

EXPERIMENTAL AND MOLECULAR ORBITAL STUDIES OF NUCLEAR SPIN–SPIN COUPLING CONSTANTS IN β -METHOXYALKYLMERCURY(II) COMPLEXES

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Summary

Nuclear spin–spin coupling constants have been measured by ^1H and ^{13}C NMR for β -methoxyalkylmercury(II) complexes, $\text{MeCH}(\text{OMe})\text{CH}_2\text{HgCl}$ (I) and $\text{Me}_2\text{C}(\text{OMe})\text{CH}_2\text{HgL}$ (II) ($\text{L} = \text{OCOCH}_3, \text{Cl}, \text{Br}, \text{SCN}, \text{I}$ and CN). The mutual polarizabilities of the valence s -orbitals in the Fermi contact expression have been calculated by extended Hückel molecular orbital theory for I and II as well as for CH_3HgL (III). The calculated mutual polarizabilities not only reproduced the signs of the coupling constants, determined experimentally for I, but also accounted well for the influence of the *trans* ligand L on $^1J(\text{Hg–C})$ and $^2J(\text{Hg–C–H})$ for II and III.

Introduction

Nuclear spin–spin coupling constants in metal complexes have attracted wide interest in recent years, since valuable information on the metal–ligand bonding is obtainable especially from the one-bond coupling constants between metal and donor atom. A number of metal–carbon one-bond coupling constants [1], $^1J(\text{M–C})$, together with geminal coupling constants, $^2J(\text{M–C–H})$, were reported for alkylmetal complexes ($\text{M} = \text{Si}$ [2], Sn [3–5], Pb [5], Pt [6] and Hg [5,7–12]). The values of both $^1J(\text{M–C})$ and $^2J(\text{M–C–H})$ for alkylplatinum(II) [6] and alkylmercury(II) complexes [5,8] are sensitive to the variation in the ligands *trans* to the alkyl group and have been discussed in terms of *trans* influence [13]. However, quantum chemical studies on the coupling constants involving heavy atoms are quite few [14–17].

According to Pople and Santry's molecular orbital theory [18], the Fermi contact interaction dominates the coupling mechanism in most cases [19,20] and the sign of the coupling constant is determined by the mutual polarizability of the valence s -orbitals of the atoms concerned (*vide infra*).

In the present work we report the Hg—C and Hg—H coupling constants in β -methoxyalkylmercury(II) complexes. The mutual polarizabilities, calculated by the extended Hückel method, are found to reproduce well the signs of the coupling constants as well as the trends of the coupling constants induced by the variation in the *trans* ligand.

Experimental

β -Methoxyalkylmercury(II) complexes, $\text{MeCR}(\text{OMe})\text{CH}_2\text{HgL}$ (I, R = H, L = Cl; II, R = Me, L = OCOCH_3 , Cl, Br, SCN, I, and CN), were prepared according to the established method [21] from β -methoxyalkylmercury(II) acetate and the corresponding salts (NaL). The chemicals were obtained from standard commercial sources and were used without further purification.

^1H NMR spectra were recorded on a JEOL PS-100 (100 MHz, 24°C) or a Hitachi R-20B (60 MHz, 35°C) spectrometer. ^1H NMR samples were examined as 1.0 mol% CDCl_3 solutions. The AMM'X₃ proton spectra of I were simulated with the LAOCN III program coded for a HITAC 5020 computer [22].

^{13}C NMR spectra at 24°C were obtained on a JEOL PS-100 spectrometer operating with the continuous wave mode or the Fourier transform mode at 25 MHz. ^{13}C NMR samples were examined as 40 mol% solutions in CDCl_3 or $(\text{CD}_3)_2\text{CO}$. The relative signs of $^nJ(\text{HgC})$ and $^{n+1}J(\text{HgH})$ ($n = 1$ or 2) for I were determined by the ^{13}C — $\{^1\text{H}\}$ selective decoupling experiments developed by Jakobson, et al. [23]. The irradiating and observing frequencies were monitored by a Takeda Riken TR-550 frequency counter with a gate time of 10 sec.

Calculation

One-electron wave functions and energies were calculated according to the extended Hückel molecular orbital (EHMO) method. The Slater type functions were used as the valence atomic orbitals and all overlap integrals were included. The Slater exponents proposed by Burns [24] were used for all atoms except mercury where Bach's values [25] were employed. The diagonal elements of the Hamiltonian matrix, Coulomb integrals, were replaced by the valence orbital ionization potentials reported by Basch, et al. [26] for donor atoms and by Bach [25] for mercury. The off-diagonal elements, resonance integrals, were evaluated by the Wolfsberg-Helmholtz expression ($K = 1.75$) [27]. The charges calculated by Mulliken's population analysis were iterated to self-consistency using a charge sensitivity factor of the Coulomb integrals, 2.0 eV/unit charge [28], for all atoms.

The spin—spin coupling constant is given by eq. (1) in Pople and Santry's approximation [18].

$$K(\text{AB}) = (64\pi^2\beta^2/9)[S_{\text{A}}(0)]^2[S_{\text{B}}(0)]^2\pi(\text{AB}) \quad (1)$$

In this equation $K(\text{AB})$ is the reduced coupling constant, defined by eq. (2) to avoid dependence on the gyromagnetic ratios γ which are individual nuclear properties, $[S_{\text{A}}(0)]^2$ is the valence *s*-electron density of the atom A at the nucleus and $\pi(\text{AB})$ is the mutual polarizability of the valence *s*-orbitals of the atom A and B (eq. 3).

$$K(AB) = 4\pi^2 J(AB) / h\gamma_A\gamma_B \quad (2)$$

$$\pi(AB) = -4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_j - \epsilon_i)^{-1} C_{iSA} C_{iSB} C_{jSA} C_{jSB} \quad (3)$$

In eq. (3) ϵ and C are the MO energies and the coefficients, respectively. Eq. (1) indicates that the sign of $K(AB)$ is determined by $\pi(AB)$ *.

EHMO calculations, including the computation of the mutual polarizabilities (eq. (3)), were carried out for $\text{MeCH(OMe)CH}_2\text{HgCl}$ (I), $\text{Me}_2\text{C(OMe)CH}_2\text{HgL}$ (II) and CH_3HgL (III) ($L = \text{OCOCH}_3, \text{Cl, Br, SCN, I}$ and CN). All the rotamers of I [22] and of II ($L = \text{Cl}$) were calculated. The ligand influence was examined for a representative rotamer holding the HgL group *anti* with respect to the OMe group in II, since the difference in the CH_2HgL bonding properties was negligible between the two rotamers in II ($L = \text{Cl}$).

The C-Hg-L moiety was fixed in a linear geometry with the C-Hg bond distance of 0.207 nm for all the complexes I-III. The Hg-L bond distances were as follows (in nm); $L = \text{OCOCH}_3$: 0.213 [29], Cl : 0.2282 [30], Br : 0.2406 [30], I : 0.2528 [31], CN : 0.205 [32] and SCN : 0.230. The distances and angles of the β -methoxyalkyl moiety were taken from ref. 33. The coordinates of the complexes were calculated using the computer program STERIC developed by Yoneda [34]. All the calculations were carried out by a HITAC 8700/8800 computer at the university of Tokyo.

Results

β -Methoxypropylmercuric chloride, $\text{MeCH(OMe)CH}_2\text{HgL}$ (I)

The carbon resonances of the β -methoxyalkylmercury(II) complexes (I and II) were assigned on the basis of both proton off-resonance experiments and ^{199}Hg satellite peaks (^{199}Hg : $I = 1/2$, natural abundance: 16.8%). Fig. 1a shows the $^{13}\text{C}\{-^1\text{H}\}$ noise decoupling spectrum of I. The coupling constants and the reduced coupling constants ** for the CHCH_2Hg moiety of I are summarized in Table 1.

We have performed relative sign determinations for ${}^nK(\text{HgC})$ and ${}^{n+1}K(\text{HgH})$ ($n = 1$ or 2) in I by use of $^{13}\text{C}\{-^1\text{H}\}$ selective decoupling experiments [10,23]. Irradiation of the high-field portion of the proton spectrum enhanced the downfield mercury satellite of the ^{13}C resonance of the methylene carbon (see Fig. 1b) and vice versa. The situation was the same for the methine carbon. Therefore, ${}^1K(\text{HgC})$ and ${}^2K(\text{HgC})$ were determined to be opposite in sign to ${}^2K(\text{HgH})$ and ${}^3K(\text{HgH})$, respectively.

* According to the well-known mean excitation energy approximation, $\pi(AB)$ is replaced by $\alpha_A^2\alpha_B^2/\Delta E$:

$$K(AB) = (64\pi^2\beta^2/9)[S_A(0)]^2[S_B(0)]^2\alpha_A^2\alpha_B^2/\Delta E$$

In this equation α^2 is the s -character of the hybrid orbital used to form the $A-B$ bond and ΔE is the average excitation energy. This approach, however, yields no negative sign of any reduced coupling constant.

** Since the gyromagnetic ratios of H, C and Hg are all positive in sign, the coupling constants in this paper have the same signs as the reduced coupling constants.

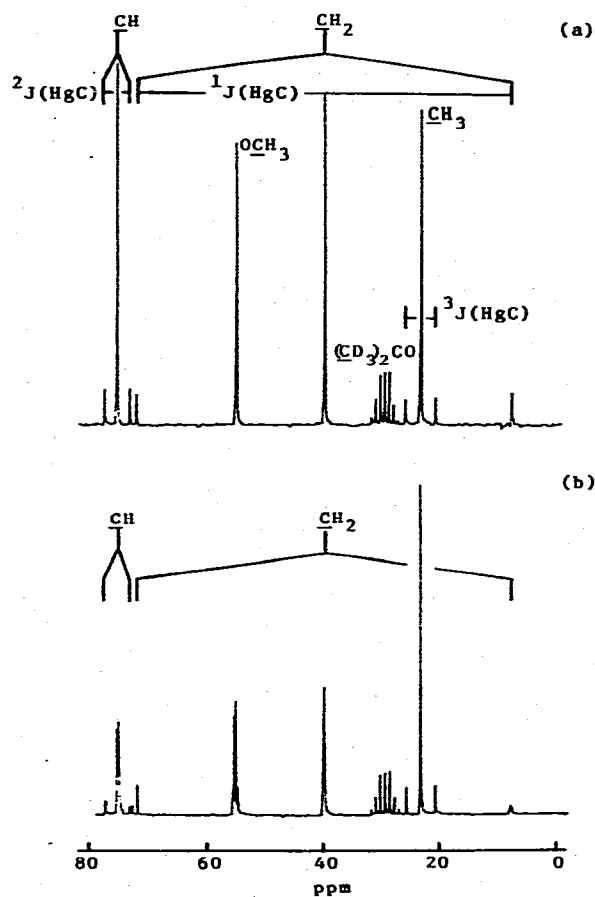


Fig. 1. ^{13}C NMR spectra (25.03 MHz) of β -methoxypropylmercuric chloride, $\text{MeCH}(\text{OMe})\text{CH}_2\text{HgCl}$ (I), in $(\text{CD}_3)_2\text{CO}$ solution. The spectra were taken under the conditions of (a) the noise decoupling of proton and (b) the selective decoupling of proton nearly at the resonance frequency of the methyl proton, which was chosen so as to be lower than those of both the methylene and methine protons.

TABLE 1

COUPLING CONSTANTS AND VALENCE s -ORBITAL MUTUAL POLARIZABILITIES FOR THE CHCH_2Hg MOIETY OF β -METHOXYPROPYLMERCURIC CHLORIDE, $\text{MeCH}(\text{OMe})\text{CH}_2\text{HgCl}$ (I)

Coupled nuclei	Coupling constant ^a			Mutual polarizability ^b
	$ J $ (Hz)	$ K $ (nm^{-3})	sign ^c	π (10^{-3} eV^{-1})
Hg—C	1606	297.5	+	+3.80
Hg—C—C	109	20.2	—	-0.46
Hg—C—H ^d	204.5	9.52	—	-1.96
Hg—C—C—H	306.3	14.26	+	+1.35
C—H(CH_2)	136	4.50	+	+8.01
C—H(CH)	134	4.46	+	+8.00
H—C—H	11.8	0.098	—	-1.92
H—C—C—H ^e	5.65	0.047	+	+1.15

^a Solvent CDCl_3 . ^b Values calculated for the three rotamers were averaged on the basis of their populations [22]. ^c See text. ^d Average value of Hg—C—H_M and $\text{Hg—C—H}_{M'}$ couplings in $\text{AMM}'X_3$ system.

TABLE 2
REDUCED COUPLING CONSTANTS AND MUTUAL POLARIZABILITIES FOR β -METHOXYISO-BUTYLMERCURY(II) COMPLEXES, $\text{Me}_2\text{C}(\text{OMe})\text{CH}_2\text{HgL}$ (II)

L	Hg—C		Hg—C—H		C—H(CH ₂)	
	K ^a	π ^b	K	π	K	π
OCOCH ₃	316	+6.15	9.84	-1.92	4.50	+8.53
Cl	304	+4.53	9.57	-1.78	4.54	+8.66
Br	288	+4.49	9.21	-1.78	4.50	+8.83
SCN	282	+4.36	9.08	-1.66	4.50	+8.67
I	278	+3.11	8.87	-1.61	4.50	+9.06
CN	269	+3.47	8.41	-1.45	4.44	+8.42

^a Units in nm⁻³, solvent CDCl₃. ^b Units in 10⁻³ eV⁻¹.

The mutual polarizabilities of the valence s-orbitals corresponding to the eight coupling constants in I were calculated by the EHMO method and are given in the last column of Table 1.

β -Methoxyisobutylmercury(II) complexes, $\text{Me}_2\text{C}(\text{OMe})\text{CH}_2\text{HgL}$ (II) and methylmercury(II) complexes, CH_3HgL (III) (L = OCOCH₃, Cl, Br, SCN, I and CN)

The six kinds of coupling constants for II (Hg—C, Hg—C—C, Hg—C—C—C, Hg—C—H, Hg—C—C—H and C—H coupling of the methylene group) were reported previously [8]. Among them, the values of ¹K(HgC) and ²K(HgH) were sensitive to the *trans* ligand L, whereas ¹K(CH) of the methylene group bound to mercury were affected little. These coupling constants, together with the corresponding mutual polarizabilities of the valence s-orbitals, are given in Table 2.

Since the effects of the ligand L on ²K(HgH) for II and III were quite similar [8], the EHMO calculations for III, the representative alkylmercury(II) complexes, were carried out as well as II. As shown in Table 3, the ligand effects on the total electron densities and the bond overlap populations of III are similar to those of II.

TABLE 3
TOTAL ELECTRON DENSITIES AND OVERLAP POPULATIONS IN THE Hg—C BOND OF $\text{Me}_2\text{C}(\text{OMe})\text{CH}_2\text{HgL}$ (II) AND CH_3HgL (III)

L	Total electron density				Hg—C overlap population	
	Hg		C		II	III
	II	III	II	III		
OCOCH ₃	10.76	10.84	4.19	4.22	0.49	0.52
Cl	10.96	11.06	4.33	4.35	0.38	0.40
Br	11.04	11.15	4.30	4.32	0.37	0.39
SCN	10.94	11.04	4.34	4.36	0.34	0.37
I	11.28	11.43	4.46	4.49	0.19	0.21
CN	10.88	10.96	4.38	4.40	0.32	0.35

Discussion

β-Methoxypropylmercuric chloride, MeCH(OMe)CH₂HgCl (I)

Some relative signs of the coupling constants in alkylmercury(II) complexes have been determined by double resonance experiments [12]. Based on the assumption that $^1K(\text{CH})$ is positive [19], absolute signs of $^1K(\text{HgC})$ (positive) and $^2K(\text{HgH})$ (negative) are obtained for both $(\text{CH}_3)_2\text{Hg}$ [35] and CH_3HgNO_3 [36]. Since $^2K(\text{HgH})$ and $^3K(\text{HgH})$ for $\text{CH}_3\text{CH}_2\text{HgCl}$ and $^3K(\text{HgH})$ and $^2K(\text{HgC})$ for dialkylmercury are both opposite in sign, the signs of $^3K(\text{HgH})$ and $^2K(\text{HgC})$ are determined to be positive [36] and negative [10], respectively. In the case of the complex I, we have also confirmed that $^2K(\text{HgC})$ is opposite in sign to $^3K(\text{HgH})$ (see Fig. 1b) and hence negative. The signs of $^2K(\text{HH})$ (negative) and $^3K(\text{HH})$ (positive) in alkyl groups are generally accepted [37]. The signs of the coupling constants for the CHCH_2Hg moiety of the complex I are given in Table 1 based on these considerations.

The calculated mutual polarizabilities $\pi(\text{AB})$ for I are also included in Table 1. The signs of the eight kinds of $K(\text{AB})$ are thus clearly reproduced by the present calculation on $\pi(\text{AB})$.

Unknown valence s-electron densities $[S_A(0)]^2$ for the five kinds of atoms in the CHCH_2Hg moiety of I can be estimated by solving five simultaneous equations for eq. (1) obtained from the five experimental reduced coupling constants and the corresponding calculated mutual polarizabilities. The Fermi contact mechanism has been reported to be dominant for $\text{Hg}-\text{C}-\text{H}$ coupling [15] as well as for $\text{C}-\text{H}$, $\text{H}-\text{C}-\text{H}$ and $\text{H}-\text{C}-\text{C}-\text{H}$ couplings [19,20]. Then the five kinds of couplings ($\text{C}-\text{H}$ of the methylene and the methine groups, $\text{H}-\text{C}-\text{H}$, $\text{H}-\text{C}-\text{C}-\text{H}$ and $\text{Hg}-\text{C}-\text{H}$) were employed to solve the simultaneous equations, yielding the following values of $[S_A(0)]^2$ (in 10^3 nm^{-3}): methylene hydrogen 3.68, methine hydrogen 2.94, methylene carbon 40.5, methine carbon 50.3 and mercury 350. The mercury atom in I can be regarded as Hg^+ , since the calculated charges of the mercury averaged for the three rotamers of I is +1.03. It is to be noted therefore that the values of $[S_{\text{Hg}}(0)]^2$, $350 \times 10^3 \text{ nm}^{-3}$, agreed closely with that of $[S_{\text{Hg}^+}(0)]^2$, $320 \times 10^3 \text{ nm}^{-3}$, obtained from the average hyperfine structure constant of Hg^+ , $A_{\text{Hg}^+} = 4.05 \times 10^{20} \text{ Hz}$ [38]. The values of both $[S_{\text{H}}(0)]^2$ and $[S_{\text{C}}(0)]^2$ are reasonable, comparing with those reported by Pople, et al. (H, 2.51, C $27.2 \times 10^3 \text{ nm}^{-3}$) [39].

Three kinds of couplings involving mercury remain unused: $\text{Hg}-\text{C}$, $\text{Hg}-\text{C}-\text{C}$ and $\text{Hg}-\text{C}-\text{C}-\text{H}$. The magnitudes of these couplings constants are evaluated from eq. (1) by using the estimated values of $[S_A(0)]^2$ and the calculated values of $\pi(\text{AB})$. The calculated values are as follows and are in good agreement with the observed values given in parentheses (in nm^{-3}): $^1K(\text{HgC}) = +202.9 (+297.5)$, $^2K(\text{HgC}) = -30.6 (-20.2)$, $^3K(\text{HgH}) = +5.23 (+14.26)$.

The present results concerning the signs and the magnitudes of both the mercury-carbon and the mercury-hydrogen couplings confirm that these couplings are dominated by the Fermi contact mechanism.

β-Methoxyisobutylmercury(II) complexes, Me₂C(OMe)CH₂HgL (II) and methylmercury(II) complexes, CH₃HgL (III) (L = OCOCH₃, Cl, Br, SCN, I and CN)

The dominance of the Fermi contact mechanism was also suggested by the

linear relationship between ${}^1K(\text{HgC})$ and ${}^2K(\text{HgH})$ in the complex II passing through the origin [8] as was found for neopentylmercury(II) complexes [5]. Positive signs for ${}^1K(\text{HgC})$ and ${}^1K(\text{CH})$ and a negative sign for ${}^2K(\text{HgH})$ in II as well as I were obtained from the calculations of the corresponding mutual polarizabilities (Table 2).

The magnitudes of the observed coupling constants are correlated to those of the calculated mutual polarizabilities (Table 2). Fig. 2 shows a linear relationship between ${}^2K(\text{HgH})$ and ${}^2\pi(\text{HgH})$. It is therefore probable that the effects of the *trans* ligand L on ${}^1K(\text{HgC})$ and ${}^2K(\text{HgH})$ are closely related to the changes in the mutual polarizabilities of the valence *s*-orbitals (${}^1\pi(\text{HgC})$ and ${}^2\pi(\text{HgH})$).

It has been reported that Hg(II) and Pt(II) complexes show similar NMR-*trans* influence and that the variation in the coupling constants for these complexes can be related to α_M^2 term (the *s*-character of the metal orbitals) [13]. It is to be noted that the α_M^2 term corresponds to the part of the metal *s*-orbital coefficients of the mutual polarizabilities in eq. (1). On the other hand, Henneke has suggested that the mercury valence *s*-electron density is an important term for the NMR *trans* influence of L on ${}^2K(\text{HgH})$ in CH_3HgL (III) [15]. If the changes in $[S_M(0)]^2$ were dominant, the NMR *cis* influence of ligand would be comparable to its *trans* influence for square-planar platinum(II) complexes. This is not so and the NMR *cis* influence is much smaller than the *trans* influence [13,40,41]. It is therefore reasonable to conclude that the variation in the mutual polarizability is dominant for the *trans* influence of L on ${}^1K(\text{MC})$ and ${}^2K(\text{MH})$ in alkylplatinum(II) and alkylmercury(II) complexes.

Fig. 3 shows a_1 symmetry molecular orbitals in which the coefficients of *s*-orbitals for H, C and Hg of CH_3HgCl are nonzero. In this figure, *s*-orbital coefficients and their products are presented, together with the orbital energies. The molecular orbitals of no. 1–5 and no. 6–8 are occupied and unoccupied, respectively. It is apparent that the C–H coupling (${}^1\pi(\text{CH})$) is determined solely by the $2(\sigma_{\text{CH}}) \rightarrow 8(\sigma_{\text{CH}}^*)$ excitation. Since the energies and *s*-orbital coefficients of C and H of $2(\sigma_{\text{CH}})$ and $8(\sigma_{\text{CH}}^*)$ orbitals are almost unaffected by the variation in the *trans* ligand L, ${}^1\pi(\text{CH})$ or ${}^1K(\text{CH})$ (Table 2) is insensitive to the ligand L [15].

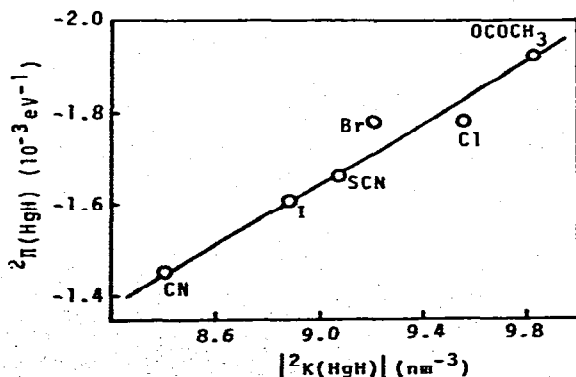


Fig. 2. Correlation of ${}^2\pi(\text{HgH})$, calculated valence *s*-orbital mutual polarizabilities, with ${}^2K(\text{HgH})$, observed reduced coupling constants, for $\text{Me}_2\text{C}(\text{OMe})\text{CH}_2\text{HgL}$ (II).

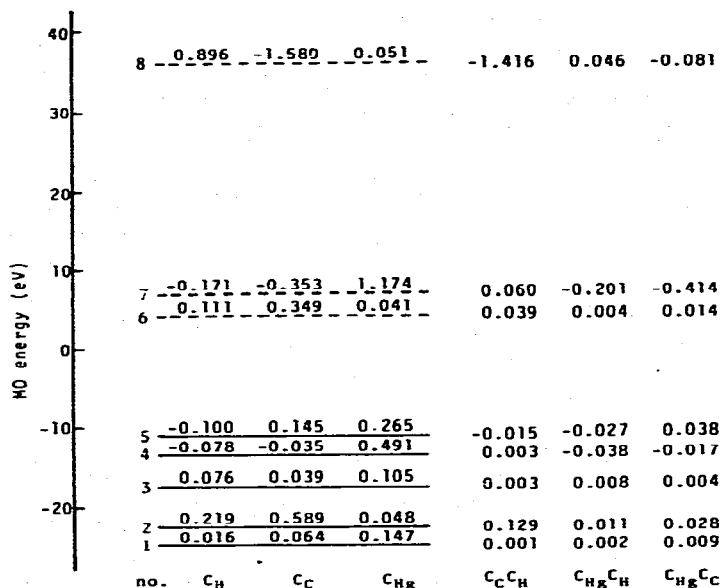


Fig. 3. Valence s-orbital coefficients of Hg(6s), C(2s) and H(1s), together with their products, in the a_1 symmetry molecular orbitals of CH_3HgCl .

The 4 (Hg_{sd}) \rightarrow 7 (σ_{HgC^*}) and the 5 (σ_{HgC}) \rightarrow 7 excitations are mainly responsible for the Hg—C—H coupling (${}^2\pi(HgH)$), where the products $C_{Hg} \times C_H$ are negative in these orbitals. The double products $C_{Hg} C_H$ (occupied MO) \times $C_{Hg} C_H$ (unoccupied MO) are consequently positive in both 4 \rightarrow 7 and 5 \rightarrow 7 excitations, yielding the negative sign of ${}^2\pi(HgH)$ or ${}^2K(HgH)$. The Hg—C coupling (${}^1\pi(HgC)$) depends on the 2 (σ_{CH}) \rightarrow 7 (σ_{HgC^*}) and the 5 (σ_{HgC}) \rightarrow 7 excitations. The positive sign of ${}^1\pi(HgC)$ or ${}^1K(HgC)$ is apparent from the signs of $C_{Hg} C_C$ in these orbitals [note the negative sign in eq. (3)].

It is to be noted that the values of ${}^1\pi(HgC)$ for III vary almost linearly with

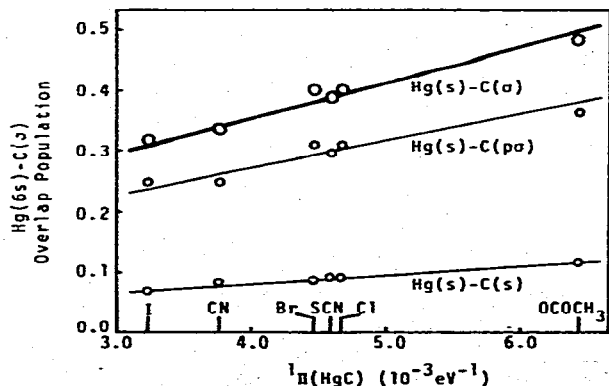


Fig. 4. Correlation of Hg 6s orbital-C σ orbital overlap populations with Hg—C valence s-orbital mutual polarizabilities for CH_3HgL (III). [$Hg(s) - C(\sigma) = Hg(s) - C(p\sigma) + Hg(s) - C(s)$]

Hg 6s orbital-C σ orbital overlap populations (Fig. 4), reflecting the effect of the ligand L on the 6s coefficients of the σ_{HgC} orbital. This variation in the Hg 6s coefficients of the σ_{HgC} orbital is certainly the most important factor contributing to the *trans* influence of the ligand L on $^1\pi(\text{HgC})$ and $^2\pi(\text{HgH})$.

The population analyses of the complexes III indicate that neither the Hg 5d nor the Hg 6p orbitals play any significant role in the Hg—C bonding. It is therefore reasonable that $^1K(\text{HgC})$ or $^2K(\text{HgH})$ is a good measure of the strength of the mercury—carbon bonding in a series of alkylmercury(II) complexes.

The present molecular orbital approach to the nuclear spin—spin coupling constants for the alkylmercury(II) complexes will be applicable to other organometallic complexes in order to obtain valuable information on the metal—carbon σ bonding.

References

- 1 B.E. Mann, *Adv. Organometal. Chem.*, **12** (1974) 135.
- 2 R.K. Harris and B.J. Kimber, *J. Magnet. Resonance*, **17** (1975) 174.
- 3 H.G. Kuivila, J.L. Considine, R.H. Sarma and R.J. Mynott, *J. Organometal. Chem.*, **111** (1976) 179.
- 4 J.D. Kennedy and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, (1974) 983.
- 5 G. Singh, *J. Organometal. Chem.*, **99** (1975) 251.
- 6 M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers and J.E.H. Ward, *J. Amer. Chem. Soc.*, **95** (1973) 8574.
- 7 G. Singh and G.S. Reddy, *J. Organometal. Chem.*, **42** (1972) 267.
- 8 T. Ibusuki and Y. Saito, *Chem. Lett.*, (1974) 311.
- 9 T. Ibusuki and Y. Saito, *Chem. Lett.*, (1973) 1255.
- 10 F.J. Weigert and J.D. Roberts, *Inorg. Chem.*, **12** (1973) 313.
- 11 L.A. Fedrov, L.A. Stumbrevichute, A.K. Prokofyev and E.I. Fedin, *Dokl. Akad. Nauk SSSR*, **209** (1973) 134.
- 12 V.S. Petrosyan and O.A. Reutov, *J. Organometal. Chem.*, **76** (1974) 123.
- 13 T.G. Appleton, H.C. Clark and L.E. Manzer, *Coord. Chem. Rev.*, **10** (1973) 335.
- 14 G. Klose, *Ann. Phys. (Leipzig)*, **9** (1962) 262.
- 15 H.F. Henneike, *J. Amer. Chem. Soc.*, **94** (1972) 5945.
- 16 P.A. Scherr and J.P. Oliver, *J. Amer. Chem. Soc.*, **94** (1972) 8026.
- 17 H. Kato, *Bull. Chem. Soc. Japan*, **44** (1971) 348.
- 18 J.A. Pople and D.P. Santry, *Mol. Phys.*, **8** (1964) 1.
- 19 W. McFarlane, *Quart. Rev.*, **23** (1969) 187.
- 20 J.N. Murrell, *Progr. NMR Spectroscopy*, **6** (1971) 1.
- 21 K. Ichikawa, H. Ouchi and S. Arai, *J. Amer. Chem. Soc.*, **82** (1960) 3880.
- 22 T. Ibusuki and Y. Saito, *Org. Magnet. Resonance*, **6** (1974) 436.
- 23 H.A. Jakobsen, T. Bundgaard and R.S. Hansen, *Mol. Phys.*, **23** (1972) 197.
- 24 G. Burns, *J. Chem. Phys.*, **41** (1964) 1521.
- 25 R.D. Bach, *J. Amer. Chem. Soc.*, **91** (1969) 1771.
- 26 H. Basch, A. Viste and H.R. Gray, *Theoret. Chim. Acta*, **3** (1965) 458.
- 27 M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20** (1952) 837.
- 28 F.A. Cotton and C.B. Harris, *Inorg. Chem.*, **6** (1967) 369.
- 29 R. Allmann and H. Musso, *Chem. Ber.*, **106** (1973) 3001.
- 30 W. Gordy and J. Sheridan, *J. Chem. Phys.*, **22** (1954) 92.
- 31 C. Feige and H. Hartman, *Z. Naturforsch.*, **22A** (1967) 1268.
- 32 J.C. Mills and H.S. Preston, *J. Organometal. Chem.*, **14** (1968) 23.
- 33 *Tables of Interatomic Distances and Configurations in Molecules and Ions*, *Chem. Soc., Spec. Publ.*, No. 11 (1958); Suppl., No. 18 (1965).
- 34 Y. Yoneda, Yuki Gosei Kyokaiishi (J. Soc. Org. Syn. Chem., Tokyo), **29** (1971) 449.
- 35 W. McFarlane and R.R. Dean, *Mol. Phys.*, **13** (1967) 343.
- 36 F.A.L. Anet and J.L. Sudmeier, *J. Magnet. Resonance*, **1** (1969) 124.
- 37 J.W. Emsley, J. Feeney and L.H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, London, 1965, Vol. 2, p. 681.
- 38 J.V. Hatton, W.G. Schneider and W. Siebrand, *J. Chem. Phys.*, **39** (1963) 1330.
- 39 J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970, p. 154.