Long-range H–H Spin–Spin Coupling in Methyl Sulphide Derivatives of Silane and Germane

By J. T. WANG and C. H. VAN DYKE*

(*Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania* 15213)

LONG-RANGE H–H spin–spin coupling has been observed in the ^{13}C and ^{29}Si satellites of the proton nuclear magnetic resonance (n.m.r.) spectra of Me_2S and $(SiH_3)_2S$.[1,2] It has not been possible to measure this coupling in the germanium analogue, since proton–germanium coupling has not been observed in the ^1H n.m.r. spectra of substituted derivatives of germane.[3,4] Information about the magnitude of long-range proton coupling through sulphur in germanium hydride systems can easily be obtained from the high-resolution ^1H n.m.r. spectrum of an unsymmetrical sulphur derivative such as germyl methyl sulphide, GeH_3SMe. We report the preparation and high-resolution ^1H n.m.r. data for this new compound.

Germyl methyl sulphide was prepared in a standard high-vacuum system by the interaction of GeH_3Cl with solid NaSMe at room temperature. The material could not be completely purified by low-temperature fractionation and was purified by vapour-phase chromatography using a 20% benzyl ether–Chromosorb W column. The molecular weight (found, 122·7; calc. 122·7), mass-spectral fragmentation pattern, and infrared spectrum are all in agreement with the formulation of the compound as GeH_3SMe.

The high-resolution ^1H n.m.r. spectrum of GeH_3SMe was determined on 20% and 90% solutions (by volume) in cyclohexane with a drop of tetramethylsilane added.† The spectrum consisted of two absorptions at τ 7·95 ±0·01 (CH_3 protons) and 5·52 ± 0·01 (GeH_3 protons), each of which had the appearance of a 1 : 3 : 3 : 1 quartet. It is obvious that long-range proton spin–spin coupling was occurring. The measured coupling constant, $J(HH')$, is 0·60 ± 0·05 c./sec. No ^{73}Ge–H coupling was observed. Chemical shifts are given at infinite dilution; $J(HH')$ did not vary with concentration.

In order to establish the trend of this long-range proton coupling through sulphur in these parent Group IV hydride systems, the high-resolution ^1H n.m.r. spectrum of SiH_3SMe[5] was also determined under the same conditions. For this compound, $J(HH')$ was found to be 0·45 ±0·05 c./sec. The values of $J(HH')$, in Me_2S and $(SiH_3)_2S$ are 0·30 ±0·05 and 0·70 ±0·02 c./sec. respectively.[1,2] It is apparent from these data that the absolute magnitude of the proton–proton spin–spin coupling constant through the C–S–M linkage (M = C, Si, and Ge) *increases* as the Group IV element is changed from carbon to silicon to germanium. The same trend is reflected in the relative magnitude of the analogous coupling in Me_2S and $(SiH_3)_2S$.

Although structural information is not available for all of these compounds, it is reasonable to assume that a simple H–H distance factor is not responsible for this trend. The long-range coupling appears to be dependent on the presence of a sulphur atom in the molecule, since the analogous coupling in $(SiH_3)_2O$, SiH_3OMe, and GeH_3OMe has not been observed, even though in certain cases attempts were made to find it.[1,4,6] If it is present in the oxygen derivatives, its magnitude is evidently considerably less than it is in the sulphur analogues. Long-range proton coupling in other hydride derivatives of the Group IV elements is currently under investigation.

We thank Mrs. Margaret Gjertsen and Mr. Gerst Gibbon for obtaining the n.m.r. spectra.

(*Received, May* 12*th*, 1967; *Com.* 465.)

---

† N.m.r. spectra were determined on a Varian Associates A-60 spectrometer at room temperature. Calibration was by the standard side-band technique.

[1] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, 1962, **36**, 2628.
[2] N. van Meurs, *Spectrochim. Acta*, 1963, **19**, 1695.
[3] E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, *J. Mol. Spectroscopy*, 1964, **19**, 299.
[4] G. A. Gibbon, Y. Rousseau, C. H. Van Dyke, and G. J. Mains, *Inorg. Chem.*, 1966, **5**, 114.
[5] B. Sternbach and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1961, **23**, 225.
[6] H. J. Campbell-Ferguson, E. A. V. Ebsworth, A. G. MacDiarmid, and T. Yoshioka, *J. Phys. Chem.*, 1967, **71**, 723.

Printed by W Heffer & Sons Ltd Cambridge England