^{73}Ge NMR spectra of 2-thienyl-, 2-furyl- and 2-(4,5-dihydrofuryl)germanes

E. Liepiņš, I. Zicmane, L.M. Ignatovich, and E. Lukevics *

Institute of Organic Synthesis, Latvian SSR Academy of Sciences, Riga (U.S.S.R.)

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Abstract

The ^{73}Ge NMR spectra of 2-thienyl, 2-furyl- and 2-(4,5-dihydrofuryl)germanes have been studied. The comparison of ^{73}Ge chemical shifts with those of ^{29}Si and ^{119}Sn in isostructural silicon and tin derivatives confirms the existence of additional effects in these compounds. The contribution of these effects to chemical shifts of central atom is different for germanium, silicon and tin compounds.
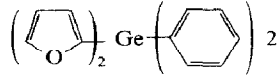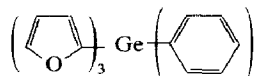
Introduction

For a long time the observation of ^{73}Ge NMR signals for germanium compounds with double or triple bonds α to the germanium atom was deemed impossible. Recently Takeuchi et al. [1] published the ^{73}Ge NMR spectra of methylvinylgermanes $Me_{4-n}Ge(CH=CH_2)_n$, i.e., of compounds with an α-double bond. In order to extend the scope of these compounds we report on the ^{73}Ge NMR spectra of 2-thienyl, 2-furyl- and 2-(4,5-dihydrofuryl)germanes R_nGeMe_{4-n} ($R = C_6H_5$; C_4H_3O; C_4H_3S; C_4H_5O; $n = 1–4$), which have from 1 to 4 hetaryl groups at the germanium atom.

Results and discussion

The linewidth of ^{73}Ge resonance signal ($\Delta\nu$) is determined by the quadrupole relaxation time which in turn depends on the rotational correlation time of the molecule (τ_c) and electric field gradient (eq) [2]. Since τ_c is directly proportional to the size of the molecule, it is suggested that the broadening of ^{73}Ge resonance signals displayed in all cases with an increased number of heteroaromatic substituents in the molecule is due to the increase of τ_c. At the same time the transition to the symmetrically substituted germanes R_4Ge causes pronounced narrowing of the ^{73}Ge signals (despite the fact that these compounds are more voluminous). Since the electric field gradient in R_4Ge should be close to zero, we assume that the $\Delta\nu_{1/2}$

Table 1

^{73}Ge, ^{29}Si, ^{119}Sn NMR data for isostructural heteroaromatic compounds R_nMMe_{4-n} (M = Ge, Si, Sn)

No	R	n	^{73}Ge		$\delta\,^{29}$Si (ppm)	$\delta\,^{119}$Sn (ppm)
			δ (ppm)	$\delta\nu_{1/2}$ (Hz)		
1		1	−22.1	140	−11.5 [b]	−54.2 [b]
2		2	−56.1	340	−24.7 [b]	−115.8 [b]
3		3	−79.5	390	−39.2 [b]	−184.7 [b]
4		4	−115.0 [a]	30	−56.0 [b]	−260.1 [b]
5		1	−10.1	200	−6.0 [c]	−27.5 [c]
6		2	−23.5	450	−15.0 [c]	−69.3 [c]
7		3	−39.4	600	−24.1 [c]	−104.5 [c]
8		4	−56.5 [d]	18	−34.1 [c]	−148.6 [c]
9		1	−25.5	180	−11.0 [e]	–
10		2	−59.5	250	−23.2 [e]	–
11		3	−89.7	440	−37.1 [e]	–
12		4	−119.1	65	−51.9 [e]	–
13		2	−18.5	120	−9.4 [f]	−60 [g]
14		4	−32.9 [h]	15	−13.9 [f]	−137 [g]
15			−73.0	400	–	–
16			−93.9	320	–	–

[a] −112.8, Ref. 12. [b] Ref. 6. [c] Ref. 17; [d] −95.5 ppm, Ref. 12. [e] Ref. 18; [f] Ref. 19; [g] Ref. 9. [h] −31.6 ppm, Ref. 12.

changes in the R_4GeMe_{4-n} series are chiefly because of variation in the electric field gradient; differences in correlation times are less important.

The range of ^{73}Ge chemical shifts (CS) of the compounds studied is large, viz., about 100 ppm (Table 1). Increases in the number of heteroaromatic substituents cause almost additive high-field shifts of the resonance signals (Fig. 1). From trivial assumptions about CS based on the shielding effects of electrons, low-field shifts with an increase in the number of electronegative substituents at the germanium atom should be expected. MNDO calculations for methylvinylgermanes [1] have shown that electron density at germanium atom decreases with sequential vinyl substitutions in the molecule, but the ^{73}Ge signal is shifted upfield, as in our case. Thus there is no simple correlation between the ^{73}Ge CS and electron density. A similar phenomenon has been described [3–5] for ^{29}Si and ^{119}Sn CS in isostructural silicon and tin compounds.
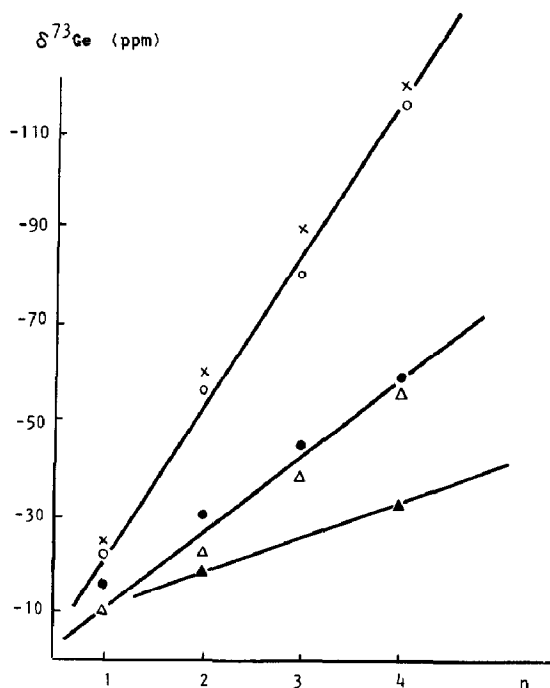
Fig. 1. The dependence of ^{73}Ge CS in hetaryl- and vinylgermanes R_nGeMe_{4-n} on the number of unsaturated substituents: $R = C_4H_3O$ ($\circ$); C_4H_5O ($\times$); $H_2C=CH$ ($\bullet$); C_4H_3S ($\triangle$); C_6H_5 ($\blacktriangle$).

In the isostructural series R_4MMe_{4-n} (M = Ge, Si, Sn) the resonance signal of the central atom is more sensitive to the number of substituents when R is 2-furyl- or 2-(4,5-dihydrofuryl) group. Both these substituents have an oxygen atom in the ring. In silicon compounds [6,7] the enhanced sensitivity of the central atom is explained by specific interactions between silicon atom and substituent. Firstly, energetically more favourable conditions for $(\pi-d)_\pi$ interaction in 2-furylsilanes as compared with thienyl- and phenylsilanes have been postulated. Secondly, $(p-d)_\pi$ bonding between silicon and oxygen atoms may occur.

Variation in the CS for 2-(4,5-dihydrofuryl)derivatives, which also have double bonds in the α-position and an oxygen atom in the ring confirm these assumptions. The effects of the 2-furyl- and 2-(4,5-dihydrofuryl) substituents on the ^{73}Ge CS are almost equal (Fig. 1), consequently, hence the germanium compounds also show the specific interactions between the group 14 atom (Si) and substituent, mentioned earlier.

We have not found any correlations between ^{73}Ge CS and inductive constants of the substituents (σ^*) for each separate series with fixed number of hetaryl substituents. The same was noted previously for alkylgermanes [8]. On the other hand, linear relationships of the type $\delta^{73}Ge/\sigma^*$ are observed for series R_nGeMe_{4-n} in which substituent R is fixed, but n varies, i.e. analogous with the relation $\delta^{73}Ge/n$. Two different correlations are evident (Fig. 2). We think that the inductive constants for the hetaryl substituents, previously determined for carbon compounds might not adequately reflect the electronic effects of these groups in the germanium compounds.

In 1983 Mitchell [9] suggested that if the paramagnetic shielding term (σ^{para}) dominates the CS, then the slope of the plots between CS of central atoms in
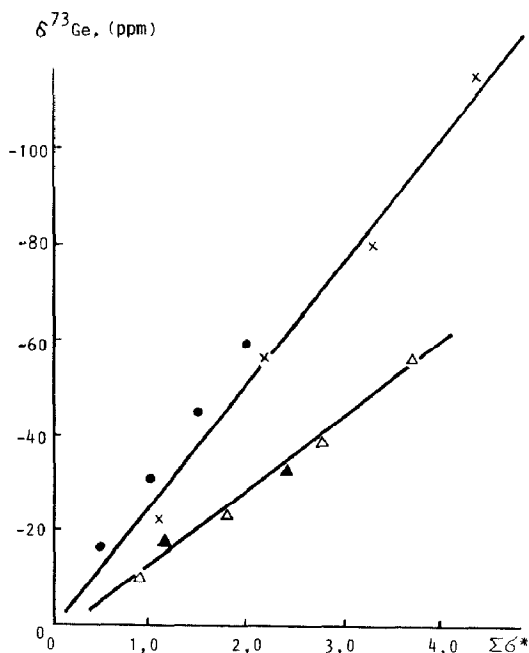
Fig. 2. The dependence of ^{73}Ge CS of hetaryl and vinylgermanes R_nGeMe_{4-n} on the sum of substituent inductive constants: $R = C_4H_3O$ ($\times$); C_4H_3S ($\triangle$); C_6H_5 ($\blacktriangle$); $H_2C=CH$ ($\bullet$).

isostructural compounds should match the ratio of p-orbital radii ($\langle r^{-3} \rangle_{np}$) for the relevant pairs of elements. Mitchell showed that this assumption was true for the pairs Sn/Si and Pb/Sn, and also for the Si/C pair.

A little later on [10] the correlations noted by Mitchell had been extended to include germanium:

$$\delta^{73}Ge = 3.32 \, \delta^{29}Si + 39.9; \quad r = 0.967; \quad n = 29 \tag{1}$$

$$\delta^{119}Sn = 1.56 \, \delta^{73}Ge - 87.4; \quad r = 0.991; \quad n = 26 \tag{2}$$

Since oxygen-containing species cause deviations from eq. 1 exclusion of these compounds from the data improves the correlation:

$$\delta^{73}Ge = 3.29 \, \delta^{29}Si + 13.3; \quad r = 0.995; \quad n = 26 \tag{3}$$

The ratios of p-orbital radii are calculated to be 3.3 ± 0.5 for Ge/Si pair and 1.3 ± 0.1 for Sn/Ge pair [11].

A comparison of the ^{73}Ge CS of the compounds studied (including the published data for vinylgermanes [1] and trimethylethynylgermane ($\delta^{73}Ge = -34.0$ ppm, $\Delta\nu_{1/2} = 300$ Hz)) with the ^{29}Si and ^{119}Sn CS of isostructural compounds yielded the following equations:

$$\delta^{73}Ge = 2.2 \, \delta^{29}Si + 3.9; \quad r = 0.975; \quad n = 18 \tag{4}$$

$$\delta^{119}Sn = 2.2 \, \delta^{73}Ge - 11.3; \quad r = 0.984; \quad n = 14 \tag{5}$$

It can be seen that the slopes of the plots differ somewhat from those predicted. The same has been noted elsewhere for other series of compounds [1,8,12,13]. Evidently, changes in the nuclei shielding are determined not only by the $\langle r^{-3} \rangle_{np}$ term of the

paramagnetic shielding, but also by the changes in the ΔE and Q_{AB} terms; the latter characterises the degree of double-bonding by the central atom.

Thus we assume that the deviations in the experimental correlations between CS of ^{73}Ge and ^{29}Si (or ^{119}Sn) from theoretically predicted ones confirms the existence of additional effects, which are present in some compounds and absent or greatly reduced in others. The contribution of these effects differs for germanium, silicon and tin compounds.

Experimental

^{73}Ge NMR spectra were recorded on a Bruker WM-360 spectrometer operating at 12.56 MHz in CDCl$_3$ solutions at 338 K. Pulse width 50 μs, sweep width 6000 Hz. CS were measured relative to external tetramethylgermanium, the accuracy was estimated as $\Delta\nu_{1/2}/100$ ppm, $\Delta\nu_{1/2}$ being the halfwidth of the signal in ppm. Synthesis of tetraphenyl-, dimethyldiphenyl-, 2-furyl- and 2-thienylgermanes has been described elsewhere [14–16].

Diphenyldi(2-furyl)germane

A solution of n-butyllithium in hexane (53 ml of 1.6 N) was added dropwise to the solution of furan (5.1 g; 0.08 mol) in absolute ether, previously cooled to $-20°$C. The mixture was stirred for 4 h at room temperature, then cooled to $-10°$C, the solution of diphenyldichlorogermane (12.5 g; 0.04 mol) in absolute ether (20 ml) was added dropwise, and mixture was left to warm to room temperature. The lithium chloride was removed by filtration, and the solvent was distilled off. Recrystallisation from ethanol yielded 4.8 g (35%) of diphenyldi(2-furyl)germane, m.p. 98–100°C. Found: C, 66.51; H, 4.0. C$_{20}$H$_{16}$GeO$_2$ calc.: C, 66.61; H, 4.50%. ^{1}H NMR: δ(ppm) 6.49 (dd, J 3.2 and 1.8 Hz, 1 H; H^4); 6.83 (dd, J 3.2 and 0.6 Hz, 1 H; H^3); 7.77 (dd, J 1.8 and 0.6 Hz, 1 H; H^5); 7.3–7.6 (m, 5 H; C$_6$H$_5$).

Phenyltri(2-furyl)germane was synthesized similarly from 2-furyllithium and phenyltrichlorogermane. Yield 17%, m.p. 92–94°C. Found: C, 64.80; H, 3.90. C$_{18}$H$_{14}$GeO$_3$ calc.: C, 64.61; H, 4.0%. ^{1}H NMR: δ(ppm) 6.48 (dd, J 3.2 and 1.6 Hz, 1 H; H^4); 6.78 (dd, J 3.2 and 0.9 Hz, 1 H; H^3); 7.78 (dd, J 1.6 and 0.9 Hz, 1 H; H^5); 7.4–7.7 (m, 5 H; C$_6$H$_5$).

Acknowledgement

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