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PMR SPECTRA OF HEXAMETHYL DERIVATIVES OF GROUP IV-M ELEMENTS, $(CH_3)_3MM'(CH_3)_3$

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SUMMARY

Proton chemical shifts and spin–spin coupling constants are presented and discussed for the compounds, $(CH_3)_3MM'(CH_3)_3$, where M and M′ are C, Si, Ge and Sn.

INTRODUCTION

The series of compounds, $(CH_3)_3M\text{–}M'(CH_3)_3$, where M and M′ represent C, Si, Ge and Sn, was prepared during an investigation[1] of cleavage of bonds between the elements of Group IV-M. The present report was prompted by observations of trends of the NMR spectral parameters.

RESULTS AND DISCUSSION

Proton chemical shifts and ${}^1J({}^{13}CH)$ coupling constants are presented in Tables 1 and 2, respectively. Values of ${}^2J({}^{29}SiH)$, ${}^2J(SnH)$, ${}^3J(SnH)$, and δ and ${}^1J({}^{13}CH)$ for $(CH_3)_4M$ are collected in Table 3. Long-range silicon–hydrogen coupling

TABLE 1

${}^1H$ CHEMICAL SHIFT DATA OF $(CH_3)_3MM'(CH_3)_3$ COMPOUNDS[a]

$(CH_3)_3C\text{–}\underline{C(CH_3)_3}$ 0.868	$(CH_3)_3C\text{–}\underline{Si(CH_3)_3}$ −0.053	$(CH_3)_3C\text{–}\underline{Ge(CH_3)_3}$ 0.041	$(CH_3)_3C\text{–}\underline{Sn(CH_3)_3}$ −0.005
$(CH_3)_3Si\text{–}\underline{C(CH_3)_3}$ 0.872	$(CH_3)_3Si\text{–}\underline{Si(CH_3)_3}$ 0.034	$(CH_3)_3Si\text{–}\underline{Ge(CH_3)_3}$ 0.120	$(CH_3)_3Si\text{–}\underline{Sn(CH_3)_3}$ 0.040
$(CH_3)_3Ge\text{–}\underline{C(CH_3)_3}$ 0.926	$(CH_3)_3Ge\text{–}\underline{Si(CH_3)_3}$ 0.103	$(CH_3)_3Ge\text{–}\underline{Ge(CH_3)_3}$ 0.198	$(CH_3)_3Ge\text{–}\underline{Sn(CH_3)_3}$ 0.115
$(CH_3)_3Sn\text{–}\underline{C(CH_3)_3}$ 1.079	$(CH_3)_3Sn\text{–}\underline{Si(CH_3)_3}$ 0.228	$(CH_3)_3Sn\text{–}\underline{Ge(CH_3)_3}$ 0.332	$(CH_3)_3Sn\text{–}\underline{Sn(CH_3)_3}$[b] 0.210[a]

[a] Positive shifts are downfield from the reference tetramethylsilane. [b] Ref. 3.

($^3J(^{29}SiH)$ 6.0 Hz) occurs in $(CH_3)_3CSi(CH_3)_3$. Measurements for $(CH_3)_3SiSn(CH_3)_3$ and $(CH_3)_3GeSn(CH_3)_3$ agree with values reported earlier[2]. For $(CH_3)_3PbPb(CH_3)_3$ in benzene, Clark *et al.* reported δ(H) (1.01 ppm), $^1J(^{13}CH)$ (134.4 Hz), $^2J(^{207}PbH)$ (−42.1 Hz), $^3J(^{207}PbH)$ (22.9 Hz) and other spectral parameters[7].

Several trends in chemical shifts can be noted. For each $M'(CH_3)_3$ group in $(CH_3)_3MM'(CH_3)_3$, variation of M from C to Si to Ge to Sn (columns in Table 1) shifts the proton resonance downfield. This downfield shift with congeners of higher atomic number in the β position has been observed also for the methyl resonances of CH_3CH_2X[8a,8b], $(CH_3)_2CHX$[9], $(CH_3)_3CX$[10], $(CH_3)_3SiX$[11], $[(CH_3)_3Si]_2Y$[11], $(CH_3)_3GeX$[12], $[(CH_3)_3Ge]_2Y$[12], $(CH_3)_3SnX$[12], $(CH_3)_2SnX_2$[13], CH_3SnX_3[13], $[(CH_3)_3Sn]_2Y$[12], $(CH_3)_3PbX$[13], and $(CH_3)_3MS\underline{CH}_3$*[14]. The dominant contribution to chemical shift differences of methyl groups within each of these series including $(CH_3)_3MM'(\underline{CH}_3)_3$ appears to be magnetic anisotropy[8b,10].

TABLE 2

$^1J(^{13}CH)$[a] COUPLING CONSTANTS OF $(CH_3)_3MM'(CH_3)_3$ COMPOUNDS

$(CH_3)_3C–C(\underline{CH_3})_3$	$(CH_3)_3C–Si(\underline{CH_3})_3$	$(CH_3)_3C–Ge(\underline{CH_3})_3$	$(CH_3)_3C–Sn(\underline{CH_3})_3$
124.2	118.6	124.3	126.9
$(CH_3)_3Si–C(\underline{CH_3})_3$	$(CH_3)_3Si–Si(\underline{CH_3})_3$	$(CH_3)_3Si–Ge(\underline{CH_3})_3$	$(CH_3)_3Si–Sn(\underline{CH_3})_3$
125.0	118.7	125.3	127.9
$(CH_3)_3Ge–C(\underline{CH_3})_3$	$(CH_3)_3Ge–Si(\underline{CH_3})_3$	$(CH_3)_3Ge–Ge(\underline{CH_3})_3$	$(CH_3)_3Ge–Sn(\underline{CH_3})_3$
124.5	120.0	125.7	128.5
$(CH_3)_3Sn–C(\underline{CH_3})_3$	$(CH_3)_3Sn–Si(\underline{CH_3})_3$	$(CH_3)_3Sn–Ge(\underline{CH_3})_3$	$(CH_3)_3Sn–Sn(\underline{CH_3})_3$
124.1	120.1	126.0	+128.0[b]

[a] Hz. [b] Ref. 4.

TABLE 3

MISCELLANEOUS NMR SPECTRAL PARAMETERS

M	$(CH_3)_3MSi(CH_3)_3$ $^2J(^{29}SiH)$ (Hz)	$(CH_3)_3MSn(CH_3)_3$		$(CH_3)_4M$	
		$^3J(^{119}SnH)$[a] (Hz)	$^2J(^{119}SnH)$[a] (Hz)	δ (ppm)[b]	$^1J(^{13}CH)$ (Hz)[c]
C	6.3[d]	65.8	49.6	0.927	124.3
Si	6.40	30.8	47.1	0.000	118.2
Ge	6.1	26.9	48.7	0.127	124.4
Sn	6.9	−17.3[e]	49.5[e]	0.070	127.7
Pb				0.72[f]	134.2

[a] Also $J(^{117}SnH)$ was observed in each case. $J(^{117}SnH)$ 0.954 × $J(^{119}SnH)$. [b] In dilute CCl_4 with TMS as the reference. Ref. 3. [c] Ref. 5. [d] $^3J(^{29}SiH)$ 6.0 Hz. [e] Ref. 4. [f] Ref. 6.

Another trend may be seen by comparing the chemical shifts of $(CH_3)_4M$ (column 4, Table 3) and $(\underline{CH}_3)_3(t\text{-}C_4H_9)M$ (row 1, Table 1). In each case substituting

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* The value for $\delta[(CH_3)_3CS\underline{CH}_3]$ is slightly anomalous.

a tert-butyl group for a methyl group shifts the resonance of the remaining methyls to higher field.

As M' is varied with M constant in the $(CH_3)_3M{-}M'(\underline{CH}_3)_3$ series, $\delta[M'(CH_3)_3]$ shifts upfield in the order $C < Ge < Sn < Si$ (rows in Table 1)**. The same order was observed for the $(CH_3)_4M'$ series, Table 3, and interpreted in terms of electronegativities of M'[15]. Different sequences, depending upon whether changes at the β position or the contiguous position occur, are expected owing to attenuation of the inductive effect by approximately one-tenth[16] thru each bond. For the $(CH_3)_6M_2$ series (diagonal of Table 1), the contiguous and the β metal atom are being changed, and both M–M bond anisotropy and inductive effects apparently determine the order of $\delta(CH_3)$. Since for compounds having a tert-butyl bonded to C, N, O or F, $\delta[(CH_3)_3C{-}]$ increases monotonically with increasing electronegativity of the first-row element (0.25 ppm/χ unit)[10], it is interesting to compare available[10] $\delta[(CH_3)_3C]$ values for other rows in the periodic system: $\delta[(\underline{CH}_3)_3C{-}Si(CH_3)_3]$ (0.872 ppm), $\delta\{[(CH_3)_3C{-}S]_2\}$ (1.280 ppm), $\delta[(CH_3)_3CCl]$ (1.592 ppm); $\delta[(\underline{CH}_3)_3CGe(CH_3)_3]$ (0.926 ppm), $\delta[(CH_3)_3CBr]$ (1.778 ppm); and $\delta[(\underline{CH}_3)_3CSn(CH_3)_3]$ (1.079 ppm), $\delta[(CH_3)_3CI]$ (1.940). Thus within rows in the periodic system, proton resonance shifts downfield with increasing electronegativity of the substituent bound to the tert-butyl group although the magnitudes of the shifts are much too great to be accounted for by inductive effects alone.

For each of the four series of $(CH_3)_3M{-}M'(CH_3)_3$ having M constant and M' variable, $^1J(^{13}CH)$ increases as M' changes from Si to C to Ge to Sn. This variation of $^1J(^{13}CH)$, evident within rows of Table 2, is the same as that reported for the $(CH_3)_4M$ series. No other simple patterns of $^1J(CH)$ values are obvious. McFarlane[17] concluded that variations in $^1J(CH)$ could be accounted for by changes in *s*-character if the substituent electronegativities are similar, or by variations in the substituent electronegativities if the bulk of the substituent varies only slightly. Although compounds in each column in Table 2 roughly fulfill both conditions, no simple trend emerges. The absence of trends within columns in Table 2 contrasts with observations[11] of the series $(CH_3)_3SiX$ [$^1J(^{13}CH)$ 118.8 Hz (F), 120.5 (Cl), 121.0 (Br), and 121.5 (I)] and $[(CH_3)_3Si]_2Y$ [$^1J(^{13}CH)$ 118.0 (O), 119.5 (S), and 120.5 (Se)]. For four analogous series, $(CH_3)_3GeX$, $[(CH_3)_3Ge]_2Y$, $(CH_3)_3SnX$, and $[(CH_3)_3Sn]_2Y$, there are irregular variations[12].

For the $(CH_3)_3SnM(CH_3)_3$ series, $^3J(^{119}SnH)$ decreases markedly as the size of M increases while $^2J(^{119}SnH)$ varies only slightly and irregularly. For both trimethyl-tert-butylsilane and trimethyl-tert-butyltin, $^2J(MH)$ is less than the corresponding reported values for $(CH_3)_4M$. Dimethyldi-tert-butyltin exhibits[18] an even smaller $^2J(MH)$ value (45 Hz). A strange variation in $J(^{119}Sn{-}H)$ with increasing numbers of intervening bonds occurs in the series: $Sn(CH_3)_4$, $^2J(^{119}Sn{-}H)$ 54.0 Hz[19], $(CH_3)_3SnC(CH_3)_3$, $^3J(^{119}Sn{-}H)$ 65.8 Hz, $Sn[CH_2C(CH_3)_3]_4$, $^4J(^{119}Sn{-}H)$ 107.9 Hz[20], and $Sn[CH_2CH_2C(CH_3)_3]_4$, $^5J(^{119}Sn{-}H)$ is not observable[21].

EXPERIMENTAL

Trimethyl-tert-butylsilane was prepared by the reaction of tert-butyllithium

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** There is a minor exception in the 4th row, Table 1.

(0.16 mole) with trimethylfluorosilane (0.13 mole) at 0° under a helium atmosphere. The volatile products were removed from lithium fluoride under vacuum, and trimethyl-tert-butylsilane was purified by trap-to-trap distillation; m.p. 76° (lit[22]. 77°), 82% yield. (Found: C, 64.54; H, 14.02; Si, 21.35. $C_7H_{18}Si$ calcd.: C, 64.52; H, 13.92; Si, 21.56%).

Trimethyl-tert-butylgermane was prepared from the combination of tert-butyllithium (0.063 mole) in hexane (35 ml) with trimethylbromogermane (0.037 mole) under a helium atmosphere. The mixture was refluxed for 2 h and products distilling above 70° were collected. A solid was isolated by vapor phase chromatography (VPC) and recrystallized from ethyl ether at −78°[23], m.p., 71–72°. (Found: C, 47.56; H, 10.95; Ge, 41.99; $C_7H_{18}Ge$ calcd.: C, 48.09; H, 10.38; Ge, 41.52%.)

Trimethyl-tert-butyltin was obtained by the dropwise addition of trimethyltin chloride (0.05 mole) dissolved in pentane (15 ml) to tert-butyllithium (0.06 mole) in pentane under a helium atmosphere. The solution was refluxed for 1 h. A fraction containing the desired product was obtained by fractional distillation and purified by VPC, low temperature recrystallization[23], and finally trap-to-trap distillation; m.p. 31.5° 41%, yield. (Found: C, 38.31; H, 8.19. $C_7H_{18}Sn$ calcd.: C, 38.06; H, 8.21%.)

Hexamethylethane[24] and the other compounds were prepared previously[1].

A Hewlett–Packard Model 5752 gas chromatograph with a thermal conductivity detector and variable oven temperature control was used to purify the compounds. Separations and analyses were performed on columns packed with Apiezon L on firebrick (analytical, 1/8″ × 12′, and preparative, 1/2″ × 8′). Retention times relative to hexamethylethane were measured at 100° with a helium flow rate of 66 ml/min for $(CH_3)_6MM'$ where MM′ = CC (1.00), CSi (0.68), CGe (1.03), SCn (1.77), SiSi (0.45), SiGe (1.03), SiSn (2.01), GeGe (1.22), and GeSn (2.57).

NMR measurements were made with a Bruker Scientific HXF-10 spectrometer operating at 90 MHz with a probe temperature of 30°. Unless stated otherwise, NMR data are for solutions containing carbon tetrachloride, approximately 5% v/v $(CH_3)_6$-MM′, and 5% v/v chloroform which served as the internal standard and as the lock-signal. In this solvent system, $\delta(TMS/CHCl_3)$ is 7.233 ppm. All chemical shifts are reported with respect to TMS. $^1J(^{13}CH)$ values are for pure liquids or saturated $CCl_4/(CH_3)_6MM'$ solutions.

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