The Sign of the Se–H Spin–Spin Coupling Constant in Benzyl Selenol

By W. McFARLANE
(*Chemistry Department, Sir John Cass College, Jewry Street, London, E.C.3*)

CALCULATIONS of nuclear spin–spin coupling constants are an important way of testing quantitative theories of chemical bonding, but valid comparisons of theory and experiment can be made only if the signs of the coupling constants are known. It has been suggested[1] that Karplus's proposal[2] that the directly bonded ^{13}C–H coupling constant is absolutely positive can be extended to other X–H couplings but may break down when neither nucleus involved is hydrogen. There is some evidence for this in that all *determined* signs of reduced directly-bonded coupling constants [the reduced coupling constant is defined[3] as $K(\mathrm{X{-}Y}) = J(\mathrm{X{-}Y})\cdot 2\pi/\hbar\gamma_\mathrm{X}\gamma_\mathrm{Y}$] involving hydrogen are positive[4–6] whereas $K(\mathrm{P^{III}{-}C})$, $K(\mathrm{Se{-}C})$, and $K(\mathrm{Te{-}C})$ are negative.[7,8] The molecular oribtal treatment of coupling constants of Pople and Santry[3] suggests that there is a parallelism between H and C coupling constants, and that negative values are most likely to occur with elements in the last groups of the periodic table.

The low abundance and quadrupole moment of ^{17}O, together with the tendency of protons attached to oxygen to be involved in chemical exchange, make the determination of the sign of $^1K(\mathrm{O{-}H})$ difficult. However selenium does not suffer from these disadvantages, and benzyl selenol, $\mathrm{PhCH_2SeH}$, was chosen for the determination of the sign of $^1K(\mathrm{Se{-}H})$. The compound was made, following Foster's general procedure,[9] by the reaction between benzylmagnesium chloride and selenium, followed by treatment with hydrochloric acid, and was distilled at 96—97°/18 mm.

The ^{1}H n.m.r. spectrum, which was recorded on a Varian HA 100 spectrometer equipped for heteronuclear double resonance experiments,[10] consisted of a multiplet at τ 2·8 (aromatic protons), a doublet at τ 6·51 [methylene protons, $^3J(\mathrm{H{-}SeC{-}H}) = 6{\cdot}4$ c./sec.], and a 1:2:1 triplet at τ 10·09 (proton attached to Se). Molecules containing the isotope ^{77}Se (spin $I = \frac{1}{2}$, abundance = 7·5%) gave satellites of the doublet [$|^2J(^{77}\mathrm{Se{-}H})| = 12{\cdot}8$ c./sec.] and of the triplet [$|^1J(^{77}\mathrm{Se{-}H})| = 42{\cdot}2$ c./sec.]. Irradiation with a weak r.f. field [amplitude given by $\mathrm{H_2}\gamma(\mathrm{Se})/2\pi \simeq 1$ c./sec.] at the ^{77}Se resonant frequency (*ca.* 19·07 Mc./sec.) and observations of these satellites showed that the ^{77}Se spectrum consisted of the expected triplet of doublets, and established that all three coupling constants are of the same sign. It is reasonable to assign a positive value to $^3J(\mathrm{H} \cdots \mathrm{H})$ since in similar molecules such couplings are positive and are quite insensitive to the nature of the intervening atoms. The positive sign of the geminal ^{77}Se–H coupling is then in agreement with that found[8] in $\mathrm{Me_2Se}$ and $\mathrm{Me_3Se^+}$, and is of similar magnitude. The reduced directly bonded Se–H coupling is therefore positive and has a magnitude of $18{\cdot}8 \times 10^{20}$ cm.$^{-3}$. This is quite small for a coupling involving an element in the third row of the Periodic Table (compare $^1K(\mathrm{O{-}H}) = \pm\ 45$, $^1K(\mathrm{P^{III}{-}H}) = +\ 40$, $K(\mathrm{Si{-}H}) = +\ 90$, and $^1K(\mathrm{Ge{-}H}) = (+)\ 233$, all $\times\ 10^{20}$ cm.$^{-3}$) and to this extent the predictions of Pople and Santry are borne out, although there is clearly no parallelism between the C and H couplings.

Part of this work was done at the National Physical Laboratory, Teddington, in the Division of Molecular Science, and I thank Dr D. H. Whiffen for advice.

(*Received, July 20th,* 1967; *Com.* **747.**)

---

[1] S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *J. Amer. Chem. Soc.*, 1963, **85**, 2664.
[2] M. Karplus, *J. Amer. Chem. Soc.*, 1962, **84**, 2458.
[3] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.
[4] E. L. Mackor and C. MacLean, *J. Chem. Phys.*, 1966, **44**, 64.
[5] W. McFarlane, *J. Chem. Soc.*, (*A*), 1967, 1275.
[6] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, 1966, **88**, 2689.
[7] W. McFarlane, *Chem. Comm.*, 1967, 58.
[8] W. McFarlane, *Mol. Phys.*, 1967, **12**, 243.
[9] D. G. Foster, "Organic Syntheses", Vol. 24, p. 89.
[10] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 528.