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THE PROTON MAGNETIC RESONANCE SPECTRA OF SOME ETHYLGERMANIUM COMPOUNDS

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The proton magnetic resonance spectra of the ethylgermanes have been studied as a preliminary stage in work on the reaction between germanes and ethylene. The results led us to study other substituted ethylgermanes and we report the spectra of the compounds $(C_2H_5)_{4-n}GeX_n$, where X = Cl, Br, I, H and ½O, and n = 0, 1, 2, 3.

In earlier studies on ethyl compounds, $(C_2H_5)_mM$, it has been shown[1,2,3] that there was an approximately linear relationship between Δ, the difference between the methyl and methylene proton shifts in the ethyl group, and the electronegativity, x, of the substituent M:

$$x = 0.62\Delta_{(ppm)} + 2.07 \qquad (1)$$

However, when an ethyl group in $(C_2H_5)_mM$ is replaced to give $(C_2H_5)_{m-1}MX$, work on $(C_2H_5)_2AlX$[4] and on $(C_2H_5)_3SiX$[5,6] shows there are considerable deviations from eqn. (1). Similar effects appear in ethyl-thallium[7] and ethyl-mercury[8] compounds. These deviations from eqn. (1) were ascribed to effects on the chemical shifts arising from the magnetic anisotropy of the M–X bond, or of the X atom[4,6]. Spiesecke and Schneider[9] earlier accounted for the individual methyl and methylene proton and ^{13}C chemical shifts in CH_3CH_2X compounds in a similar way. However, alternative explanations of the CH_3CH_2X shifts have been put forward in terms of the inductive effect and of a "C–C bond shift"[10] or in terms of an intramolecular Van der Waals forces effect[11].

The effects of further substitution in $(C_2H_5)_{m-1}MX$ have been discussed for two sets of compounds. Narasimhan and Rogers[12] found a linear relation between Δ and n in the ethylchlorosilanes, $(C_2H_5)_{4-n}SiCl_n$, later verified for the mono-chloride[5,6],

$$\Delta_{(ppm)} = -0.420 + 0.205\,n \qquad (2)$$

Verdonck and Van der Kelen[13], found a similar but much less regular effect in the ethylchlorostannanes, $(C_2H_5)_{4-n}SnCl_n$.

In the compounds discussed in this paper, a much wider range of substituents has been covered than in earlier work. With substituents ranging from H to O and Cl in inductive power, and from the monohydride to the triiodide in magnetic anisotropic effects (and also in the size of intramolecular dispersion forces), it has been possible to assess the relative importance of these different effects.

The only proton resonance spectra of ethyl-germanium compounds previously reported are those of $(C_2H_5)_4Ge$[12] and of $(C_2H_5)_3GeOSi(CH_3)_3$[14].

EXPERIMENTAL

The halides[16] were prepared by treating the corresponding oxide with strong aqueous hydrohalic acid. The oxides were prepared by hydrolysis of triethylbromogermane (from bromine on tetraethylgermane), diethyldibromogermane (from tetraphenylgermane) or ethyltriiodogermane (from ethyl iodide and germanium diiodide) respectively. A second, satisfactory route to ethylgermanes was via ethyltrichlorogermane prepared by the action of tetraethylstannane on $GeCl_4$ (*cf.* ref. 17). All the hydrides were prepared by $LiAlH_4$ reduction of a halide in dimethyl ether or in tetraglyme. All compounds were characterised by their distillation behaviour, infra-red spectra and by analysis. Conventional micro-combustion methods with careful and extended heating proved reasonably satisfactory. In a number of cases, homogeneity was confirmed by vapour phase chromatography. The NMR spectrum was also, of course, a good criterion of purity.

Infra-red spectra were measured as gases, liquid films or as KBr discs and nujol mulls, as appropriate, on a Perkin–Elmer 521 grating spectrometer in the range 4000–250 cm^{-1}. The spectrum of ethylgermane showed considerable rotational detail and a full study of this compound will be published elsewhere. Table 1 lists the observed bands.

The proton magnetic resonance spectra of all compounds were recorded at 60 Mc/s on a Perkin Elmer R10 spectrometer. A number of compounds were also run at 100 Mc/s on a Jeol JNM-4H-100 instrument. Tetramethylsilane was used as an internal standard throughout. All the halides and the triethyl and diethyl oxides were run as 10 % solutions in CCl_4. A number of samples were also run in 50 % and 5 % concentration and as neat liquids. The mono-ethyl oxide, $[(C_2H_5GeO)_2O]_x$ was insoluble in CCl_4 and was run as a saturated solution in D_2O. The three hydrides reacted with CCl_4, forming $CHCl_3$, and these had to be run in benzene solution. A careful study of dilution effects was made and samples were also run in carbon disulphide to check for solvent effects. Some of the halides were also run in benzene to estimate the comparability of the hydride and halide results. Analysis of the spectra of $C_2H_5GeH_3$, $(C_2H_5)_2GeH_2$, and $(C_2H_5)_3GeH$ was aided by double irradiation at the GeH frequency.

Most of the spectra were of the second order A_3B_2 type and were analysed by a number of complementary methods. Where $|\Delta|$ was greater than 10 cps, the spectra could be analysed accurately by the method of Narasimhan and Rogers[2], giving $|\Delta|$ to $\pm$ 0.2 cps and the ethyl proton–proton splitting, J_{AB}, to $\pm$ 0.1 cps. When $|\Delta|$ was less than 10 cps, the spectra were very complex and accurate determinations of Δ and J together were not possible. However, using Corio's[15] calculated A_3B_2 values a plot was constructed of the separation of line B_4 from A_6 (the centre of the methyl peak) against Δ for each of a series of J values. As B_4 and A_6 could always be identified, Δ could be obtained by assuming a suitable J value. For the triethyl compounds, it was assumed that $J = 7.8$ c/s, the value found for $(C_2H_5)_4Ge$[12]. A variation in J of 0.2 c/s affected Δ by less than 1 % so the Δ value is accurate: however, the J value has an error of $\pm$ 0.3 c/s. This analysis, carried out on the 60 Mc/s spectra, could be verified by comparison with the 100 Mc/s spectra and by examining the shifts on dilution. Fig. 1 shows some representative experimental and calculated spectra.

In the cases where the ^{13}C–H satellites were observed, a further check on J and

TABLE 1

CHARACTERISTIC INFRA-RED BANDS OF ETHYLGERMANIUM COMPOUNDS

Et_3GeCl	Et_2GeCl_2	$EtGeCl_3$	Et_3GeBr	Et_2GeBr_2	$EtGeBr_3$	Et_3GeI	Et_2GeI_2	$EtGeI_3$	*Assignment*
1461 vs	1462 vs	1462 vs	1462 vs	1456 vs	1454 vs	1462 vs	1455 vs	1452 vs	$\delta_{as}(CH_3)$
1422 s	1426 m	1433 m	1421 s	1423 m	1430 w	1422 s	1420 m	1425 vw	$\delta_{as}(CH_2)$
		1399 w			1392 sh			1390 sh	
1380 m	1384 s	1386 s	1380 s	1382 s	1381 s	1381 s	1380 s	1380 s	$\delta_s(CH_3)$
	1322 vw	1322 vw		1315 vvw		1320 vw		1320 vw	
		1260 shw		1260 shw	1255 shw			1270 vw	
1229 m	1233 m	1229 s	1226 m	1222 s	1220 vs	1222 m	1219 s	1206 vs	$\delta_s(CH_2)$
1120 bw	1160 vw	1188 w	1150 bvw	1145 vw	1155 vw			1120 bw	
1025 vs	1028 sh	1028 vs	1028 vs		1022 vs	1028 vs	1030 sh	1022 vs	
1012 s	1022 vs		1010 vs	1021 vs		1014 vs	1018 vs		
972 s	977 m	979 m	971 m	974 ms	973 s	972 m	969 s	967 s	
955 sh			955 sh			960 sh	955 sh		
700 bvs	708 vs	710 vs	705 bvs	704 vs	707 vs	705 bvs	704 vs	708 vs	
588 vs	613 s	594 vs	583 vs	604 s	578 vs	580 vs	590 m	563 s	$\nu_{as}(Ge–C)$
542 s	568 s		539 m	560 s		533 s	547 s		$\nu_s(Ge–C)$
		542 vvw							
385 sh	420 sh	490 w							ν(Ge–Cl)
362 vs	400 sh	422 vvs							
	395 vvs	415 sh							
		370 m							
319 mw	345 m	310 sh		394 w	410 w				
		294 mw	360 sh	355 sh	330 vs	322 m	320 m	308 vs	ρ(Ge–C–C) (plus ν(Ge–Br) in bromides)
			322 s	318 vs	310 vs	290 m	305 m		
			293 s	310 sh	280 s				
			267 s	290 vs	?245				
				280 sh					
				265 sh					
								255 sh	ν(Ge–I)
								< 245 vs	

TABEL 1 (*continued*)

Et_4Ge	*Et_3GeH*	*Et_2GeH_2*		*$EtGeH_3$*		*Assignment*
	2016 vs	2085 sh		2090 vs	B	ν(Ge–H)
	(1452 Ge-D)	2044 vs		2080 vs		
1464 s	1470 m	1468 m		1470 w	C	$\delta_{as}(CH_3)$
	1435 sh					
1428 s	1432 w	1430 sh				$\delta_{as}(CH_2)$
1378 m	1384 w	1380 w				$\delta_s(CH_3)$
1235 w	1235 wb	1228 w	B	1250 w	A	$\delta_s(CH_2)$
1100 vw	1135 vvw					
1020 s	1019 s	1020 m		1028 w	A	ν(C–C)
1003 sh						
969 m	969 ms	968 m		975 w	B	ν(C–C)
		872 s	B	890 m	B	δ(Ge–H)
		865 sh		884 m		+
		830 w	A	833 vs	A	ρ(Ge–Et)
	751 vs	763 vs		738 m	C	
706 vs	700 sh					
685 sh	665 sh	688 w	C			
		630 wb		620 m	B	ν(Ge–C) and
578 vs	568 vs	567 m		522 m	A	$\rho(GeH_x)$
not examined below 400		448 m		438 w	C?	

Δ was possible. Fig. 2 illustrates the experimental and calculated satellite spectrum of $(C_2H_5)_2GeH_2$ where there is the additional complication of the H–Ge–C–H coupling.

RESULTS AND DISCUSSION

NMR spectra

Effect of solvent and concentration. The spectra measured in carbon tetrachloride showed only slight concentration effects. On dilution, the methylene signal remains almost the same and the methyl signal shifts by about 5–10 %. Fig. 3 shows typical changes. Standard conditions were chosen as 10 % concentration in CCl_4: extrapolation to infinite dilution would leave the methylene positions essentially the same and affect the methyl positions by not more than 0.5 cps. It will be seen that the methyl position shifts by 3–5 cps on dilution from 100 % to 10 % concentration and this shift was useful in confirming the identification of the methyl absorption A_6 in spectra like that of Fig. 1a.

When the spectrum of $C_2H_5GeI_3$ was measured in benzene, very large dilution effects were observed in both the methyl and the methylene signals. These were in the opposite sense to those in CCl_4 and at least ten times larger (Fig. 3). Benzene would obviously be an unsatisfactory solvent, although the effects are less for the bromides and chlorides. Unfortunately, benzene was the only solvent found which did not react with hydrides and yet did not obscure regions of the spectrum. It was therefore used for the hydride spectra, and as Fig. 3 shows, concentration effects were not too large for the hydrides. (Similar dilution effects were found for ethyl–aluminium compounds in benzene[4].) Further, a solution of mono-germane, GeH_4, in benzene showed a chemical shift of 6.93 τ compared with 6.85 τ in cyclohexane[18] or of 6.83 τ at —20° in CCl_4[19] (though the latter value must be treated with reserve in view of the reaction

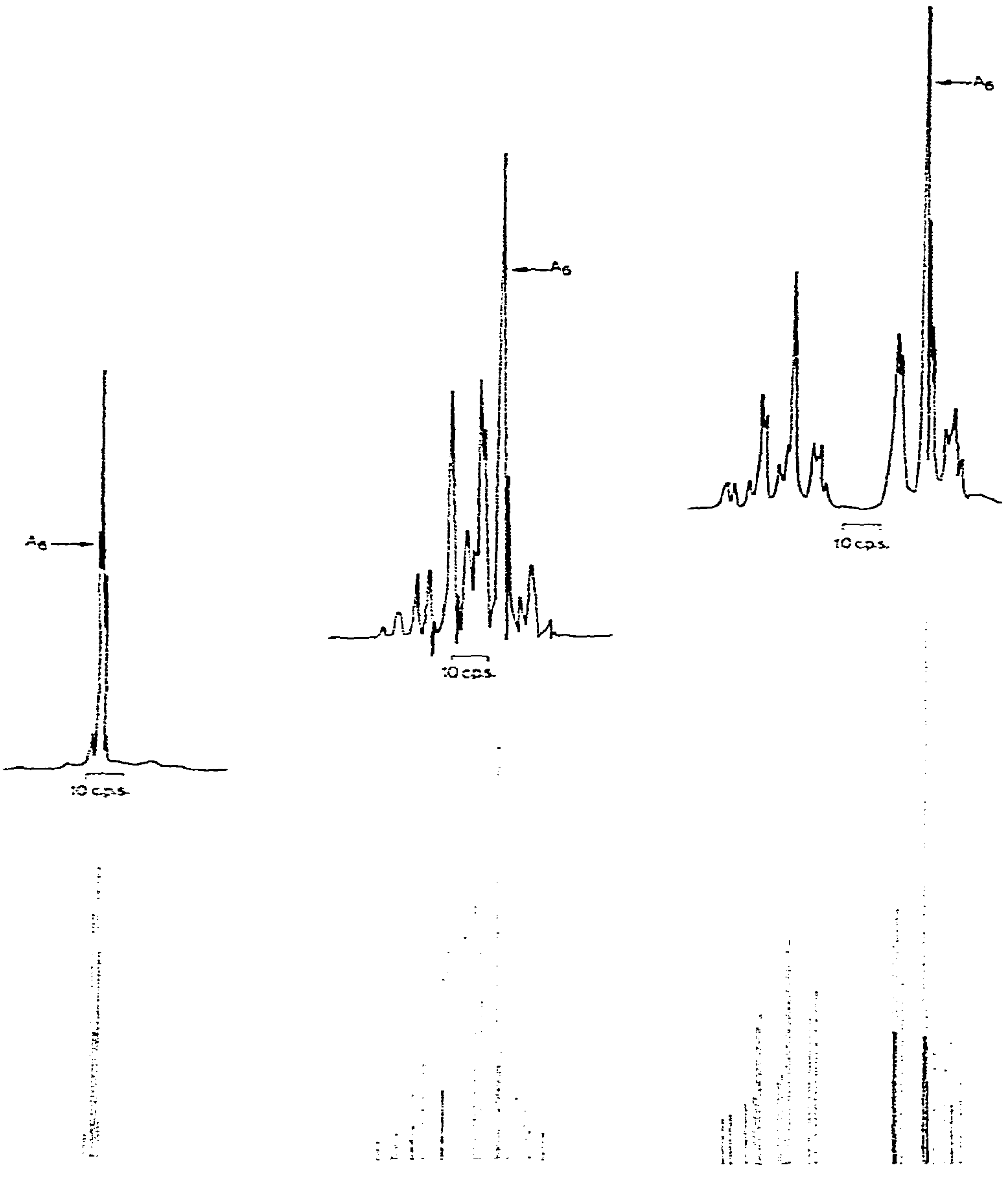

Fig. 1. Representative experimental and theoretical PMR spectra: (a) $(C_2H_5)_3GeCl$, (b) $(C_2H_5)_2GeCl_2$, (c) $C_2H_5GeCl_3$. The lines marked A_6 are the $\delta(CH_3)$ positions corresponding to the values given in Table 2.

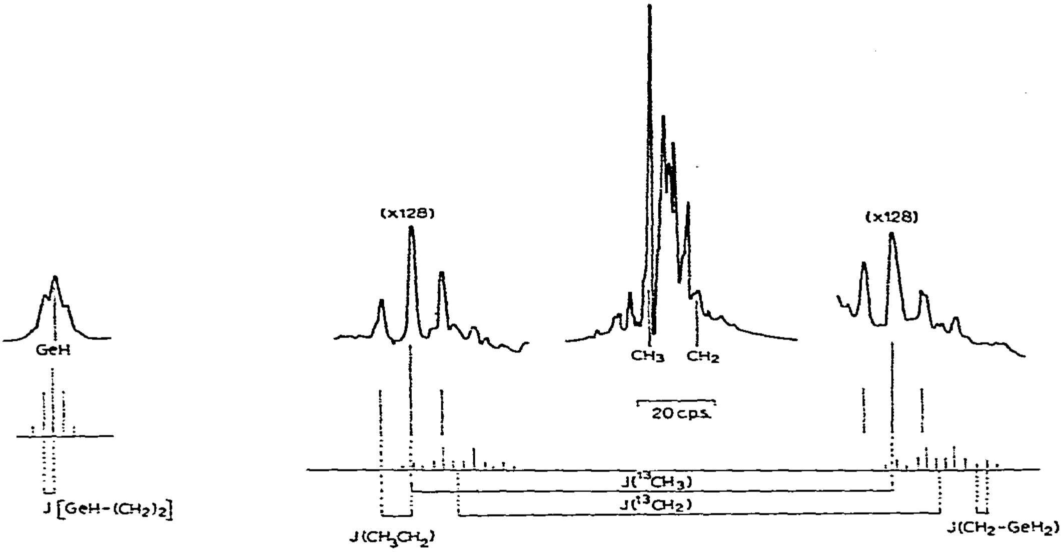

Fig. 2. The PMR spectrum of $(C_2H_5)_2GeH_2$ showing the $^{13}C–H$ satellites.

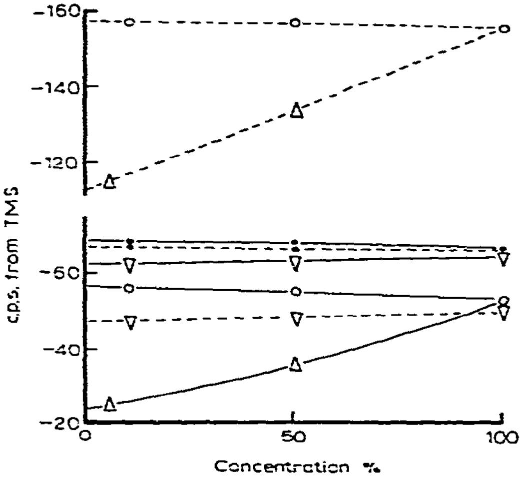

Fig. 3. Dilution effects in carbon tetrachloride and benzene. Dotted lines ----, CH_2; solid lines ———, CH_3. ● = $(C_2H_5)_3GeCl$ in carbon tetrachloride; ⊙ = $C_2H_5GeI_3$ in carbon tetrachloride; △ = $C_2H_5GeI_3$ in benzene; ▽ = $(C_2H_5)_3GeH$ in benzene.

found between ethylgermanes and CCl_4). It thus seems that the results for the hydrides in benzene are comparable with those obtained for the halides in carbon tetrachloride, but the solvent effect must be kept in mind.

The internal chemical shift of the ethyl group, Δ. Table 2 gives the NMR parameters of all the compounds studied. It will be seen that the values of Δ [$\delta(CH_3) - \delta(CH_2)$] measured at 60 Mc/s and at 100 Mc/s are in good agreement. The parameters for tetraethylgermane agree closely with the literature values[12]. The variation of Δ

TABLE 2

THE PROTON MAGNETIC RESONANCE SPECTRA DATA FOR ETHYL–GERMANIUM COMPOUNDS

Compound	*Chemical shifts*			*Coupling constants*			*Frequency*
	δ(CH₃) (cps)	*δ(CH₂) (cps)*	*Δ*[a] *(ppm)*	*J(AB) (cps)*	*J(¹³C¹H₃) (cps)*	*J(¹³C¹H₂) (cps)*	*(Mc/s)*
Solutions in CCl_4							
$(C_2H_5)_4Ge$	− 60.0	− 41.6	−0.307	7.8	125.5	124.0	60
	−101.3	− 70.8	−0.305	7.8			100
$(C_2H_5)_3GeCl$	− 68.0	− 66.5	−0.025	7.9	127.0	127.0	60
			−0.027	7.9			100
$(C_2H_5)_3GeBr$	− 67.9	− 71.2	0.053	7.8	127.3	127.8	60
	−113.0	−118.0	0.050	7.8			100
$(C_2H_5)_3GeI$	− 66.3	− 75.8	0.158	7.7			60
	−111.5	−127.2	0.157	7.7	129.0	129.0	100
$[(C_2H_5)_3Ge]_2O$	− 61.5	− 47.4	−0.236	7.8			60
	−103.8	− 79.6	−0.242	7.8			100
$(C_2H_5)_2GeCl_2$	− 76.1	− 92.2	0.268	7.7	128.5	130.0	60
	−126.7	−154.3	0.276	7.7			100
$(C_2H_5)_2GeBr_2$	− 72.5	−100.0	0.458	7.7			60
	−124.8	−170.1	0.453	7.7			100
$(C_2H_5)_2GeI_2$	− 68.3	−112.0	0.729	7.8			60
$[(C_2H_5)_2GeO]_n$	− 66.2	− 57.4	−0.147	7.7			60
$C_2H_5GeCl_3$	− 82.3	−121.7	0.657	7.9			60
	−137.8	−202.9	0.651	7.9			100
$C_2H_5GeBr_3$	− 75.4	−135.2	0.996	7.8			60
	−126.3	−226.1	0.998	7.8			100
$C_2H_5GeI_3$	− 56.2	−156.0	1.662	7.7			60
$[(C_2H_5GeO)_2O]_n$	− 70.5	− 82.7	0.204	7.7			60
Solutions in C_6H_6							
$(C_2H_5)_2GeH$	− 62.8	− 47.2	−0.260	7.8	127.0	123.5	60
$(C_2H_5)_3GeD$	− 64.7	− 49.4	−0.255	7.8			60
$(C_2H_5)_2GeH_2$	− 61.6	− 46.8	−0.247	7.8	126.2	126.3	60
$C_2H_5GeH_3$	− 58.3	− 44.6	−0.228	7.8			60

[a] $\Delta = \delta(CH_3) - \delta(CH_2)$.

with n, in $(C_2H_5)_{4-n}GeX_n$, is shown in Fig. 4: it will be seen that the relation is not, in general, linear. The points for the ethylchlorosilanes[12,5,6], which fit eqn. (2) are included for comparison (although these were measured on the neat liquids).

The curve for the oxides is clearly anomalous. The point for the monoethyl oxide is abnormal as this was measured in D_2O and the oxide has a polymeric structure. The values for $[(C_2H_5)_3Ge]_2O$ and $[(C_2H_5)_2GeO]_n$, which were measured in CCl_4, do appear to fit the general pattern.

Among the halides, the curve for the iodides shows a clear upward curvature with the Δ values for $C_2H_5GeI_3$ and $(C_2H_5)_2GeI_2$ being larger than expected for a linear relation like eqn. (2). The curves for the bromides and chlorides show similar, but decreasing, curvatures, the points for $C_2H_5GeBr_3$ and $C_2H_5GeCl_3$ being respectively about 0.2 ppm and 0.1 ppm above the best straight lines through the points for the less-substituted members. These differences, though small, are definitely significant for the bromides and probably significant for the chlorides. It therefore appears that the linear relationship between Δ and n found for the ethylchlorosilanes (eqn. 2) corresponds only to a special case. The plot of Δ versus n becomes increasingly non-linear in the order Cl < Br < I, and, probably, in the order Si < Ge < Sn. The position of tin is less clear as the published values for Δ in the ethylchlorostannanes[13] were recorded on neat liquids and the possibility of polymeric structures exists.

The curve of Δ versus n for the hydrides is slightly irregular, possibly reflecting solvent effects. It is approximately linear and of zero slope.

It is clear that the changes in Δ may not be explained on the basis of inductive effects alone. For example, application of eqn. (1) to the trihalides gives group electronegativities of 3.0 for $-GeI_3$, 2.7 for $-GeBr_3$ and 2.5 for $-GeCl_3$. To examine the basis of the changes in Δ, it is necessary to examine the variations in the methyl and methylene shifts separately.

Methylene shifts. Fig. 5 shows the plot of the CH_2 chemical shift against n for

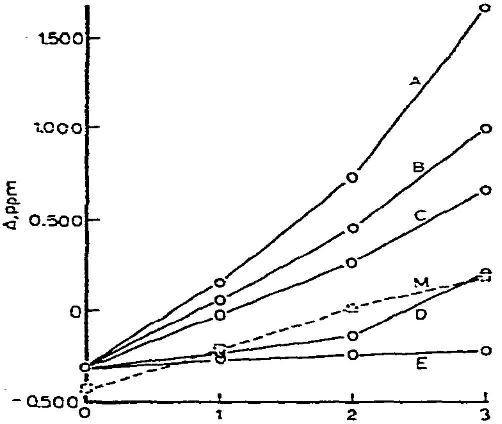

Fig. 4. The variation of Δ [$\delta(CH_3) - \delta(CH_2)$] with n for $(C_2H_5)_{4-n}GeX_n$. Curve A is for X = I, B for X = Br, C for X = Cl, D for X = $\frac{1}{2}$O, E for X = H. Curve M shows the values for $(C_2H_5)_{4-n}SiCl_n$ (refs. 5, 6, 12).

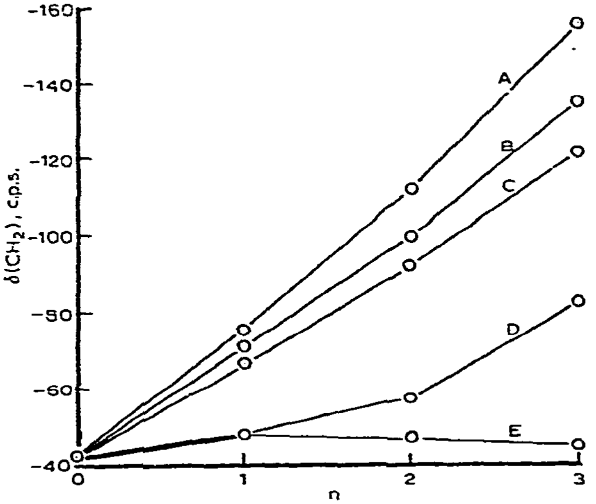

Fig. 5. The variation of the CH_2 chemical shifts with n for $(C_2H_5)_{4-n}GeX_n$. A, B, C, D, E as in Fig. 4.

each series of compounds. As expected, the chemical shift of the CH_2 proton changes markedly with substitution at the germanium atom and makes the dominant contribution to the Δ value changes. The methylene shifts follow the same pattern as the Δ shifts, but the curvature of the plots is less pronounced, (see the discussion of methyl shifts below). The curve for the oxides is irregular, reflecting solvent and composition changes.

For the halides, the methylene shift to low field increases in the order $Cl < Br < I$. The shifts in the trihalides are more than three times the shifts in the monohalides, and similarly for the dihalides. It is thus necessary to find an effect which causes a shift to low field in this order and where the presence of more than one halogen atom causes a mutual enhancement of the effect. The inductive effect does not account for the order within the series of halides, although it could account for their low field shift relative to the hydrides and tetraethylgermane. However, all these effects can be explained qualitatively in terms of the magnetic anisotropy effect: the application of the alternative theory of intramolecular dispersion forces is treated later.

Fig. 6 shows a representation of the magnetic anisotropy effect. As the induced field parallel to the Ge–X bond is greater than the perpendicular component, the total effect of the magnetic anisotropy may be represented by a magnetic dipole in the Ge–X bond. The resulting field at the methylene proton positions reinforces the applied field, causing a shift of the resonance to low field. As the induced field increases in the order $H < O < Cl < Br < I$, the relative positions of the resonance signals may be understood. Furthermore in, say, a GeX_2 unit, the field resulting from the magnetic dipole in one Ge–X bond reinforces the applied field at the second X atom, which would lead to a larger induced magnetic dipole in the second Ge–X bond, and *vice-versa*. Thus the enhancement of the shifts in the di- and trihalides may be explained in terms of this second order interaction between the induced magnetic dipoles. Clearly the enhancement is greatest for the iodides, where the anisotropic field is greatest. This presentation is similar to that used by Spiesecke and Schneider[9] in their discussion of the ethyl halides. Further, in the ethyl halides, the differences between the methylshifts of C_2H_5Cl, C_2H_5Br and C_2H_5I are, respectively, 12 and 18 cps (at 60 Mc/s) while, in the $(C_2H_5)_3GeX$ compounds, the corresponding differences in the methylene shift (*i.e.* comparing the protons β to X in both cases) are 6 and 5 cps. Thus the effect at the β protons in the C–C–X system is two to three times that in the C–Ge–X system which is reasonable allowing for the longer Ge–X bond. It is also found that there is a good linear relation between the methyl shifts in $(CH_3)_3GeX$ compounds[20] and the methylene shifts in the corresponding $(CH_3CH_2)_3GeX$ compounds.

However, two factors have so far been left out of consideration. The first is whether there is any residual inductive effect and the second is whether the anisotropy effect is confined to the X atom or Ge–X bond, or whether it is to be looked for in the germanium atom (or in the Ge–C bond) as well.

An estimate of the contribution to the methylene shift of inductive effects of the substituents X may be made by using Spiesecke and Schneider's results for the methyl shifts of CH_3CH_2X compounds. These shifts, for substituents X which show no anisotropy effect, showed a small variation with electronegativity of X, of the order of 0.2 ppm per electronegativity unit. As this change may involve contributions from other effects than the inductive one, and as the inductive effect in an H–C–C–X system is larger than in the corresponding H–C–Ge–X system, a reasonable guess for the inductive contribution to the methylene shift in the germanium compounds would be 0.1 ppm per electronegativity unit. Thus, in triethylchlorogermane, about 10% of the methylene shift relative to that of tetraethylgermane may be ascribed to inductive effects. The inductive contribution would drop to about 3% for triethyliodogermane, and would be even less in the diethyl and monoethyl compounds. These rough estimates of the magnitude of the inductive effect are supported by the relatively small changes observed in the carbon-13 coupling to the methylene protons.

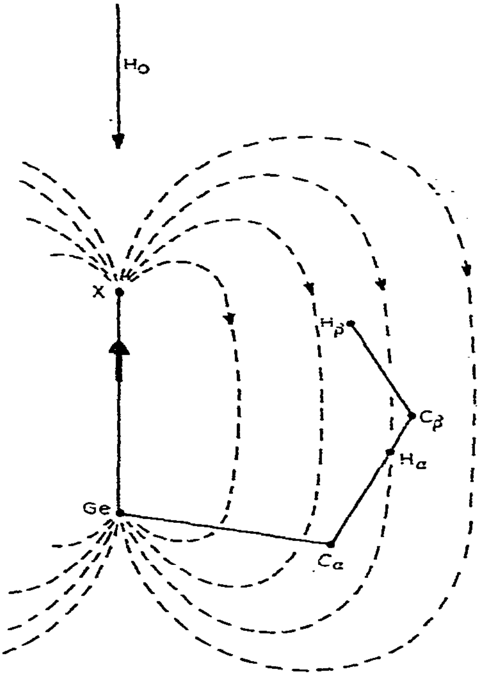

Fig. 6. Representation of the magnetic anisotropy effect due to the substituent X in the system CH_3–CH_2–Ge–X. The diagram shows both the methyl and the methylene protons in their positions of closest approach to X.

In assessing the importance of magnetic anisotropy contributions arising from the germanium atom, or in the Ge–C bond, attention must be confined to the ethylgermanes (*i.e.* the hydrides) and oxides, where anisotropy effects at the substituent atom are slight or absent. An immediate estimate of the size of the magnetic anisotropy effect associated with the germanium atom may be obtained by comparing the methylene proton shift in the ethylgermanes with those of other $(C_2H_5)_mM$ compounds reported by Spiesecke and Schneider (Fig. 8 of ref. 9). The uncertainty which exists in the electronegativity value of germanium leads to a rather wide range in the proportion of the methylene shift of the ethylgermanes which is to be ascribed to the inductive effect, but the comparison indicates that a contribution of 30 ± 20 cps (at 60 Mc/s) to the methylene shift in the ethylgermanes is to be ascribed to the magnetic anisotropy effect. This is found by taking the electronegativity of germanium in the range 1.8 to 2.1, and the error in the figure includes an allowance for the comparison of the liquid phase spectrum of the ethylgermanes with the gas phase spectra of ref. 9. There are further indications that this figure of 30 cps is of the correct order of magnitude. A comparison of the methylene proton shifts in silanes and germanes $(C_2H_5)_3MH$ and $(C_2H_5)_3MOM(C_2H_5)_3$, where the substituents, H and O, should show little anisotropy effect, shows that the difference between germanium and silicon[5] compounds is around 15 cps. As silicon itself appears to show a weak anisotropy effect[9], this would lead to a value of about 20 cps. Further, the difference in the methylene shifts of tetraethylgermane and of triethylbromogermane amounts to 30 cps for the effect of substitution of one bromine atom. The anisotropy effects of germanium and bromine should be similar, and the value includes the inductive effect of the bromine, so that this confirms that the order of magnitude is correct. Taking all the evidence together, it is reasonable to assign a value in the range 20–30 cps at 60 Mc/s to the contribution to the low field shift of methylene protons arising from magnetic anisotropy effects at the germanium atom.

Thus anisotropy effects at the germanium atom provide a significant contribution to the methylene proton shifts in the ethylgermanium compounds. If the substituent has relatively few electrons and a low anisotropy effect, the germanium contribution becomes the dominant one. This applies in the case of the hydrides and oxides, and probably for the mono- and dichlorides. On the other hand, in all the iodides, and in the di- and tribromides, the dominant effect is the magnetic anisotropy effect of the halogen atom. The small and irregular shifts found for the hydrides probably reflect a balance between two shifts in opposite directions: an inductive shift to high field increasing with the number of hydrogen atoms, and the anisotropy shift of the germanium atom to low field.

The rather irregular changes found for the three ethylchlorostannanes[13] probably reflect the balance of anisotropy effects at the chlorine atoms and a pronounced effect at the tin atom.

Thus the methylene proton shifts may be interpreted as arising from low-field shifts caused by magnetic anisotropic effects at the germanium atom, or in the germanium–carbon bond, reinforced by anisotropy effects arising at the halogens. The latter make the major contribution in the iodides and bromides and second-order effects occur in such compounds. Inductive effects provide only a small part of the shifts.

Methyl shifts. In Fig. 7, the methyl proton shifts in $(C_2H_5)_{4-n}GeX_n$ are plotted

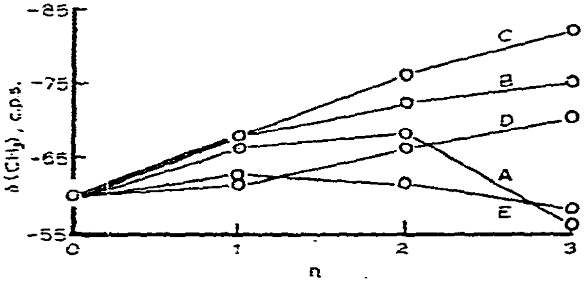

Fig. 7. The variation of the CH_3 chemical shift with n for $(C_2H_5)_{4-n}GeX_n$. A, B, C, D, E as in Fig. 4. (Note the increased ordinate scale compared with Figs. 4 and 5.)

against n (note the increased scale). Although these shifts are relatively small, they are not negligible and the overall changes at least are thought to be real. The basic pattern is a shift to low field paralleling the methylene shifts and about one quarter as large. These shifts are attributed to the magnetic anisotropy effects of the germanium, and of the substituents, diminished by the greater distances. Inductive effects probably contribute only marginally.

The methyl shifts for the iodides do not fall into this pattern, and it is proposed that they arise from a shift to high field, falling in the order $I_3 > I_2 > I$, superimposed on the low field shift. A similar effect is seen in the tribromide, and possibly for the dibromide and trichloride. This high field shift is thought to arise as the methyl protons come into direct contact with the halogen atoms, and experience the field arising from its induced electronic circulation (compare Fig. 8). Models show that the effect is particularly marked in the triiodide as the methyl protons are in contact with the iodine atoms over the major part of their figure of rotation about the C–C and Ge–C bonds. The effect decreases as the number, or size, of the halogen atoms in the molecule decreases. It will be noted that this shift arising from direct contact is interpreted as a high field shift, while the dispersion forces theory (see below) would appear to require a low field shift.

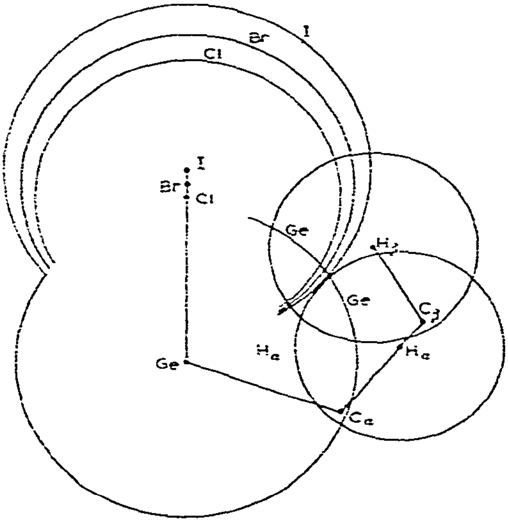

Fig. 8. The overlap of Van der Waals radii in the system CH_3–CH_2–Ge–X (for X = Cl, Br, I). The configuration of closest approach of either set of protons to Ge and X is shown.

As all the methyl shifts are relatively small, there is little profit in trying to distinguish the relative contributions to the magnetic anisotropy effect of the germanium atom and the substituent atom. It is reasonable to suppose that the contributions are in similar proportions as to the methylene shifts.

In the spectra of the oxides, the methyl shift of the monoethyl oxide falls in line with those of the diethyl and triethyl oxides. This suggests that the abnormal methylene shift of the monoethyl oxide could result from coordination of D_2O molecules at the germanium atom.

From this discussion it follows that the shapes of the Δ *versus* n plots (Fig. 4) are the resultant of large shifts in the methylene proton resonances and smaller effects at the methyl positions. The general upward curvature results mainly from second-order effects in the methylene shifts but with a contribution from the small shifts to high field in the methyl resonances of the heavier halides.

Intramolecular Van der Waals dispersion forces. In the discussion above, it was shown that the chemical shifts could be explained in terms of the magnetic anisotropy effect, following the treatment of Spiesecke and Schneider. Recently, Schaefer, Reynolds and Yonemata[11] proposed that the proton chemical shifts in the ethyl halides might be explained in terms of intramolecular dispersion forces, as an alternative to the Spiesecke and Schneider approach. The effect arises as the methyl and methylene protons are both in Van der Waals contact with the halogens in the ethyl halides giving rise to an interaction which is not averaged to zero by rotations or vibrations. This would cause the observed low field shifts, whose size would increase with the number of electrons in the halogen atom.

The magnetic anisotropy theory and this dispersion forces theory both predict low field proton shifts, the main qualitative difference being that dispersion forces should decrease more quickly with increasing distance. There is at present no quantitative treatment of the ethyl halides which allows a decision to be made about the relative importance of the two effects.

It is possible to decide qualitatively between the two theories in the case of the ethylhalogermanes studied here. Fig. 8 shows the Van der Waals radii for the various atoms in CH_3-CH_2-Ge-X (X = Cl, Br or I) for the position of closest approach of either the CH_2 or the CH_3 hydrogens to X. The use of spherical Van der Waals envelopes is an approximation but should serve for purposes of comparison. It is seen that, while the methyl protons come into contact with any of the halogen atoms, the methylene ones do not. Both sets of protons overlap with the germanium atom to a similar degree.

As the intramolecular Van der Waals effect depends on the number of electrons, it falls off in the order I > Br ≈ Ge > Cl. It follows that the size of the effect is limited to the size of the methyl shifts in the iodides, and these are small. Thus the theory of Schaefer, Reynolds and Yonemata does not account for the principal features of the pattern of methylene shifts in these ethyl-germanium compounds. Intramolecular dispersion forces arising at the halogen atom could account for part, at least, of the methyl shifts, and forces arising at the germanium atom could make minor contributions to both the methyl and methylene shifts. However, the principal contribution in the methylene shifts must come from magnetic anisotropy effects.

The Ge-H resonance. The Ge-H parameters are shown in Table 3. In the ethylgermanes, the Ge-H signals appear about 6 τ and show the expected multiplet structures from coupling with the methylene protons. There is little indication of interaction with the methyl protons, possibly a slight broadening of the peaks: any coupling is under 0.1 cps.

The Ge-H shifts in $(C_2H_5)_{4-n}GeH_n$ are shown plotted against n in Fig. 9, for 10 % solutions in benzene. The corresponding methylgermane values[21] (for the neat liquids) are also shown. The GeH_4 value is for a solution in benzene at about two atmospheres pressure. The monogermane shift in benzene differs by about 0.1 ppm from the shifts quoted above in cyclohexane[18] or in carbon tetrachloride[19]. The shift

TABLE 3

Ge–H CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE ETHYL–GERMANES

Compound	*δ(GeH) (cps)*	*$J(H_2CGeH)$ (cps)*	*Concentration*
$(C_2H_5)_3GeH$	−235.5	2.6	10%
	−230.2		50%
$(C_2H_5)_2GeH_2$	−230.1	2.7	10%
	−225.7		50%
$C_2H_5GeH_3$	−213.0	3.0	10%
GeH_4	−184.0	—	2 atm. pressure

from the value in the gas phase of 7.02 τ at five atmospheres pressure[22] to the solution value is similar to that found for methane[24].

The positions of the Ge–H resonances in these $R_{4-n}GeH_n$ compounds go to low field with decreasing *n*, and when methyl is replaced by ethyl, as expected. The irregularity of the variation of the shift with *n* for the benzene solutions supports the earlier suggestion that the methyl and methylene shifts in the ethylgermanes are showing solvent effects.

Coupling constants. The values of the various coupling constants are shown in Tables 2 and 3. The proton–proton coupling constants within the ethyl group, J_{AB}, vary from 7.7 to 7.9 cps, within the range of values found for ethyl–metal compounds[1–13]. The range of values is too small to show significant trends.

In the hydrides, the coupling between the protons on germanium and the methylene protons, *J*(H–Ge–C–H), decreases with increasing number of alkyl groups, as in the methylgermanes[21]. The coupling constants in the ethylgermanes are about 1 cps smaller than those in the methylgermanes, and the value of 2.6 cps for $(C_2H_5)_3GeH$ compares with 3.1 cps for $(C_2H_5)_3SiH$[5,6]. All these changes are relatively small and probably reflect small changes in *s* character in the bonding orbitals with substitution.

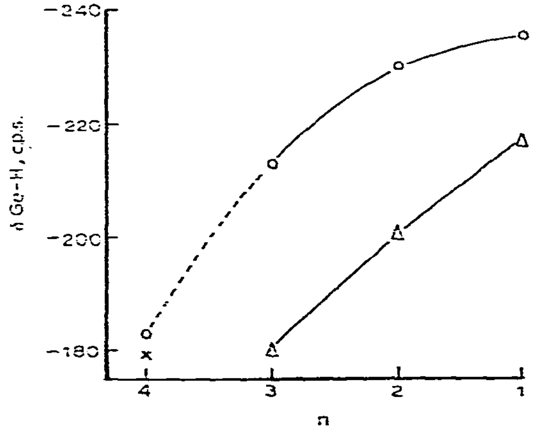

Fig. 9. The variation of the Ge–H chemical shifts with *n* for $R_{4-n}GeH_n$. The values for R = C_2H_5, in benzene, are shown by circles (○), and those for R = CH_3, as neat liquids[21], by triangles (△). The gas phase value for GeH_4[22] is shown by the cross (×).

The carbon-13–proton couplings observed were found to be of similar size in both the methyl and methylene groups. The methyl group couplings are similar to the carbon-13–methyl couplings of 129–130 cps found in the triethylhalosilanes[5]. The methylene group couplings are close to the carbon-13 couplings in the trimethylhalogermanes[20] of 126 to 130 cps. The carbon-13–proton couplings increase, from the values found in tetraethylgermane, on halogen substitution and the increase is in the order $Cl < Br < I$ and $Cl < Cl_2$. Similar trends are found in the hydrides. These changes with substitution reflect changes in the *s* character of the orbitals used by carbon to bond to hydrogen. All the changes are relatively small showing that substitution at the germanium has only minor effects on the bonding in the ethyl groups.

Infra-red spectra

Table 1 shows the stronger infra-red bands observed in the region from 1600–250 cm^{-1}, together with the Ge–H stretching modes of the hydrides. In addition, all compounds showed C–H stretching modes at 2960 vs, 2935 s, 2905 m and 2875 s cm^{-1}. Overtone and combination bands were observed in most spectra, in the high frequency region, at 3880 b, 3590 b, 3100 sh, 3090 sh, 2825, 2738, 2680, 2640, 2600, 2390, 2185, 1920 b, 1810–1800 vb, 1760–50 vb, 1650 b and 1600 sh cm^{-1}, all bands being weak or very weak.

The assignments given in Table 1 were arrived at by comparison with Cross and Glockling's work on organogermanes[23] and with Lohmann's[25] on ethylstannanes. The description of the vibration modes is to be regarded, in all cases, as approximate: in molecules of this type, considerable mixing of low frequency modes is to be expected. In a number of cases, interaction is so severe that assignments in terms of a single vibrational type are improper. The mode described as the Ge–C–C rock mixes with the Ge–Br stretches, and possibly with the Ge–I stretches in the mono- and di-iodides. In the hydrides, the Ge–C stretches and Ge–Et rock mix with the Ge–H deformation and rocking modes so that assignments in individual modes break down below 1000 cm^{-1}. For example, the band at 700–710 cm^{-1} which is very strong and constant in the other spectra cannot be picked out in the hydrides.

Some characteristic changes occur on increasing halogen substitution. The C–H deformation modes in the 1500–1350 cm^{-1} region show patterns characteristic of the number of ethyl groups: vs, s, m for Et_3: vs, m, s for Et_2; and vs, m–w, s (with a high frequency shoulder) for Et. Similarly characteristic changes occur in the intensity of the 1220 band, the complexity of the 1020 band and in the number and intensities of the Ge–C stretches at 520–600 cm^{-1}, most of these changes resemble those observed for the halostannanes[25].

Our assignments for $(C_2H_5)_4Ge$ and $(C_2H_5)_3GeBr$ agree with those of Cross and Glockling[23], except with regard to the Ge–Br stretch which we regard as included in the complex band at 300 cm^{-1}.

Most of the bands in the ethylgermane spectrum, measured in the gas phase, showed characteristic contours for A, B or C type modes (though most of these were distorted). A few of the diethylgermane modes showed similar contours. Full assignments of the hydride spectra will be discussed elsewhere.

The spectra of the oxides are not reported as sample handling difficulties gave rise to poor spectra of the diethyl and monoethyl oxides. The spectrum of $[(C_2H_5)_3$-

Ge]$_2$O agrees with that reported by Glockling[23] and the Ge–O bands in spectra of the other two oxides resemble those reported for analogous compounds[23]. The characteristic changes with the number of ethyl groups discussed above were found in the oxide spectra.

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SUMMARY

The PMR and IR spectra of the compounds $(C_2H_5)_{4-n}GeX_n$ are reported for $X = Cl, Br, I, H$ and $\frac{1}{2}O$, and for $n = 0, 1, 2, 3$. The effect of substitution on chemical shifts of the CH_3 and CH_2 protons is discussed and it is concluded that the principal factor is the magnetic anisotropy effect of the substituent X. A second order effect in the CH_2 shifts of the trihalides is proposed. Anisotropy effects at the germanium atom, inductive effects of X and intramolecular dispersion forces may make smaller contributions. There is some evidence for direct interaction between methyl groups and halogen atoms, especially in $CH_3CH_2GeI_3$. The Ge–H chemical shifts, the H–H and ^{13}C–H coupling constants, and the infra-red spectra are also discussed.

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