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Preliminary communication

MERCURY—MERCURY SPIN—SPIN COUPLING IN AN ORGANOMERCURY COMPOUND

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Summary

The ^{199}Hg NMR spectrum of 2-methoxy-1-nitro-3,5-bis(trifluoroacetatomercurio)benzene, prepared by mercuration of 1-methoxy-2-nitrobenzene with mercuric trifluoroacetate in trifluoroacetic acid, shows an AB system attributable to ^{199}Hg^{199}Hg coupling with $^{4}J(^{199}\text{Hg}^{199}\text{Hg})$ 2163 Hz.

Although spin—spin coupling is well established between ^{199}Hg (spin $I = ½$) and isotopes of other Main Group elements with spin $I = ½$, e.g. ^{29}Si [1], ^{117,119}Sn [2], the first example of ^{199}Hg^{199}Hg coupling has only recently been observed, viz. for the compound $Hg_3(AsF_6)_2$ in liquid sulfur dioxide [3]. The coupling was observed as the inner two lines of an AB system (the outer lines being too weak for observation) for which $^{1}J(^{199}\text{Hg}^{199}\text{Hg})$ was calculated to be ca. 140 000 Hz [3]. The assignment was confirmed by measurements at two different field strengths. We now report the first example of ^{199}Hg^{199}Hg coupling in an organomercury compound with observation of a complete AB system.

Reaction of mercuric trifluoroacetate with 1-methoxy-2-nitrobenzene (mol ratio 2/1) in refluxing trifluoroacetic acid for 2 h yielded a yellow precipitate of 1-methoxy-2-nitro-4-trifluoroacetatomercuriobenzene (36%). The filtrate was heated under reflux for a further 8 h giving a yellow precipitate of 2-methoxy-1-nitro-3,5-bis(trifluoroacetatomercurio)benzene, 1 (16%), which was analytically pure with a ^{1}H NMR spectrum [$(CD_3)_2SO$]: 7.84, d, with satellites $^{3}J(^{199}\text{HgH})$ 233 Hz, 1H, H(6); 7.73, d. with satellites $^{3}J(^{199}\text{HgH})$ 229 Hz, 209 Hz, 1H, H(4); 3.91, s, 3H, OMe.

The proton-decoupled ^{199}Hg NMR spectrum of 1 in $(CD_3)_2SO$ is shown in Fig. 1. The major peaks are attributable to molecules with only one ^{199}Hg atom (δ (A) Hg(3); δ (B) Hg(5)), and ν_1, ν_2, ν_3, ν_4 are an AB system from molecules in which both mercury atoms are ^{199}Hg isotopes. The ^{199}Hg^{199}Hg coupling constants (below) are of similar magnitude to the chemical shift difference between δ(A) and δ(B), thus second order effects give a highly distorted AB pattern. From the spectrum with a JEOL FX200 instrument, an observed value of $^4J(^{199}\mathrm{Hg}^{199}\mathrm{Hg})$ 2163 Hz was obtained compared with a calculated value (δ(A), δ(B), ν_3, ν_2 determined from the experimental; ν_1, ν_4 values by $\delta(\mathrm{A}) - \delta(\mathrm{B}) = \sqrt{(\nu_4 - \nu_1)(\nu_3 - \nu_2)}$ [7] with $J = \frac{\nu_1 - \nu_4}{2} - \frac{\nu_2 - \nu_3}{2}$) of 2110 Hz. Confirmation of mercury—mercury coupling was provided by relative changes in the chemical shifts of ν_2 and ν_3 when the spectrum was recorded with a JEOL FX100 spectrometer. In this case, no lines due to ν_1 and ν_4 were observed, but values calculated as above give $^4J(^{199}\mathrm{Hg}^{199}\mathrm{Hg})$ 2155 Hz in good agreement with the observed value (JEOL FX200).

A programme of synthesis of other unsymmetrically disubstituted benzenes is underway in particular to establish values of $^3J(^{199}\mathrm{Hg}^{199}\mathrm{Hg})$ and $^5J(^{199}\mathrm{Hg}^{199}\mathrm{Hg})$. The present $^4J(^{199}\mathrm{Hg}^{199}\mathrm{Hg})$ coupling is expectedly considerably smaller than the reported $^1J(^{199}\mathrm{Hg}^{199}\mathrm{Hg})$ coupling [3].

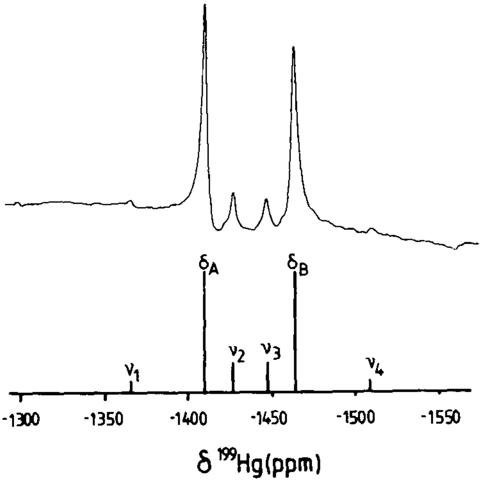

Fig. 1. Proton decoupled ^{199}Hg NMR spectrum of 1 at 35.64 MHz referenced to neat $(\mathrm{CH_3})_2\mathrm{Hg}$. The above spectrum was recorded with an internal d_6 dimethylsulphoxide lock on the sample which was spun. The spectral width was 20 kHz. A delay time of 50 μs caused the rolling baseline, however longer delay times made accurate phasing of the spectrum impossible. Chemical shift values were measured relative to 1 *M* phenylmercuric acetate in dimethylsulphoxide [4], the sample replacement method being used. Subtraction of 1437 ppm gives a value referenced to neat dimethylmercury [5]. The poorly phased signal at ca. −1560 ppm is an impurity due to 1-methoxy-2-nitro-3,4-bis(trifluoroacetatomercurio)benzene where the two Hg atoms have coincident chemical shifts. The identity of the species which gives rise to the small resonance at ca. −1330 ppm has not yet been established [6].

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