Journal of Organometallic Chemistry, 410 (1991) 287–291
Elsevier Sequoia S.A., Lausanne
JOM 21589

^{73}Ge, ^{13}C and ^{1}H NMR spectra of methylethynylgermanes

E. Liepiņš *, M.V. Petrova
Institute of Organic Synthesis, Latvian Academy of Sciences, Riga 226006 (USSR)

E.T. Bogoradovsky and V.S. Zavgorodny
LENSOVET Leningrad Technological Institute, Leningrad (USSR)

(Received November 22nd, 1990)

Abstract

The ^{73}Ge, ^{13}C and ^{1}H NMR spectra of methylethynylgermanes have been studied. The chemical shifts were compared with those of the corresponding isostructural tin compounds and a good correlation has been found. The origin of the chemical shifts could not simply be attributed to the electron densities as estimated by MNDO calculations.

Introduction

Ethynylgermanes offer a challenge for spectroscopic investigations as well as a vast synthetic potential. The electronic structure of this class of compounds has not yet been fully understood, an intriguing aspect being the presence or absence of d_π–p_π backbonding between *d*-orbitals of germanium and the π-systems of triple bonds. Similarities or differences with respect to acetylides of the other Group IV elements also deserve attention.

Whether or not ^{73}Ge NMR signals can be obtained from compounds with a triple bond in the α-position towards the central atom has also been unclear due to the well known difficulties of determinating resonance signals of quadrupolar nuclei. Bearing this in mind we prepared methylethynylgermanes $(CH_3)_{4-n}Ge(C{\equiv}CH)_n$ and recorded their ^{1}H, ^{13}C and ^{73}Ge NMR spectra.

Results and discussion

The results obtained are summarized in Table 1. For the sake of comparison some of the existing literature data on isostructural tin compounds are also included in Table 1 [1–7].

Compounds with *n* equal to 1, 2, or 3 have an asymmetric electric field gradient at the germanium nucleus which might cause excessive broadening of the ^{73}Ge

Table 1

NMR spectra parameters of methylethynylgermanes and -stannanes $(CH_3)_{4-n}M(C^{\alpha}\equiv C^{\beta}H)_n$

M	n	$\delta(^1H)$ (ppm)		$\delta(M)$ (ppm)	$\delta(^{13}C)$ (ppm)			SSCC (J, L, Hz)		
		CH_3	$\equiv CH$		CH_3	C_{α}	C_{β}	$^{13}C-^1H_3$	$^{13}C_{\beta}-^1H$	$^{13}C_{\alpha}-^1H$
Ge	0	–	–	0(2)	−0.60	–	–	125.1	–	–
	1	0.31	2.20	−34(300)	−0.62	89.13	91.90	127.1	236.7	42.0
	2	0.53	2.31	−77(750)	0.08	85.32	92.90	129.1	239.7	42.9
	3	0.75	2.41	−118(800)	1.27	81.44	93.57	131.1	242.8	43.7
	4	–	2.53	−173(14)	–	78.24	94.18	–	245.9	44.7
Sn	0	–	–	0	−8.6	–	–	–	–	–
	1	0.28[1]	2.25[2]	−68.3[1]	−7.46[1]	89.25[1]	97.30[1]	–	233.5 [a][3]	40.5 [a][3]
	2	0.49[4]	2.29[2]	−154.4[4]	−5.96[4]	85.70[4]	97.87[4]	–	235.6 [a][3]	41.5 [a][3]
	3	0.68[4]	2.33	−252.3[4]	−4.53[4]	82.98[4]	98.84[4]	–	–	–
	4	–	2.36[5]	−353.1[6]	–	79.4[7]	98.8[7]	–	242.2[7]	43.0[7]

[a] For $Et_{4-n}Sn(C\equiv CH)_n$ [3].

signals. Fortunately, the broadening was not large and signals could be accumulated. This is the first successful measurement of the ^{73}Ge NMR spectra of organogermanium compounds where germanium is surrounded by ethynyl groups.

The obtained ^{73}Ge CS for ethynylgermanes can be compared with the data on ethynylstannanes (see Table 1). The comparison of ^{73}Ge NMR CS with ^{119}Sn ones in isostructural ethynyl compounds reveal a linear correlation between these parameters: $\delta(^{73}Ge) = 0.481\delta(^{119}Sn) - 0.892$ $(r = 0.997,\ n = 4)$

The slope of this correlation is close to 0.5, which differs considerably from the value of 1.3 [8] predicted on the assumption that the valence level of the p-orbital dominates the values of these chemical shifts.

The MNDO method has acquired a considerable reputation as a simple and highly successful semiempirical molecular orbital calculation technique [9]. That is why we have applied this method to study methylethynylgermanes. The electron densities calculated at various atoms of the compounds under question are given in Table 2.

It is noticeable that the electron densities calculated on the germanium atom are much too low. This probably comes from the fact that the parameters were chosen so that the heat of formation, rather than the electron density, can be reproduced more appropriately. It is expected, however, that the calculated electron density will reflect the relative electron density at the atom in these compounds.

Table 2

The calculated charges (Δq) in methylethynylgermanes $(CH_3)_{4-n}Ge(C\equiv CH)_n$

n	CH_3		Ge	$C\equiv CH$		
	H	C		C^{α}	C^{β}	H
0	0.9965	4.3315	2.7091	–	–	–
1	0.9950	4.3514	2.5259	4.4990	4.1108	0.8557
2	0.9942	4.4176	2.3475	4.5123	4.1070	0.8535
3	0.9927	4.4770	2.1934	4.5231	4.1034	0.8547
4	–	–	2.0476	4.5328	4.1010	0.8547

When the number of ethynyl groups increases the electron density decreases and the ^{73}Ge signal moves upfield. This is in line with previous investigations of methylvinylgermanes [10] and methylvinylsilanes [11] where the same relationships between the nuclear shieldings of ^{73}Ge and ^{29}Si and their electron densities were found. However, both the range of ^{73}Ge chemical shifts and variations in electron density in methylethynylgermanes (Table 2) are larger than those for methylvinylgermanes, consistent with the electronegativity of the ethynyl group being higher than that of vinyl.

Similarly to what is seen in ^{73}Ge resonance, the carbon-13 nuclei signals of methyl group also move downfield with increasing electron density. This tendency appears to be reversed in methylvinylgermanes [10]: the increase in electron density on these carbons is associated with high field shift of ^{13}C NMR signals.

Both the above observations of ethynylgermanes are contrary to what would be predicted knowing the shielding effect of electrons on the chemical shifts.

The increase in number of ethynyl groups in the molecule increases the polarity of the triple bond $C_\alpha^{\delta-}{\equiv}C_\beta^{\delta+}H$; as one would assume from the differences between $^{13}C_\alpha$ and $^{13}C_\beta$ chemical shifts.

$^{13}C_\alpha$ and $^{13}C_\beta$ carbon shieldings were inversily related to the number of ethynyl groups in the molecule: $^{13}C_\alpha$ signals move upfield and $^{13}C_\beta$ downfield in the series $n = 1 \rightarrow 4$ (Table 1). This corresponds to the changes in the electron density of these nuclei (Table 2).

The $^{13}C_\alpha$ or $^{13}C_\beta$ chemical shifts and electron densities of these atoms are mutually related:

$$\delta(^{13}C_\alpha) = 1542.2 - 323.1\Delta q_{C_\alpha} \quad (r = 0.999,\ n = 4)$$

$$\delta\left(^{13}C_\beta\right) = 915.6 - 200.3\Delta q_{C_\beta} \quad (r = 0.996,\ n = 4)$$

Occurrence of two independent correlation lines for C_α and C_β carbons probably indicates extra factors governing the chemical shifts of both ethynyl carbons. Such additional factors may be as follows: (1) anisotropy of triple bond, and (2) σ–π conjugation between triple bond and methyl group at germanium. One would expect that anisotropy of the ethynyl bond would affect further deshielding of the C_α-atom in step with the increase of n from 1 through 4.

The σ–π conjugation must exert its main influence on the $^{13}C_\beta$ chemical shift decreasing as n increases from 1 through 4. Perhaps the latter effect may be responsible for the inverse relationship between ^{13}C chemical shifts and electronic charges of methyl groups, too.

The difference in $\delta(^{13}C_{CH_3})/\Delta q$ and $\delta(^{13}C_\alpha)/\Delta q$, $\delta(^{13}C_\beta)/\Delta q$ relationships can be explained (following Fliszar [12]). In the latter case ($\delta(^{13}C_\alpha)$, $\delta(^{13}C_\beta)$) the gain in π-charge is obviously more important than the loss in σ-population. In the case of $\delta(^{13}C_{CH_3})$ increase in charge is dominated by the σ-population.

As for $\delta(^{73}$Ge) the situation is more complicated: the considerable influence of $4p$, $3f$, $3p$ AO electron interactions must be taken into consideration.

Therefore, the full analysis of the electronic structure and bonding situation must take into account all factors affecting the interactions between the orbitals of the various fragments of these molecules in order to obtain comprehensive explanations for the changes occurring in germanium-73 chemical shifts. These calculations have not been carried out owing to the absence of satisfactory theory.

^1H NMR spectra demonstrate downfield shifts for both methyl and methine proton signals when the number of ethynyl groups increases (see Table 1). This is consistent with the decrease of electron density in the vicinity of hydrogen nuclei as n increases from 0 through 4. However, one can observe the greater sensitivity of ^1H chemical shifts when the methyl group is replaced by ethynyl (Table 1) as compared with the similar substitution in methylvinylgermanes [10]. This corresponds to the larger electronegativity of the ethynyl group compared with that of the vinyl group.

We have measured $^{13}C-^1H$ coupling constants for the title compounds, too (Table 1). Increasing the number of attached ethynyl groups results in an increase of the absolute value of $^nJ(^{73}Ge-^1H)$ coupling constants. This is in accordance with the increase in electronegativity of substituents. The same tendencies can be observed in methylethynylstannanes (Table 1).

^{73}Ge NMR signal of tetraethynylgermane $Ge(C{\equiv}CH)_4$ is sufficiently narrow and this allowed us to measure $^1J(^{73}Ge-^{13}C_\alpha)$ coupling constant, obtaining a value of 59.2($\pm$0.3) Hz. Up to now this type of coupling constant has only been measured in tetramethylgermane $^1J(^{73}Ge-^{13}C) = -18.7$ Hz [13].

The change in carbon atom hybridization from sp^3 to sp significantly increases the $^1J(^{73}Ge-^{13}C)$ coupling constant in line with theoretical predictions and experimental findings for $^1J(M-^{13}C)$ ($M = {}^{119}Sn$, ^{29}Si) in isostructural stannanes and silanes. Therefore, it can be assumed that the Fermi-contact mechanism is predominant and determines this coupling constant.

Experimental

Ethynylgermanes were obtained by reaction between the corresponding germanium halides and trimethylethynylstannane in hexamethyltriamidophosphate solution as described in [14].

The ^1H spectra were recorded on a Bruker WM-360 spectrometer as $CDCl_3$ solutions containing a small amount of TMS as internal standard.

Also recorded were natural abundance ^{13}C (frequency 90.5 MHz, 30° pulse (15 μs), spectral width 20 KHz, number of scans 200 ÷ 300), and ^{73}Ge (frequency 12.56 MHz, 90° pulse (50 μs), spectral width 6 KHz, number of scans 50000 ÷ 100000).

^{13}C CS were measured relative to TMS internal standard with an accuracy of $\pm$0.03 ppm. ^{73}Ge CS were measured relative to an external tetramethylgermanium standard, the accuracy was estimated as $\pm\Delta\nu_{1/2}/100$ ppm, where $\Delta\nu_{1/2}$ is the halfwidth of signals in ppm.

The AMPAC program [15] was used for MNDO calculations. Geometrical parameters were taken from [16].

We are grateful to Dr. L. Ignatovich for the generous gift of some germanium halides.

References

1 V.A. Pestunovich, E.O. Tsetlina, M.G. Voronkov, E. Liepiņš, E.T. Bogoradovsky, V.S. Zavgorodny, V.L. Maksimov and A.A. Petrov, Dokl. Akad. Nauk SSSR, 243 (1978) 149.

2 B. Wrackmeyer, Rev. Silicon, Germanium, Tin and Lead Compounds, 6 (1982) 75.

3 A. Sebald and B. Wrackmeyer, Spectrochim. Acta, Part A, 37 (1981) 365.

4 E.O. Tsetlina, V.A. Pestunovich, M.G. Voronkov, E. Liepiņš, V.N. Cherkasov, E.T. Bogoradovsky, V.S. Zavgorodny and A.A. Petrov, Dokl. Akad. Nauk SSSR, 245 (1979) 400.

5 E.T. Bogoradovsky, V.P. Novikov, V.S. Zavgorodny and A.A. Petrov, J. Gen. Chem., 45 (1975) 2650.

6 V.S. Zavgorodny, V.N. Cherkasov, E.T. Bogoradovsky, A.A. Petrov, V.A. Pestunovich, E.O. Tsetlina and M.G. Voronkov, Abstracts of the All-Union Conference: "Heavy nucleus" NMR Study of Organoelemental Compounds, Irkutsk, 1979, p. 38.

7 B. Wrackmeyer, Z. Naturforsch. B, 37 (1982) 1524.

8 P.I. Watkinson and K.M. Mackay, J. Organomet. Chem., 275 (1984) 39.

9 M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc., 99 (1977) 4899.

10 Y. Takeuchi, H. Inagaki, K. Tanaka and S. Yoshimura, Magn. Res. Chem., 27 (1989) 72.

11 L. Delmulle and G.P. van der Kelen, J. Mol. Struct., 55 (1980) 309.

12 S. Fliszar, Charge distributions and Chemical effects, Springer-Verlag, New York, 1983, p. 205.

13 D.K. Dalling, H.S. Gutovsky, Gov. Rep. Announce. (U.S.), 71 (1971) (Chem. Abstr., 75 (1971) 82238).

14 E.T. Bogoradovsky, V.S. Zavgorodny, B.V. Polozov and A.A. Petrov, J. Gen. Chem., 46 (1976) 1659.

15 Available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405.

16 M.J.S. Dewar and C. Jie, Organometallics, 8 (1989) 1544.