bon (and hence affect the relative energies of conformations A and B) and also have an inductive stabilizing or destabilizing effect of considerable magnitude. The falloff factor in the inductive effect is found to be approximately $^2/_3$ for each interposed CH_2 group.

(4) Substituent effects observed in primary cations are also operative in secondary and tertiary cations and only slightly diminished in magnitude.

(5) Calculated heats of formation, relative energies, and stabilization energies are in reasonable agreement with available gas-phase experimental data.

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A Semiempirical Molecular Orbital Study of ^{199}Hg–^1H Coupling Constants. I. The Method and Aliphatic Systems

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Abstract: An extended Hückel procedure for calculating ^{199}Hg–^1H coupling constants is outlined and results for a variety of methylmercury (CH_3HgX) systems are given. These results suggest that orbital contraction for the 6s orbital of mercury with increasing electronegativity of the substituent X is an important contributing factor to the large range spanned by these coupling constants. The calculated vicinal and geminal coupling constants in the ethylmercury moiety agree well with experimental values. It is suggested that this agreement might be useful in some conformational studies of organomercurials. No support for significant employment of mercury 5d orbitals in bonding is found in these systems.

In recent years a great deal of information on heavy atom proton spin–spin couplings has been accumulated,[1,2] particularly for mercury systems.[3,4] Perhaps the most outstanding general features of these couplings are their large absolute magnitudes and the degree to which they are influenced by substitution at the heavy atom.[4,5]

Hatton, Schneider, and Siebrand[4] have shown that the relative magnitudes of the geminal coupling constants in methane (^1H–C–^1H) and dimethylmercury (^{199}Hg–C–^1H) are approximately accounted for by assuming that both are due solely to the Fermi contact mechanism and including the relative optical hyperfine structure constants for hydrogen and mercury.

Evans, *et al.*,[5,6] have shown that the pattern of ^1H–^1H coupling constants in benzene is largely reproduced by ^{205}Tl–^1H couplings and ^{199}Hg–^1H couplings in the appropriate metal-substituted benzene.

These and other studies strongly suggest that the magnitudes of heavy metal proton spin–spin coupling constants are largely determined by the Fermi contact mechanism although several authors have questioned this.[6,7]

Orgel[8] has argued that one of the principal causes of the different stereochemical preferences of Hg (linear) and Zn (tetrahedral) is the involvement of the d_{z^2} orbital of mercury in forming digonal hybrids with a significant amount of d orbital character. Baldeschwieler[9] has interpreted the relative magnitudes of $J(M–H_\alpha)$ and $J(M–H_\beta)$ in ethyl compounds of Sn, Pb, Tl, and Hg as evidence for involvement of the metal d orbitals in bonding. However, a recent esr study[10] of radical anions of several arylmercury systems gave little evidence that the d orbitals of mercury play a significant role in bonding.

Because of these divergent views we have undertaken to calculate the Fermi contact contribution to $J(^{199}Hg$–$^1H)$ for a variety of systems. Mercury was chosen for this investigation because of the accuracy and variety of both structural and nuclear magnetic resonance data available. The low coordination number of mercury also makes the MO calculations easier and less expensive. Extended Hückel semiempirical MO methods have been shown to provide reasonable results for many proton proton couplings.[11,12]

Method

In the one-electron MO approximation the Fermi contact contribution, $J^{(3)}{}_{AB}$, to the coupling of nuclei

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(6) W. McFarlane, *J. Chem. Soc.*, 725 (1967).

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(12) S. Polezzo, P. Cremoschi, and M. Simonetta, *Chem. Phys. Lett.*, **1**, 357 (1967).

A and B is given by the following equation

$$J^{(3)}{}_{\mathrm{AB}} = -(128/9)\pi h\beta^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}} \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{unocc}} (E_j - E_i)^{-1} \times \sum_{\mu\nu\lambda\sigma} C_{i\lambda}C_{j}C_{j}C_{i\sigma}\langle\phi_\lambda|\delta(r_{\mathrm{A}})|\phi_\mu\rangle\langle\phi_\nu|\delta(r_{\mathrm{B}})|\phi_\sigma\rangle \quad (1)$$

which was derived by Pople and Santry.[13]

The author's use of eq 2 was modified by including not only one-center integrals over valence shell s orbitals but all multicenter integrals over valence shell orbitals with the only restriction being that the origin for orbitals ϕ_λ and ϕ_μ must be less than 3.0 Å from atom A while ϕ_ν and ϕ_σ are centered less than 3.0 Å from atom B.

One-electron wave functions and energies are computed according to the extended Hückel theory, using the following valence orbital ionization potentials (VOIP's) in electron volts for the diagonal elements of the Hamiltonian matrix: $H_{\mu\mu}$(H 1s) = −13.60, $H_{\mu\mu}$(C 2s) = −19.41, $H_{\mu\mu}$(C 2p) = −10.64, $H_{\mu\mu}$(N 2s) = −25.56, $H_{\mu\mu}$(N 2p) = −13.19, $H_{\mu\mu}$(O 2s) = −32.26, $H_{\mu\mu}$(O 2p) = −15.87, $H_{\mu\mu}$(F 2s) = −40.12, $H_{\mu\mu}$(F 2p) = −18.65, $H_{\mu\mu}$(S 3s) = −20.66, $H_{\mu\mu}$(S 3p) = −11.58, $H_{\mu\mu}$(Cl 3s) = −25.27, $H_{\mu\mu}$(Cl 3p) = −13.69, $H_{\mu\mu}$(Br 4s) = −24.03, $H_{\mu\mu}$(Br 4p) = −13.19, $H_{\mu\mu}$(Hg 5d) = −15.66, $H_{\mu\mu}$(Hg 6s) = −10.44, $H_{\mu\mu}$(Hg 6p) = −5.00.[14]

All overlaps are included and are calculated using Clementi's double ζ functions[15] for all atoms except mercury where Herman and Skillman[16] functions for mercury(I) are employed. This ensures at least approximately correct behavior of the valence orbitals at all nuclei.

The off-diagonal elements are approximated by the Cusach's expression

$$H_{\mu\nu} = 0.5S_{\mu\nu}(2 - |S_{\mu\nu}|)(H_{\mu\mu} + H_{\nu\nu}) \quad (2)$$

which was handled so as to retain invariance to rotation.[17,18]

For these calculations the geometry of the H_3CHg^+ fragment was held fixed with R_{CH} = 1.095 Å, R_{CHg} = 2.07 Å and tetrahedral angles. Other distances and angles are taken from ref 19. Since the R_{CHg} values reported for $(CH_3)_2Hg$[20] and CH_3HgCl[19] are 2.094 and 2.061 Å, respectively, a constant value for these calculations seems justified and will serve to keep the choice of R_{CHg} from prejudicing the result.

Discussion

The calculated and observed coupling constants for several simple test molecules are compared at the top of Table I. It should be emphasized that these molecules represent a much wider range of substituent and geometry than is looked at in the organomercurial work. Thus the ability of the calculations to reproduce well not only trends but signs[21] and, in general, magnitudes for both direct and indirect couplings is heartening. This is especially so since the procedure is a simple one with no iteration to self-consistent charges or parameters chosen especially to fit these data.

Table I. Calculated and Observed H–H and C–H Couplings

Compound	Coupling	J^3 calcd[a]	J obsd[a]
CH_4	CH	138.4	125[b]
	HH	−10.5	−12.4[b]
CH_3F	CH	+145.4	149[g]
	HH	−8.9	−9.6[f]
$H_2C{=}CH_2$	CH	+164.0	156[b]
	HH gem	+6.4	2.5[b]
$HC{\equiv}CH$	CH	+287.7	249[b]
	HH	+29.6	9.8[b]
$H_2C{=}O$	CH	+203.6	173[e]
	HH	+29.6	41[d]
CH_3Hg^+	CH	131.3	
CH_3HgCH_3	CH	118.3	129[c]
$CH_3HgC_2H_5$	CH	118.0	
CH_3HgC_2H	CH	118.3	
CH_3HgCF_3	CH	117.9	
CH_3HgCN	CH	117.9	130[h]
CH_3HgSCN	CH	119.6	
$[CH_3HgNCS]$	CH	119.5	
CH_3HgBr	CH	119.5	
CH_3HgCl	CH	119.6	130[h]
CH_3HgF	CH	121.1	
$CH_3Hg(OH_2)^+$	CH	120.8	132[h]
CH_3HgSH	CH	119.5	

[a] Values are given to nearest 0.1 Hz. [b] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962). [c] C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, **9**, 1998 (1970). [d] B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *J. Chem. Phys.*, **39**, 3154 (1963). [e] By analogy to $CH_3{}^{13}C^1HO$. [f] H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962). [g] N. Muller and D. E. Pritchard, *ibid.*, **31**, 1471 (1959). [h] This work.

The agreement between experiment and calculation for the geminal HH couplings is especially gratifying for two reasons: first, these are analogous to the geminal Hg–H couplings we are primarily interested in as an indicator of bonding in the methyl mercurials, and, secondly, the geminal coupling constants are in general much more difficult to calculate since they are the result of near cancellation between two large numbers[22] as well as numerous smaller contributions.

Also listed in Table I are calculated and experimental values for the direct $^{13}C-^{1}H$ coupling constant in a number of methylmercurials. The calculated couplings are all lower than the experimental numbers by about 10–11 Hz but they do follow the expected pattern of generally increasing with increasing electronegativity of the substituent on mercury. Furthermore, the range (3 Hz) is identical, within experimental error, with the range found experimentally for this coupling constant. The value of $J(^{13}C-^{1}H)$ calculated for CH_3Hg^+ is significantly larger than that for the hydrated methylmercury cation $(CH_3Hg(OH_2)^+)$. After adding 10 Hz to correct the calculated value for the nearly constant error noted above, the value of 141 Hz is in poor agreement with the value of 132 Hz found for solutions of CH_3HgClO_4 in H_2O. However, correcting the calcu-

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(13) (a) All terms are defined in the original reference; (b) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(14) (a) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965); (b) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, S160 (1965); (c) D. C. Frost, *et al.*, *Chem. Phys. Lett.*, **1**, 93 (1967). The mercury VOIP's are taken directly from the photoelectron spectroscopy results in this paper. The value for Hg(5d) is taken as the mean of the ionization energies leading to the $^2D_{5/2}$ and $^2D_{3/2}$ states of the ...$5s^2$, $5p^6$, $5d^9$, $6s^2$ configuration of mercury(II).

(15) E. Clementi, *IBM J. Res. Develop., Suppl.*, **9**, 2 (1965).

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(17) L. C. Cusachs, *J. Chem. Phys.*, **43**, S157 (1965).

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(20) K. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Chem.*, **38**, 1516 (1960).

(21) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ref 2, p 681.

(22) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

lated value for $CH_3Hg(OH_2)^+$ by the same amount gives 131 Hz in good agreement with experiment. It seems intuitively appealing that the methylmercury cation would be strongly solvated by one water molecule giving a linear geometry with any subsequent solvation much weaker in character. This is consistent with the Raman spectroscopy studies of Goggin and Woodward.[23a]

Table II contains a comparison of calculated and experimental geminal $J(^{199}Hg-^1H)$ coupling constants for the organomercurials studied. The values in column 1 were obtained by the method outlined previously in the experimental portion and several points are to be noted. First, these coupling constants are all negative as is expected from comparison with experiment. Secondly, the value for the coupling constant of the methylmercury cation itself is, as found for $J(^{13}C-^1H)$, quite out of line with the other methylmercurials. In this case the calculated coupling constant even has the wrong sign. Another point to note is that while the coupling constants are of the correct sign and the general trend of increasing absolute value for the coupling constant with increasing electronegativity of the substituent is observed, in general, the magnitude of the coupling constants is too small by a factor of 2–3 and the range over which the coupling constants vary is much reduced from that observed experimentally. Experimentally the largest coupling constant observed is for methylmercury perchlorate dissolved in water where one presumably has the methylmercury aquo cation.[23a] Taking this as a reference, the range in the coupling constant observed is 102% of this coupling constant. For column 1 the largest calculated coupling constant is that for methylmercury fluoride and taking this as a reference the total range of calculated coupling constants is only 23% of this value. The range is thus calculated too small by a factor of 4.

Table II. Calculated and Observed Geminal Hg–H Couplings

Compound	$J^{(3)}$ calcd	$J^{(3)}$ calcd^{a,b}	J obsd^{a,j}
CH_3Hg^+	+17.1	+40.4	
CH_3HgCH_3	−71.4	−118.5	100.6^{d,h}
$CH_3HgC_2H_5$	−69.1, −65.3^c	−114.1, −106.2^c	94, 96^{c,i}
CH_3HgC_2H	−75.1	−133.5	143.2^{f,h}
CH_3HgCF_3	−66.7	−94.4	139^g
CH_3HgCN	−74.3	−137.0	176.0^{e,h}
CH_3HgSCN	−77.3	−138.4	197.5^{f,h}
$[CH_3HgNCS]$	−82.6	−159.5	
CH_3HgBr	−79.6	−148.8	201.3^{f,h}
CH_3HgCl	−81.4	−156.4	204.3^{f,h}
CH_3HgF	−87.6	−193.6	
$CH_3Hg(OH_2)^+$	−83.9	−175.8	259.8^{e,h}
CH_3HgSH	−78.3	−133.2	156^{f,h}

[a] Values are given to the nearest 0.1 Hz. [b] Density of Hg 6s orbital at nucleus corrected for charge on Hg; see Discussion. [c] Coupling to α-methylene protons. [d] Solvent cyclohexane. [e] Solvent benzene. [f] Reduced by 5% from value measured in pyridine to approximate benzene solvent effect. [g] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964). [h] Reference 4. [i] Reference 2, p 690. [j] Experimental value for $CH_3HgSHgCH_3$.

If we write the expression for $J^{(3)}(^{199}Hg-^1H)$ in terms of the fractional s character of the bonds involved in the coupling and an average excitation energy (ΔE) we have[24]

$$J^{(3)}{}_{HgH} = {}^1/_2 h a_H a_{Hg} F_{HgC} F_{HC}/\Delta E \qquad (3)$$

where a_H and a_{Hg} are hyperfine constants for hydrogen and mercury, respectively. F_{HC} would be $^1/_4$ for an s orbital on mercury and an sp^3 hybrid (25% s) on carbon and F_{HgC} would be $^1/_8$ for an sp hybrid (50% s) on mercury and an sp^3 hybrid on carbon. Looking at the data in Table IV, we see that the hybrid orbital on C directed at Hg remains essentially constant for all substituents on Hg while the hybrid orbital employed by Hg only varies from 57.6% s character in CH_3HgCH_3 to 69.4% s character in $CH_3Hg(OH_2)^+$. This is only slightly smaller than the per cent increase in $J^{(3)}(^{199}Hg-^1H)$ noted in the calculations. This is to be contrasted with the results of Table III where the expected large changes in hybridization for carbon in the test molecules are indeed found.

Table III. Overlap Populations, Per Cent Character. Test Molecules

Compound	C–H	C–X	% s_{C-X}	% s_{C-H}
CH_4	0.8141	0.8141	26.9	26.9
CH_3F	0.8026	0.3481	49.6	27.4
$H_2C{=}CH_2$	0.8128	1.400	50.4	28.5
$H_2C{=}O$	0.8037	0.8105	41.8	31.6
$HC{\equiv}CH$	0.8172	2.022	61.0	37.9

The values for per cent s character of the mercury hybrids seem reasonable. Since the 6s orbital is more nearly matched in energy to the valence orbitals of all the ligands, it is reasonable that the 6s orbital makes a large contribution to all bonds. Raman spectral studies[23a,25] indicate a significant amount of covalency to the HgO bond and the calculated overlap population for the HgO bond is nonnegligible although only about one-third that of the Hg–C bonds. It does not seem likely that the per cent s character of the Hg orbital directed toward the methyl carbon actually varies over a wide enough range to account for the variation in $J^{(3)}(^{199}Hg-^1H)$ coupling constants observed experimentally.

The Hg–C bond of CH_3HgX is strongly covalent and apparently does not change much in strength as is evidenced by the small change in force constant for this bond as a function of X. For CH_3HgCl a value of 2.69 mdyn/Å is found while for CH_3HgCH_3 the force constant is 2.45 mdyn/Å.[23b] Since the 6p orbitals of mercury are so relatively unstable, this small change suggests that no large change in hybridization is taking place.

The simplified expression (3) for $J^{(3)}$ employs a constant term for the excitation energies between occupied and virtual orbitals. The actual calculations were carried out using eq 1 where the calculated energies of the relevant MO's are used. A possible source for the small range in calculated coupling constants might be that the calculated orbital energies show the wrong trend with substituent changes.

The following considerations suggest that this is almost certainly not the major source for the discrepancy. To account for the full range of coupling con-

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(23) (a) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, *ibid.*, **58**, 1495 (1962); (b) *ibid.*, **62**, 1423 (1966).

(24) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(25) R. P. J. Cooney and J. R. Hall, *Aust. J. Chem.*, **22**, 337 (1969).

Table IV. Overlap Populations, Charges, and % s Character. CH_3HgX Molecules

Compound	C–Hg	Hg–X	Q Hg	% s_C	% s_{HgC}	% s_{HgX}	% s_X
CH_3Hg^+	0.5749	0.0000	1.201	33.4	92.0		
$CH_3HgC_2H_5$	0.5791	0.5944	0.936	19.3	57.0	55.1	19.3
CH_3HgCH_3	0.5813	0.5813	0.956	19.3	57.6	57.6	19.3
CH_3HgC_2H	0.5895	0.5554	1.026	19.4	59.6	55.3	30.6
CH_3HgCF_3	0.5673	0.6922	0.800	19.5	51.1	56.2	28.3
$CH_3HgC{\equiv}N$	0.5883	0.5739	1.064	19.3	56.6	55.9	32.2
CH_3HgSH	0.5875	0.5195	0.980	19.4	61.4	53.4	15.5
CH_3HgSCN	0.5932	0.4606	0.980	19.4	63.9	52.9	22.7
CH_3HgBr	0.5983	0.4033	1.080	19.5	64.6	53.4	13.3
CH_3HgCl	0.6000	0.3639	1.110	19.4	65.2	54.8	13.8
$[CH_3HgNCS]$	0.6064	0.3615	1.114	19.3	65.0	53.2	26.3
$CH_3Hg(OH_2)^+$	0.6128	0.2182	1.207	19.2	69.4	58.1	14.0
CH_3HgF	0.6205	0.1153	1.269	19.4	70.1	68.6	10.1

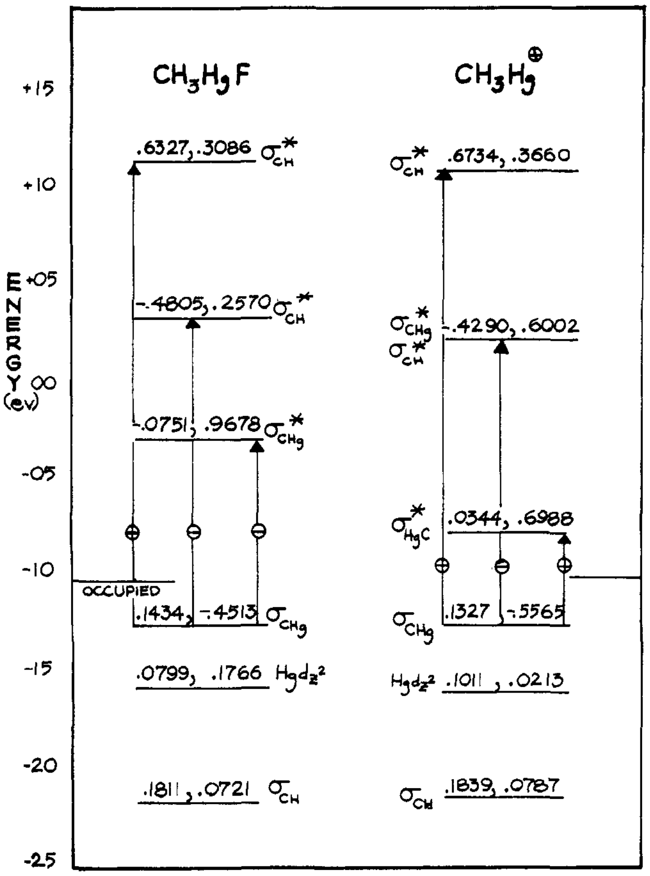

Figure 1. Energy levels and orbital descriptions for major contributions to $J^{(3)}$ (^{199}Hg–^{1}H) in CH_3HgF and CH_3Hg^+. The coefficients of H 1s and Hg 6s orbitals in each MO are listed in that order right to left. The labels designate the principal nature of the orbital, *i.e.*, bonding, antibonding, etc. The sign associated with a transition between levels indicates the sign of the contribution of that orbital pair to $J^{(3)}$ (^{199}Hg–^{1}H).

stants ΔE would have to decrease by a factor of more than 2 from the least electronegative substituent to the most electronegative substituent. Looking at Figure 1 we see that the individual MO's which account for the major contributions to $J^{(3)}(^{199}Hg$–$^{1}H)$ are primarily C–H and C–Hg bonding and antibonding in nature. There is good reason to believe that the C–H bonds change little throughout the series of CH_3HgX molecules studied here. The substitutions are taking place two bonds away from the CH bond and, as noted before, the value of $J(^{13}C$–$^{1}H)$ is essentially constant at 131 ± 2 Hz. In agreement with this, the calculated energies of the σ_{CH} and σ_{CH^*} levels remain almost unaffected by changes in substituent groups X as indicated in Figure 1.

The C–Hg bond is more strongly affected by these substitutions but again there is evidence available showing that this change is small relative to the change in coupling constants or even in the wrong direction. Experimentally it is found that the dissociation energy for the process $CH_3HgX \rightarrow CH_3\cdot + \cdot HgX$ *increases* with increasing electronegativity of the ligand X.[26,27] The following values (kcal/mol) have been reported: for $X = CH_3^-$ (51.5 ± 2), $X = I^-$ (58.5 ± 3), $X = Br^-$ (61.3 ± 3), and $X = Cl^-$ (63.8 ± 3). If these values are interpreted in terms of increasing C–Hg bond energy, then they should also correspond to increasing values of ΔE due to increasing stabilization of σ_{C-Hg} and destabilization of σ_{C-Hg^*}. But this is, of course, contrary to the observed trend in coupling constants. In any case the changes in dissociation energy span about 12 kcal/mol or ~25% of the average bond energy while the coupling constants vary over a considerably wider range.

It is interesting to note that the calculated MO energies vary in a manner just opposite to that expected in that σ^*_{CHg} is most stable (−2.41 eV) in CH_3HgF and least stable (+0.31 eV) in CH_3HgCH_3 with the other cases falling in between (except for CH_3Hg^+). In the actual calculation of $J^{(3)}(^{199}Hg$–$^{1}H)$ the variation in energy of σ^*_{CHg} then serves to slightly increase the range of values for this coupling constant. While predominantly C–Hg antibonding in nature these levels also contain some σ^*_{C-H} and σ^*_{HgX} character and it is apparently the latter which controls the trend in energy. The HgF bond, for instance, is very weakly covalent and any C–F antibonding interaction is also expected to be weak. The effect of mixing σ^*_{CF} character into the predominantly σ^*_{CHg} levels is thus to lower their energy noticeably.

The methylmercury cation represents the extreme example of the above. With no ligand X present, the distribution of σ^* character changes significantly. In particular, the sign of the contribution to $J^{(3)}$ for the lowest energy transition now becomes positive and results in a positive sign for the calculated coupling constant. The unoccupied level involved in the transition is mainly an sp hybrid on Hg directed away from the methyl group. A change of only 0.10 in the co-

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(26) T. Charnley and H. A. Skinner, *J. Chem. Soc.*, 1921 (1951).
(27) H. O. Pritchard, *J. Chem. Phys.*, 25, 267 (1956).

efficient of the 1s orbital from the CH_3HgF case has resulted in a reversal of the sign of the contribution to the overall coupling constant.

If neither the changes in MO coefficients or energies can account for the observed range of coupling constants, there is only one possibility left within the framework of the Fermi contact mechanism and that is the density of the valence s orbitals at their nuclei. Since the H atom is situated two bonds away from the site of substitutions we can direct our attention solely toward the mercury 6s orbital.

From the reported values for the average[4] hyperfine structure constants of Hg^0 (3p), $A_{\mathrm{Hg}} = 1.5 \times 10^{10}$ Hz, and Hg^+ ($^2s_{1/2}$), $A_{\mathrm{Hg}^+} = 4.05 \times 10^{10}$ Hz and eq 4[28] we can determine the expectation value of the mercury 6s orbital at the nucleus for Hg^0 and Hg^+.

$$A_{\mathrm{N}} = (8\pi/3h)g_{\mathrm{e}}\beta_{\mathrm{e}}g_{\mathrm{N}}\beta_{\mathrm{N}}\langle\psi_{\mathrm{N}}|\delta_{(r_{\mathrm{N}})}\psi_{\mathrm{N}}\rangle^2 \tag{4}$$

The results are: $\langle\psi_{6s}|\delta_{(\mathrm{Hg})}|\psi_{6s}\rangle = \pm 4.33$, $\langle\psi_{6s}|\delta_{(\mathrm{Hg}^+)}|\psi_{6s}\rangle = \pm 7.12$ while the Herman–Skillman 6s function for Hg^+ gives -5.922.

In order to at least partially include the effects of the contraction of the Hg 6s orbital, the following procedure was employed. Since the expectation value of the Herman–Skillman function is almost midway between that expected for Hg^0 and Hg^+, it was arbitrarily taken to correspond to a calculated charge (Mulliken population analysis) on mercury of 0.5. Expectation values for other calculated charges (Q_i) were then interpolated or extrapolated linearly according to

$$\langle\psi_{6s}|\delta|Q_i|\psi_{6s}\rangle = -5.922 - (Q_i - 0.5)[\langle\psi_{6s}|\delta|_{(\mathrm{Hg}^+)}|\psi_{6s}\rangle - \langle\psi_{6s}|\delta|_{(\mathrm{Hg})}|\psi_{6s}\rangle] \tag{5}$$

This revised expectation value for the 6s orbital is then used in the coupling constant calculation. The actual MO calculation in each case employs the Herman–Skillman wave function which means that the effect of orbital contraction on the overlaps is being neglected. This is necessitated by the difficulties inherent in trying to interpolate all the coefficients and exponents in the linear combination of Slater-type orbitals being used. The calculated coupling constants of Table II labeled $J^{(3)\prime}$ are the result of this approach.

Allowing for the 6s orbital contraction on a partially cationic mercury center increases the magnitude of all coupling constants as expected but also serves to increase the range of values to something approaching that observed experimentally. Furthermore, the ordering of substituents by increasing coupling constants now resembles that found experimentally much more closely. The order based on calculated J values includes three reversals of position but that based on the J' values only includes one: that for CH_3 and CF_3 as substituents. From other observations it seems that many semiempirical MO methods are less successful with fluorine parameterizations than most other atoms. The large values of J and J' calculated for CH_3HgF are probably related to this general failure.

The very low charge on the mercury atom ($Q_{\mathrm{Hg}} = 0.800$) in CH_3HgCF_3 seems quite out of line with the usual description of the CF_3 group having a σ electron-withdrawing effect compared to CH_3.[29] There is no indication in the calculations of a hyperconjugative interaction between the CF_3 group and the empty 6p orbitals of mercury; it is solely a σ interaction. The calculated charge distribution in this molecule resembles an exaggerated charge alternation effect of the type noted by Pople in CNDO/2 calculations.[30]

In none of these calculations was there any indication that the 5d orbitals of mercury were playing any role in the bonding either to the methyl carbon or to any substituent used including F^-, CN^-, and Br^-. In all cases the overlap populations involving mercury 5d orbitals amounted to less than 8% of the total overlap population between mercury and the atom in question. The 5d orbitals of mercury are apparently best viewed as "core" rather than valence shell orbitals.

In light of this, the calculated vicinal ($J_{^{199}\mathrm{Hg}-^1\mathrm{H}\beta}$) and geminal ($J_{^{199}\mathrm{Hg}-^1\mathrm{H}\alpha}$) coupling constants for the ethylmercury group of $CH_3HgCH_2CH_3$ are particularly interesting (see Tables V and VI). The suggestion has been made that the larger absolute magnitude of the vicinal or longer range coupling constant results from the use of 5d orbitals of mercury in bonding.[9] Not only are the relative signs reproduced here but the absolute and relative magnitudes are quite good. In particular, the ratio of vicinal-to-geminal coupling constants found experimentally (−1.46) is closely reproduced in these calculations both for J's (−1.33) and J''s (−1.35).

Table V. Conformational Dependence of $J_{^{199}\mathrm{Hg}-^1\mathrm{H}\beta}$ in $CH_3HgCH_2CH_3$

Dihedral angle ϕ, deg	$J^{(3)}{}_{^{199}\mathrm{Hg}-^1\mathrm{H}\beta}$, Hz	$J^{(3)}{}_{^{199}\mathrm{Hg}-^1\mathrm{H}\beta}$, Hz
0	+96.5	+152.0
30	+69.9	+109.6
60	+17.5	+27.3
90	+2.5	+3.8
120	+72.3	+113.8
150	+188.9	+296.2
180	+245.8	+383.8

Table VI. Average[a] Coupling Constants in $CH_3HgCH_2CH_3$

	$J_{^{199}\mathrm{Hg}-^1\mathrm{H}\alpha}$	$J_{^{199}\mathrm{Hg}-^1\mathrm{H}\beta}$	$J_{^{199}\mathrm{Hg}-^1\mathrm{HCH_3}}$
Exptl[b,c]	−96	+129	−94
Calcd $J^{(3)\prime}$	−106.2	+155	+114.1
Calcd $J^{(3)}$	−65.3	+86.7	−69.1

[a] Assuming all dihedral angles equally probable for a given hydrogen atom. [b] Reference 2, p 690. [c] Absolute signs assumed although relative signs known from double resonance experiments.

The smooth curve in Figure 2 represents the calculated dependence of the vicinal coupling constant on the dihedral angle ϕ between the C–Hg bond and C–H bond of the coupled atoms. There is apparently not a great deal of experimental coupling constant data for organomercurial systems wherein the dihedral angle is accurately known. The asterisks mark approximate values taken from ref 31. These are scaled uniformly

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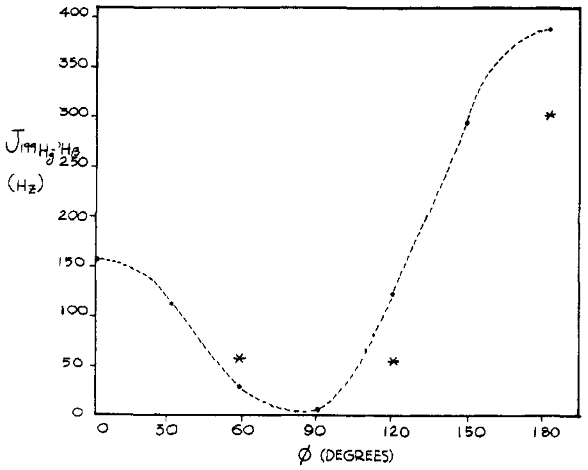

Figure 2. Conformational dependence of $J_{^{199}Hg-^1H_\beta}$ in $CH_3HgCH_2CH_3$. The asterisks mark approximate experimental values from ref 3.

down from values reported for organomercury chlorides to the data calculated for methylethylmercury. The calculated curve resembles very strongly that for vicinal H–H coupling with an exaggerated value for the trans orientation. This curve appears to be at least qualitatively consistent with the experimental data.

Conclusions

These results with inclusion of changes in the effective nuclear change of the 6s orbital of mercury suggest strongly that all the major features of ^{199}Hg–^{1}H spin coupling in saturated organomercurials can be accounted for in terms of a dominant Fermi contact term and little use of mercury's 5d orbitals in bonding. The results may well be quantitative enough to aid in configurational studies of organomercurials or other heavy metal systems such as platinum-containing complexes.

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Electron Spin Resonance Studies of Vinyl, Propargyl, and Butatrienyl Radicals Isolated in Argon Matrices

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Abstract: Electron spin resonance spectra of vinyl, propargyl, and butatrienyl radicals isolated in argon matrices at ~4°K are obtained and analyzed. The analyses were made utilizing a spectrum simulation program which incorporates the effect of the forbidden transitions. An excellent agreement is noted between the spin density distributions assessed from the anisotropies of the hyperfine coupling tensors and those obtained by INDO molecular orbital calculations.

Electron spin resonance spectra of free radicals of the form $H_2C{=}(C)_n{=}C\cdot{-}H$ have been investigated by several groups.[1-7] The specific examples reported are vinyl ($n = 0$), propargyl ($n = 1$), and butatrienyl ($n = 2$) radicals. Fessenden and Schuler[1] obtained the isotropic or " the liquid state" spectra of vinyl and propargyl radicals generated in liquid ethylene and allene, respectively, by a high-energy electron beam. Kochi and Krusic[2] obtained the istropic spectrum of propargyl radicals by abstracting hydrogen from methylacetylene and allene using photochemically induced *tert*-butoxy radicals. Cochran, *et al.*,[3] obtained the anisotropic or " the solid-state" spectrum of vinyl radicals by reacting hydrogen atoms with acetylene trapped within a solid argon matrix. The solid state spectra of propargyl radicals are observed from various organic matrices which had been irradiated with uv or γ-ray at 77°K.[4-6] As for butatrienyl radicals, only the solid-state spectrum obtained from an argon matrix is known.[7]

For a π-electron radical, when the isotropic coupling constant A_{iso} to an α proton is known, the spin density ρ at the p_π orbital of the carbon can be assessed using the relationship of McConnell and Chestnut[8]

$$A_{iso} = Q\rho \qquad (1)$$

The direct application of eq 1 to the present series of radicals is difficult, however, since the proportionality constant Q is known to vary substantially depending upon the type of hybridization of the carbon in question. The magnitude of Q has been shown to range from 23 G for a sp^2-hybridized carbon atom to 35 G

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