

OBSERVATIONS OF THE PROTON MAGNETIC RESONANCE SPECTRA OF CERTAIN GROUP IVB DERIVATIVES OF SULPHUR, SELENIUM AND ARSENIC

E. W. ABEL AND D. B. BRADY

Department of Inorganic Chemistry, The University, Bristol (Great Britain)

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Table 1 reports the chemical shifts of the compounds $(\text{CH}_3)_3\text{MSCH}_3$ and $(\text{CH}_3)_3\text{MSM}(\text{CH}_3)_3$ for $M = \text{C, Si, Ge, Sn and Pb}$. The τ values of the M-methyl protons in both series of sulphur compounds follow qualitatively the order $\text{Si} > \text{Sn} > \text{Ge} > \text{Pb} > \text{C}$, previously established¹ for the tetramethyl derivatives of the Group IVB elements. The present measurements cast no new light on the controversy^{2,3} regarding the reason for this particular order of the elements, but they do confirm the order for two other series of Group IVB compounds. The chemical shifts of the S-methyl protons in the $(\text{CH}_3)_3\text{MSCH}_3$ series vary over a much smaller range, and except for the slight anomaly in the case of carbon, the τ values decrease steadily down the group. Owing to the changes taking place in electronegativity, possible π -bonding, bond strengths, diamagnetic anisotropy etc., it would be difficult to ascribe such a steady decrease to any one reason.

As expected, the presence of substituent electronegative sulphide or methylthio groups causes a deshielding of the M-methyl protons compared with the tetramethyl derivatives. Contrary to electronegativity arguments, however, it is notable that the deshielding of the protons for each member of the series $(\text{CH}_3)_3\text{M-S-M}(\text{CH}_3)_3$ is greater than that of the corresponding member of the $(\text{CH}_3)_3\text{MOM}(\text{CH}_3)_3$ series⁴. This we believe to be due to the induced currents in the localised electrons of the M-S bonds, the larger sulphur atom causing an anisotropic deshielding greater than the

TABLE 1

PROTON CHEMICAL SHIFTS OF THE SERIES $(\text{CH}_3)_3\text{MSCH}_3$ AND $[(\text{CH}_3)_3\text{M}]_2\text{S}$
 $M = \text{C, Si, Ge, Sn and Pb}$

| $(\text{CH}_3)_3\text{MSCH}_3$ | $\tau(\text{M-CH}_3)$ | $\tau(\text{S-CH}_3)$ | $[(\text{CH}_3)_3\text{M}]_2\text{S}$ | $\tau(\text{M-CH}_3)$ |
|---------------------------------|-----------------------|-----------------------|--|-----------------------|
| $(\text{CH}_3)_3\text{CSCH}_3$ | 8.75 | 8.08 | $[(\text{CH}_3)_3\text{C}]_2\text{S}$ | 8.63 |
| $(\text{CH}_3)_3\text{SiSCH}_3$ | 9.78 ^a | 8.13 | $[(\text{CH}_3)_3\text{Si}]_2\text{S}^b$ | 9.69 |
| $(\text{CH}_3)_3\text{GeSCH}_3$ | 9.52 | 8.04 | $[(\text{CH}_3)_3\text{Ge}]_2\text{S}^b$ | 9.47 |
| $(\text{CH}_3)_3\text{SnSCH}_3$ | 9.61 | 8.00 | $[(\text{CH}_3)_3\text{Sn}]_2\text{S}^b$ | 9.61 |
| $(\text{CH}_3)_3\text{PbSCH}_3$ | 8.80 | 7.78 | $[(\text{CH}_3)_3\text{Pb}]_2\text{S}$ | 8.81 |

^a Corresponding oxygen compound $(\text{CH}_3)_3\text{SiOCH}_3$ has $\tau(\text{Si-CH}_3)$ 9.95 and $\tau(\text{O-CH}_3)$ 6.68.^b These three compounds have been previously measured and the figures of Schmidbaur^{9,10} when converted to τ values are in excellent agreement with our own.

TABLE 2

PROTON CHEMICAL SHIFTS AND TIN-PROTON COUPLING CONSTANTS FOR THE SERIES OF COMPOUNDS $(CH_3)_3A_nSn(SCH_3)_n$

| $(CH_3)_3A_nSn(SCH_3)_n$ | $\tau(M-CH_3)$ | $\tau(S-CH_3)$ | $J(^{119}Sn-C-H)$ | $J(^{117}Sn-C-H)$ | $J(^{119}Sn-S-C-H)$ | $J(^{117}Sn-S-C-H)$ |
|--------------------------|----------------|----------------|-------------------|-------------------|---------------------|---------------------|
| $(CH_3)_3Sn$ | 9.92 | | 54.0 | 51.5 | | |
| $(CH_3)_2SnSCH_3$ | 9.61 | 8.00 | 56.9 | 54.5 | 37.5 | 36.0 |
| $(CH_3)_2Sn(SCH_3)_2$ | 9.29 | 7.84 | 61.2 | 58.5 | 44.2 | 42.6 |
| $CH_3Sn(SCH_3)_3$ | 9.06 | 7.73 | 66.6 | 63.5 | 56.7 | 53.2 |
| $Sn(SCH_3)_4$ | | 7.68 | | | | 66.0 |

TABLE 3

TIN-PROTON COUPLING CONSTANTS FOR AN ORGANOTIN ARSINE AND AN ORGANOTIN SELENIDE:

| $(CH_3)_3SnNCH_3[S(CH_3)_3]^a$ | $(CH_3)_3SnSeCH_3$ | $(CH_3)_3SnAs(CH_3)_2$ |
|--------------------------------|----------------------|------------------------|
| $J(^{117}Sn-C-H)$ | $J(^{117}Sn-C-H)$ | $J(^{117}Sn-C-H)$ |
| 52.5 | 53.4 | 47.0 |
| $J(^{119}Sn-C-H)$ | $J(^{119}Sn-C-H)$ | $J(^{119}Sn-C-H)$ |
| 55.0 | 55.9 | 49.5 |
| $J(^{117}Sn-N-C-H)$ | $J(^{117}Sn-Se-C-H)$ | $J(^{117}Sn-As-C-H)$ |
| 43.0 | 30.0 | 51.0 |
| | | $J(^{119}Sn-As-C-H)$ |
| | | 53.5 |

^a Data from Ref. 11.

largely inductive deshielding of the oxygen compounds. In this respect the S-M-CH₃ protons are analogous to the β -protons of ethyl derivatives. In the case of heavier atom ethyl derivatives, while the α -protons appear to have their shielding dominated by inductive effects (though an anisotropic factor is certainly present), for geometrical reasons the shielding of the β -protons is dominated by the induced currents and usually shows opposite trends to the α -protons⁵.

This point is further brought out by a comparison of the proton shieldings in (CH₃)₃SiOCH₃ [τ (Si-CH₃) = 9.95 and τ (O-CH₃) = 6.68] and (CH₃)₃SiSCH₃ [τ (Si-CH₃) = 8.75 and τ (S-CH₃) = 8.63]. Whilst the α -protons of the alkoxy and alkylthio groups have relative shieldings in accordance with the greater electronegativity of the oxygen, the β -protons of the methylsilicon groups have the reverse relative values, showing the dominance of the sulphur-silicon bond anisotropy on protons with β -geometry.

Table 2 reports the proton chemical shifts and tin-proton coupling constants for the series (CH₃)_nSn(SCH₃)_{4-n}. Deshielding of the Sn-CH₃ protons increases steadily with successive introduction of the electronegative methylthiogroups, but in the light of the arguments above, it is likely that the anisotropy of the tin-sulphur bond also plays a part in the deshielding of these β -protons.

A steady, but much smaller, decrease of shielding is noted for the S-CH₃ protons with successive introduction of alkylthio groups from (CH₃)₃SnSCH₃ to Sn(SCH₃)₄. A steadily increasing positive charge on tin, resulting from the increasing number of attached electronegative methylthio groups, could cause such shifts.

In the series of compounds reported in Table 2 well defined satellites due to the spin active isotopes ¹¹⁷Sn and ¹¹⁹Sn are observed for both tin-methyl and sulphur-methyl protons. In the case of the sulphur-methyl protons, however, the compounds must be obtained in a state of some purity for the ¹¹⁷Sn and ¹¹⁹Sn satellites to be well resolved. (as *e.g.* in Fig. 1). Extremely small quantities of impurities

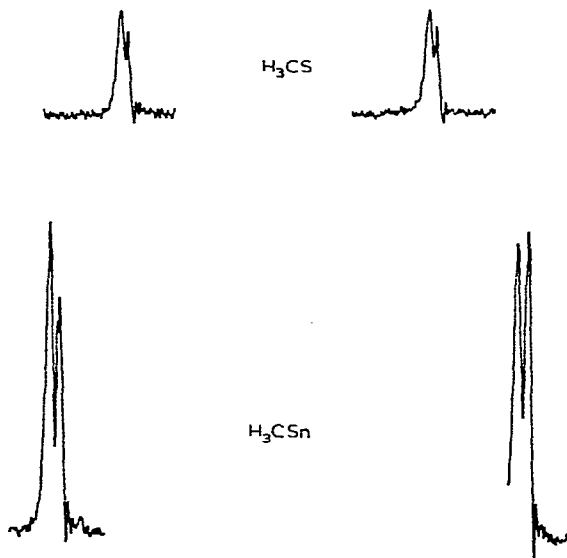


Fig. 1. ¹¹⁷Sn and ¹¹⁹Sn coupled protons in Me₃SnSMe.

such as acid or thiol cause the collapse of these separated ^{117}Sn and ^{119}Sn satellites to an unresolved single satellite*. The presence of further impurity causes the complete collapse of the satellites. It would appear that impurities allow rapid exchange of methylthio groups, which in turn causes the deterioration of the satellite spectra. We were unable to obtain $(\text{CH}_3\text{S})_4\text{Sn}$ in a sufficiently high state of purity to completely resolve the ^{117}Sn and ^{119}Sn satellites for accurate measurement, hence the centre of the poorly resolved doublet is quoted as the mean Sn-S-C-H coupling constant.

Assuming the dominant Fermi contact contribution to the coupling is proportional to the *s*-character in the $\text{CH}_3\text{-Sn}$ bond, and that *s*-character concentrates in bonds to the least electronegative substituents, the steady increase of $J(\text{Sn-C-H})$ with successive methylthio introduction is understandable.

The tin thiomethyl proton coupling is smaller, but also steadily increases with successive methylthio addition. This would appear to indicate a steady enhancement of the electron density in the Sn-S bonds with increasing methylthio content. This may be due to an increase in Sn-S π -bonding with increasing numbers of methylthio groups; a somewhat unexpected situation, but already shown to exist⁶ in the methylmethoxysilanes with increasing methoxy content.

We have also observed coupling of tin to protons over three different bonds for selenium and arsenic, as shown in Table 3. Again, the separated ^{117}Sn and ^{119}Sn couplings through selenium and arsenic could be observed, provided the samples were purified with care. It is notable that whereas the β -protons of the amino-, thio- and seleno-methyl groups have lower $J(\text{Sn-H})$ than the corresponding methyl groups directly attached to tin in the same compound, in the case of the arsenic compound the β -coupling through arsenic is larger than $J(\text{Sn-H})$ for the methyl-tin protons. Many cases of β -couplings larger than α -couplings are known^{7,8}, and usually involve opposite signs for the α and β coupling constants.

EXPERIMENTAL

All spectra were recorded with a Varian Associates A60 spectrometer as 30% solutions in carbon tetrachloride, using 1% tetramethylsilane as internal reference, except $(\text{CH}_3)_3\text{SnSeCH}_3$ and $(\text{CH}_3)_3\text{SnAs}(\text{CH}_3)_2$ for which no solvent was incorporated.

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SUMMARY

Proton magnetic resonance shieldings for the three series of compounds,

* *Note added in proof.* This point is well illustrated in a recent paper (E. V. VAN DEN BERGHE, D. F. VAN DE VONDEL AND G. P. VAN DER KELEN, *Inorg. Chim. Acta*, 1 (1967) 97), where resolution of the ^{117}Sn and ^{119}Sn to proton couplings was not observed via sulphur, presumably due to impurity.

$(\text{CH}_3)_n\text{Sn}(\text{SCH}_3)_{4-n}$, $(\text{CH}_3)_3\text{MSM}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{MSCH}_3$ ($\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and Pb), and the various tin-proton coupling constants of the compounds $(\text{CH}_3)_n\text{-Sn}(\text{SCH}_3)_{4-n}$, $(\text{CH}_3)_3\text{SnSeCH}_3$ and $(\text{CH}_3)_3\text{Sn-As}(\text{CH}_3)_2$ are recorded and discussed.

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