STUDIES ON THE BOND STRUCTURE OF THE ORGANIC ALLYL DERIVATIVES OF GROUP IV/1 ELEMENTS

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The vinyl, allyl, benzyl and phenyl derivatives of Group IV/1 elements, as well as their structure elucidation have been earlier dealt with [1, 2, 3, 4, 5, 6, 7].

For the purpose of checking the structure established for allyl derivatives the cyclic form had to be studied too. As the dipole moment of the 1,1-dimethyl-germanium-cyclopentene-3 is equal to zero, only that of 3-trimethyl-germanium-cyclopentene-1 was determined. Naturally, a further germanium compound was also necessary (trimethyl-allyl-germanium) and the work was completed by studies on 1-neopentyl-ethylene.

All in all, dipole moments of the following three compounds have been determined:

$$1.\ (CH_3)_3Ge-CH \Big\langle \begin{matrix} CH=CH_2 \\ | \\ CH_2-CH_2 \end{matrix}$$

$$2.\ (CH_3)_3Ge-CH_2-CH=CH_2$$

$$3.\ (CH_3)_3C-CH_2-CH=CH_2$$

The compounds were prepared as published in the literature by the research group directed by V. F. MIRONOV.

The purity of the compounds was checked by comparing molar refractions (MR_D) determined at 25 °C and calculated from the bond increments, as well as by gas chromatography.

Gas chromatography analysis was performed on a G CHF 18.2 Willy Giede apparatus. The packing was Chromosorb W wetted with 18% SE-30, the carrier gas was nitrogen.

The dipole moment was determined by the Onsager method [8], as our compounds were liquids at room temperature and did not tend to associate.

According to Onsager's theory, the dipole moment at 25 °C

$$\mu = 0.22123 \sqrt{P^*} \tag{1}$$

where

$$P^* = (\varepsilon_0 - \varepsilon_{\text{eff}}) \frac{2\varepsilon_0 + \varepsilon_{\text{eff}}}{\varepsilon_0(\varepsilon_{\text{eff}} + 2)^2} \cdot V \tag{2}$$

ε_0 is the measured dielectric constant
V is the molar volume (ml)

$$\varepsilon_{\text{eff}} = \frac{2R + V}{V - R} \tag{3}$$

R is the sum of atomic (P_A) and electronic polarization (P_E). Its approximate value can be calculated from the molar refraction at 25 °C by means of the following equation:

$$R = MR_D \cdot 1.05 = P_A + P_E. \tag{4}$$

The tests were performed at 25 ± 0.02 °C. The temperature was kept constant by an ultrathermostat. The density (d^{25}) was determined using graduated dilatometers, the refractive index with reference to the sodium D line (n_D^{25}) and the dispersion values $(n_F - n_C)$ by means of an Abbé refractometer.

Dielectric constants (ε^{25}) were determined at a frequency of 10 000 Hz using an apparatus constructed in our laboratories [9].

Measurement and calculation results are compiled in Table 1, including recorded refractive indices (n_D^{25}), dielectric constants (ε^{25}), molar volumes (V^{25}), densities (d^{25}), molar refractions calculated from bond increments

Table 1

Characteristic physical constants of 1-neopentyl-ethylene,
trimethyl-allyl-germanium and trimethyl-germanium-cyclopentene-1

	$(CH_3)_3-C-CH_2-CH=CH_2$	$(CH_3)_3-Ge-CH_2-CH=CH_2$	$(CH_3)_3-Ge-CH{<}^{CH=CH}_{CH_2}{>}CH_2$
n_D^{25}	1.3887	1.4289	1.4676
ε^{25}	1.997	2.400	2.299
d^{25}	0.6771	0.9859	1.0626
V^{25}	145.0249	161.0396	173.9196
$MR_{D \text{ calc}}$ (ml)	34.114	41.130	48.226
$MR_{D \text{ meas}}$ (ml)	34.2776	41.5076	48.3110
R	34.2776**	43.5830	50.7266
ε_{eff}	1.928	2.113	2.235
P^*	1.902	7.853	18.357
μD	0.305	0.620	0.948

** For carbon compounds the atomic polarization can be neglected $R = MR_D$.

($MR_{D\ calc}$/ml), measured molar refractions ($MR_{D\ meas}$/ml), sums R of atomic and electronic polarization calculated by means of Eq. (4), the value of the effective dielectric constant (ε_{eff}) calculated using Eq. (3), as well as values of the polarization of orientation (P^*) and of the dipole moment (μ), calculated using Eqs (2) and (1), respectively.

In Table 2 the dipole moments of some compounds are presented which are necessary to our studies.

Fig. 1 clearly shows the change of the dipole moments of compounds of the type $(CH_3)_3MCH_2CH{=}CH_2$, where M=C, Si, Ge, Sn. As the electronegativity of M decreases, the inductive effect increases, similarly to the analogous benzyl compounds, and the dipole moment increases, too. This is in contrast to the analogous phenyl and vinyl compounds where a —M effect is concomitant to the +I effect.

Table 2

Dipole moments of the vinyl, allyl,
phenyl and benzyl derivatives of the Group IV elements

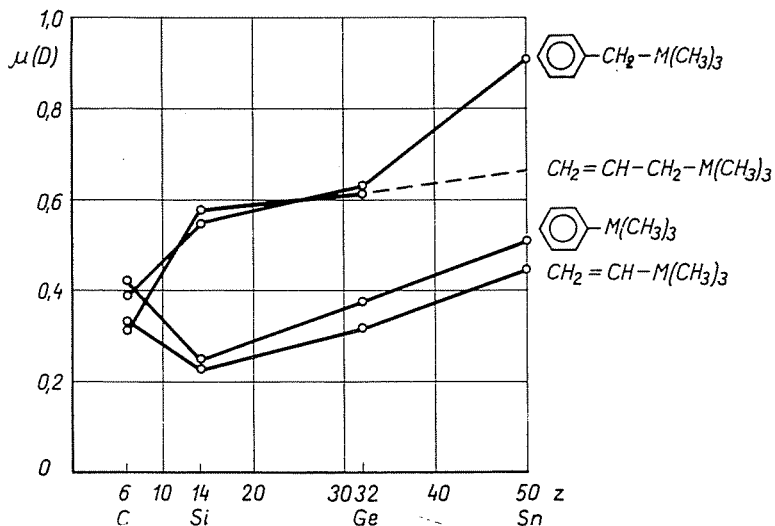| Compound	μD	Reference
$\langle\bigcirc\rangle{-}CH_2{-}C(CH_3)_3$	0.39	[13]
$\langle\bigcirc\rangle{-}CH_2{-}Si(CH_3)_3$	0.55	[10]
$\langle\bigcirc\rangle{-}CH_2{-}Ge(CH_3)_3$	0.632	[7]
$\langle\bigcirc\rangle{-}CH_2{-}Sn(CH_3)_3$	0.91	[10]
$CH_2{=}CH{-}CH_2{-}Si(CH_3)_3$	0.58	[10]
$\langle\bigcirc\rangle{-}C(CH_3)_3$	0.425	[6]
$\langle\bigcirc\rangle{-}Si(CH_3)_3$	0.248	[6]
$\langle\bigcirc\rangle{-}Ge(CH_3)_3$	0.378	[6]
$\langle\bigcirc\rangle{-}Sn(CH_3)_3$	0.51	[10]
$CH_2{=}CH{-}C(CH_3)_3$	0.330	[11]
$CH_2{=}CH{-}Si(CH_3)_3$	0.229	[11]
$CH_2{=}CH{-}Ge(CH_3)_3$	0.319	[11]
$CH_2{=}CH{-}Sn(CH_3)_3$	0.449	[7]

3*

Fig. 1. The change of dipole moment in the vinyl, phenyl, allyl and benzyl derivatives of Group IV elements

Test results on allyl compounds are similar to those obtained for benzyl compounds, attributable to their similar bond structures. This is supported, according to the rule of Karapetiantz, also by the fact that a linear correlation exists between the dipole moments of corresponding pairs of compounds (Fig. 2).

Hence, the expectable dipole moment of the allyl compound of tin might be about 1 *D*. Unfortunately, no such experimental value was available to us.
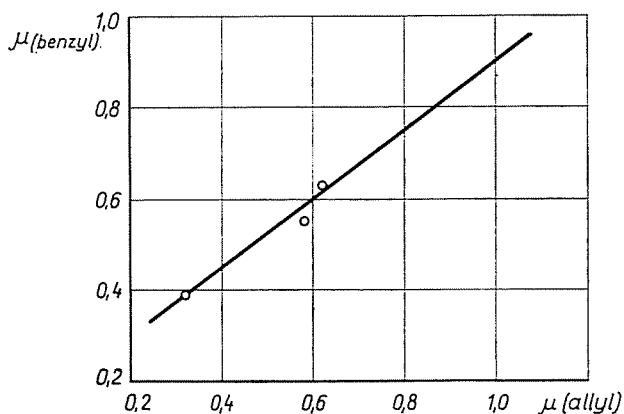

Fig. 2. Correlation between dipole moments of the allyl and benzyl derivatives of Group IV elements

It is clearly shown by both figures that the values for silicon and germanium compounds are very close what can be explained by the similar electronegativity and affinity of the two elements. As mentioned earlier [4, 5], in the case of allyl derivatives a $d - \pi$ interaction, so called long bond and the hyperconjugation of the CH_2 group have to be taken into account.
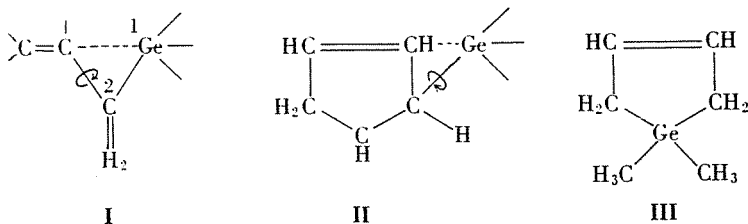
But in the case of compound III there is no long bond, in accordance with the fact that compound II exhibits a marked bathochromic shift in the ultraviolet band relative to compound I, whereas compound III exhibits a great hypsochromic shift [12]. This proves that the long bond lends to compound I, and even more to compound II a more conjugated bond system since the degree of freedom of rotation is lower, whereas in compound III the double bond is practically localized, as no long bond may occur, since germanium lies in the plane of the cyclopentene ring.

This has been stated earlier in connection with silicon compounds [1, 2, 3, 4, 5].

The bond orders calculated by the HMO-ω technique for the three types are as follows:
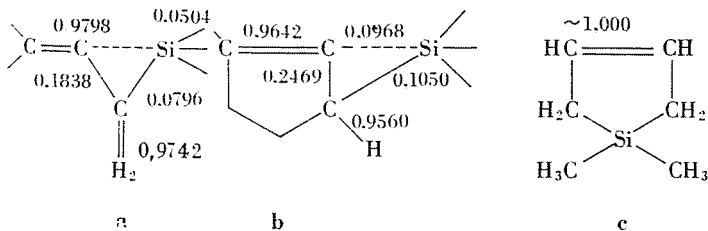
The bond order π of the long bond is seen to 5.04% for *a*, 9.68% hence greater for *b*. Therefore the bond order of the allyl group is 97.98% for *a* and 96.42% for *b*, whereas nearly 100% for *c*.

The isostructural germanium compounds are expected to behave similarly. The fact that dipole moment of the cyclopentenyl compound is much greater than that of the allyl derivative, partly due to the greater electron shift and partly to the lower degree of freedom of rotation is likely to agree with this phenomenon.

This latter statement can be proved by the following model calculation:

I   II
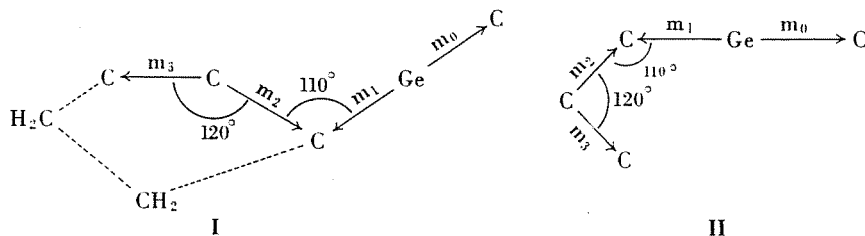
The following values were used in the calculations:

$$m_0 = 0.6 \ D$$

$$m_1 = 0.7 \ D$$

$$m_2 = 0.2 \ D$$

$$m_3 = 0.5 \ D$$

Calculations for minimum and maximum limiting values delivered

$$\mu = 0.53 \ D \ \text{for I, and}$$

$$\mu = 0.35 \ D \ \text{for II.}$$

In view of the fact that 1-trimethyl-germanium-cyclopentene-2 has only a structure corresponding to I, whereas trimethyl-allyl-germanium can assume all the rotation states between I and II including the limiting states, its dipole moment is expected to be smaller than that of the cyclic compound.

Similar statements can be made on the benzyl derivatives of silicon and germanium, as shown earlier [1, 2, 3, 4, 5].

Summary

1. Dipole moments of 1-neopentyl-ethylene, trimethyl-allyl-germanium and trimethyl-germanium-cyclopentene-1 have been determined.

2. Comparison of dipole moments led to the conclusion that a $d - \pi$ interaction occurs between the β-carbon of the allyl group and the silicon atom.

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