

Evidence for Through-space Spin-Spin Coupling Between Mercury and Fluorine

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Summary The insensitivity of ${}^4J({}^{199}\text{Hg} \cdots {}^{19}\text{F})$ in $o\text{-CF}_3\text{C}_6\text{H}_4\text{HgX}$ to the nature of X indicates that there is a substantial 'through-space' contribution to this coupling constant.

THE predominant mechanism for the electron-coupled spin-spin interaction between atomic nuclei is the Fermi contact interaction,¹ and for nuclei which are separated by three or more bonds this involves mainly the electrons and orbitals associated with the formal chemical bonds of the molecule.² In certain circumstances however, the physical separation of a pair of coupled nuclei may be abnormally small, and it has been suggested³ that there may then be a direct 'through-space' contribution to the coupling. Unfortunately, the criteria for recognising such a contribution are not well defined, and it is common to rely upon the observation of a coupling constant which is larger than might otherwise be expected.⁴ Recently Grim and his

co-workers⁵ have shown that the marked temperature dependence of ${}^4J({}^{31}\text{P} \cdots {}^{19}\text{F})$ in tris(*o*-trifluoromethylphenyl)phosphine and related compounds can also be used to provide evidence for a 'through-space' mechanism which involves the phosphorus lone pair.

This communication presents direct evidence that a 'through-bond' mechanism is not the major contributor to ${}^4J({}^{199}\text{Hg} \cdots {}^{19}\text{F})$ in *o*-trifluoromethylphenylmercury derivatives.⁶ The Table gives n.m.r. parameters of *o*-, *m*-, and *p*-($\text{CF}_3\text{C}_6\text{H}_4$)₂Hg and $\text{CF}_3\text{C}_6\text{H}_4\text{HgBr}$. These compounds were made from mercury(II) bromide and the appropriate Grignard reagent, and were examined as concentrated solutions in acetone or CDCl_3 . In all cases the identities of the satellite lines attributed to the presence of ${}^{199}\text{Hg}$ ($I = \frac{1}{2}$, abundance 17%) were confirmed by ${}^1\text{H}\text{-}\{{}^{199}\text{Hg}\}$ or ${}^{19}\text{F}\text{-}\{{}^{199}\text{Hg}\}$ double resonance experiments which were also used to give the ${}^{199}\text{Hg}$ resonance frequencies. With the exception of ${}^4J({}^{199}\text{Hg} \cdots {}^{19}\text{F})$ in the two *ortho*-derivatives, the coupling constants which involve mercury all become

approximately doubled in magnitude when an aryl group is replaced by bromine. This is in fact a quite general phenomenon, and in R_2Hg the replacement of one group R

rotation of the trifluoromethyl group) is only 240 pm. The latter distance is the more significant as it is probable that 'through space' coupling will depend upon $\langle r^{-n} \rangle$ rather

TABLE. *N.m.r. parameters of organomercury compounds*

| Compound | $J(^{199}Hg \dots ^{19}F)$ Hz | $^3J(^{199}Hg \dots H_o)$ Hz | $\Xi(^{199}Hg)$ MHz ^a | $\delta(^{19}F)$ p.p.m. ^b |
|--|----------------------------------|---------------------------------|-------------------------------------|---|
| <i>o</i> -CF ₃ -C ₆ H ₄) ₂ Hg | 26.5 | 110 | 17.89347 | -15.3 |
| <i>o</i> -CF ₃ -C ₆ H ₄ -HgBr | 28.8 | 199.5 | 17.88698 | -14.7 |
| <i>m</i> -CF ₃ -C ₆ H ₄) ₂ Hg | 9.5 | 108 | 17.89600 | -13.9 |
| <i>m</i> -CF ₃ -C ₆ H ₄ -HgBr | 18.3 | 202 | 17.88817 | -13.8 |
| <i>p</i> -CF ₃ -C ₆ H ₄) ₂ Hg | 8.0 | 104 | 17.89492 | -13.7 |
| <i>p</i> -CF ₃ -C ₆ H ₄ -HgBr | 16.7 | 190.5 | 17.88730 | -14.7 |

^a The ¹⁹⁹Hg resonant frequency corrected to a magnetic field strength in which Me₄Si would give a proton resonance of exactly 100 MHz.

^b Relative to external CF₃CO₂H: a negative sign indicates a shift to lower field.

by a much more electronegative group normally affects all the coupling constants between mercury and nuclei in the remaining R group in this way.^{7,8} Examples are $^1J(^{199}Hg-^{13}C)$, $^2J(^{199}Hg \dots H)$, $^3J(^{199}Hg \dots H)$, and $^4J(^{199}Hg \dots H)$ for R = alkyl; $^3J(^{199}Hg \dots H)$, $^4J(^{199}Hg \dots H)$, $^4J(^{199}Hg \dots H)$, $^4J(^{199}Hg \dots ^{19}F)$, and $^5J(^{199}Hg \dots ^{19}F)$ for R = aryl; and $^1J(^{199}Hg-^{31}P)$ for R = (EtO)₂P(O)-. This behaviour is due to the diversion by the more electronegative group of *s*-character into the mercury hybrid orbital used to form the bond to R; there may also be a contribution due to the greater effective nuclear charge of mercury in RHgX which will increase $\psi^2(6s)$ for the mercury atom. It is thus clear from the values for $^3J(^{199}Hg \dots H)$ that *s*-character of the Hg-R bond is varying in the expected manner in the *o*-trifluoromethylphenyl derivatives, but this has very little effect upon $^4J(^{199}Hg \dots ^{19}F)$. Furthermore the couplings between ¹⁹⁹Hg and ¹⁹F in a more distant *m*- or *p*-trifluoromethyl group behave normally. The behaviour of the *ortho*-compounds is thus consistent with domination of $^4J(^{199}Hg \dots ^{19}F)$ by a mechanism other than the normal 'through bond' one.

The mean Hg-F internuclear distance in the *ortho*-derivatives is ca. 350 pm, and the shortest instantaneous mercury-fluorine separation (on the assumption of free

than $\langle r \rangle^{-n}$ where *r* is the mercury-fluorine separation and *n* is fairly large. This short mercury-fluorine distance, and the observed insensitivity of the Hg-F coupling to the *s*-character of the Hg-R bond, therefore provides evidence that a 'through space' mechanism is the main contributor to $^4J(^{199}Hg \dots ^{19}F)$ in the *ortho*-compounds. The sum of the mercury and fluorine van der Waals radii exceeds 340 pm, so there is some steric overcrowding in the *ortho*-compounds; this is usually the case when 'through space' coupling involving fluorine is observed.⁴ This is one of the first examples for which independent experimental evidence of this is available; it also now appears that one of the elements involved may be of low electronegativity.

Geometrical considerations indicate that van der Waals penetration and concomitant 'through space' coupling to fluorine are likely for the magnetic nuclei of elements larger than helium, in their *o*-trifluoromethyl derivatives. However, this will depend upon the extent to which other substituents permit close approach of the trifluoromethyl group; mercury and to a lesser extent phosphorus(III) are particularly favourable in this respect.

I thank the S.R.C. for a grant for the purchase of the JEOL C-60-H spectrometer and other equipment.

(Received, April 20th, 1971; Com. 604.)

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