform (0.5 *M*). The proton and INDOR spectra were recorded on a XL-100-15 instrument. The ^{13}C NMR spectra were obtained with a CFT-20 spectrometer. The proton and carbon chemical shifts were measured from the chloroform signal and scaled with respect to TMS. The ^{199}Hg chemical shifts were measured using dimethylmercury as external reference.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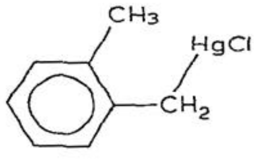
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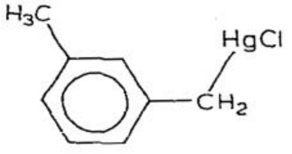
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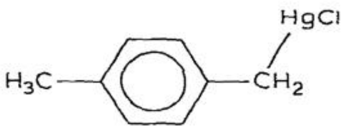
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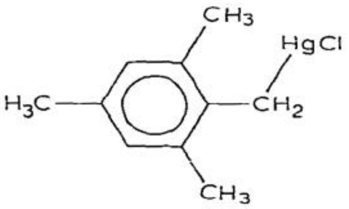

(V)

Results and discussion

Comparison of the ^{199}Hg spectra of compounds I—V (Fig. 1) reveals that the methyl substituents in the *meta* and *para* positions of the aromatic ring do not cause significant changes in the shielding of the mercury nuclei compared with benzylmercuric chloride. However, the *ortho*-methyl substituent having a similar electronic effect to the *para*-methyl one shifts the ^{199}Hg signal downfield by 30 ppm. The two *ortho*-methyl substituents produce an even stronger deshielding and the effect is nearly additive. Successive increase in the population of the nonplanar rotamer (Ia) which leads to increase of the mean (effective) θ angle provides the most reasonable explanation for these observations. Actually, any neutral substituent that favours displacement of the mercury atom from the aromatic ring plane should facilitate σ,π-conjugation thus increasing the positive charge on the mercury atom and deshielding the ^{199}Hg nuclei. The $^{5}J(^{13}C—^{199}Hg)$

TABLE 1

PROTON CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS $J(^{1}H—^{199}Hg)$ (Hz) FOR ORGANOMERCURIALS

Compound	CH_2 [a]	CH_3 [a]	$^{2}J(^{199}Hg—CH_2)$	$J(^{199}Hg—CH_3)$	$J(^{199}Hg—CH_3)$ [b]
I	3.28		259		
II	3.15	2.36	263	28	26
III	3.24	2.34	259	15	14
IV	3.25	2.33	254	43	38
V	3.11	2.38 [c]	263	30 [c]	
		2.34 [d]		51 [d]	

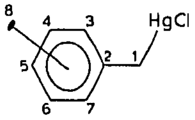
[a] Referenced to TMS using convertion $CHCl_3$ is 7.28 ppm from TMS. [b] From ref. 23. [c] o-CH_3. [d] p-CH_3.

TABLE 2

^{13}C CHEMICAL SHIFTS [a] (ppm) AND COUPLING CONSTANTS [b] $J(^{13}C—^{199}Hg)$ (Hz) FOR ORGANOMERCURIALS

Compound	C-1 [c]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
I	36.6 (1424.2)	139.2 (156.8)	128.6 (107.5)	128.7 (51.9)	125.6 (62.7)	128.7 (51.9)	128.6 (107.5)		
II	34.9 (1386.0)	137.7 (164.0)	134.9 (93.4)	130.3 (59.0)	126.1 (66.4)	126.4 (54.8)	129.1 (107.7)	20.3 (21.4)	
III	36.6 (1429.6)	139.0 (156.6)	129.4 (107.6)	138.3 (51.9)	126.3 (62.2)	128.6 (51.5)	125.6 (108.1)	21.3 (154.2)	
IV	36.3 (1418.4)	135.9 (156.9)	128.5 (108.6)	129.5 (51.4)	135.6 (65.4)	129.5 (51.4)	128.5 (108.6)	20.9 (23.8)	
V [d]	31.5 (1331.8)	132.8 (?)	134.8 (93.8)	128.9 (59.0)	135.2 (74.3)	128.9 (59.0)	134.8 (93.8)	20.7 (25.4)	20.7 (45.1)

[a] Referenced to TMS using convertion $CHCl_3$ is 75.25 ppm from TMS. [b] Coupling constants are in parentheses. [c] The carbon atom numbering is:



[d] $Cr(acac)_3$ was added.

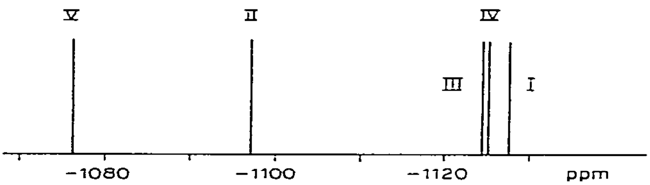


Fig. 1. ^{199}Hg chemical shifts (ppm) of organomercurials referenced to external neat dimethylmercury.

values (coupling between Hg and the *para*-carbon atoms) provide additional evidence for increasing of the effect in the series I → II → V (Tables 1, 2). These values, which are known to depend mainly on π-contributions [22], increase successively from I to II to V (62.8, 66.4, and 74.3 Hz, respectively). The ^7J-(^{1}H—^{199}Hg) values increase nearly as strongly on passing from IV to V (43 and 51 Hz, respectively); this coupling constant has a similar nature to ^5J(^{13}C—^{199}Hg). The direct constant ^1J(^{13}C—^{199}Hg) decreases in the same series indicating a decrease in electron density on the Hg—C bond. The proton and carbon chemical shifts of the CH_2-groups also show characteristic trends. Thus we conclude that the ^{199}Hg NMR technique provides the most sensitive tool for the detection of subtle electronic effects in organomercury compounds.

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