



Homo- and Heteronuclear NMR Methods for Signal Assignments in ^1H and ^{13}C Spectra of 1-Aminoacyloxygermatran

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Abstract

1-Aminoacyloxygermatran containing a hexacoordinated germanium atom and an amino acid substituent in its structure—L-valine—was synthesized and studied by high resolution ^1H and ^{13}C NMR spectroscopy for the first time. Complete signal assignment in two different parts of ^1H spectra containing 8 and 12 overlapped multiplets from $-\text{O}-\text{CH}_2-$ and $-\text{N}-\text{CH}_2-$ protons was made by using homonuclear *J*-COSY, COSY and NOESY methods and on base data of heteronuclear HMQC and HMBC experiments. The spatial structure of the studied 1-aminoacyloxygermatran was proved on the basis of data on interproton through-space interactions obtained from the NOESY spectra at different mixing times from 0.3 to 1.2 s. Simultaneously, along with cross peaks from positive NOEs, exchange cross peaks between germinal protons of different $-\text{O}-\text{CH}_2-$ groups were found in the same spectra, thus indicating the existence of a slow (in the NMR time scale) dynamic process in this compound associated with rearrangements within the atranium cycle.

1 Introduction

Chemical compounds with specific physical and chemical properties have always attracted much attention of research chemists. Undoubtedly, such compounds are hypercoordinated or hypervalent molecules, the central atoms of which are

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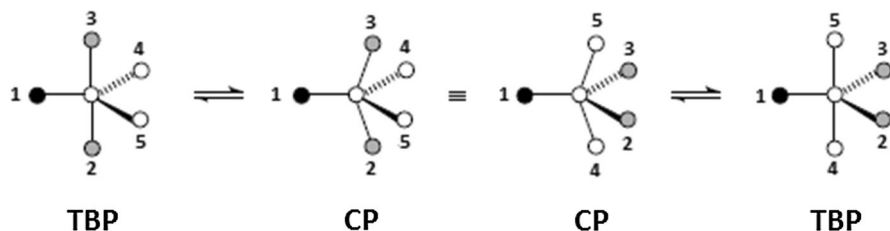


Fig. 1 Transition from TBP (trigonal-bipyramidal) configuration, through CP (square pyramid—Berry pseudo-rotation [8]) and back to TBP

the elements of group 14 of the Mendeleev table—Si, Ge, Sn. Although these elements are in the same group as carbon, their properties are significantly different. When studying the elements standing below carbon (Si, Ge, and Sn), these elements were found to have specific properties that are not typical of the carbon atom. One of the main properties is that they are able to form a coordination environment above four, due to the presence of a free d-orbital. In such compounds, the number of valence electron pairs exceeds the number of available binding orbitals. As a rule, the coordination number of the central atom of the molecule is higher than four (5 or 6) [1, 2].

Thanks to quantum chemistry, which provided an opportunity to study the electronic structure of the atoms of the 14th group elements in more detail, the model of hypervalence was proposed. According to this model, a four-electron three-center bond is formed in the axial fragment between the unshared electron pair of the donor (O), the 3p_z-electron of the central atom (Si, Ge) and the valence electron of its substitute. A donor–acceptor bond N–Ge is also formed due to the unshared electron pair of the nitrogen atom and the vacant d-orbitals of the germanium atom [3]. Nowadays, compounds of hypercoordinated germanium still attract the attention of researchers. However, a specific area of the dynamics of hypercoordinated germanium compounds—stereochemical rigidity—has been poorly studied.

In articles [4–7], the results of studies of stereochemical rigidity of hyper- and hypocoordinated silicon, germanium and tin compounds by NMR and DNMR spectroscopy on various nuclei are summarized. In particular, in work [4], it is referred to non-dissociative mechanisms manifested in pentacoordinated complexes (Fig. 1), which include Berry pseudo-rotation [8].

Methods to determine the spatial structure of new hypervalent silicon, germanium and tin derivatives containing intramolecular O→M coordination bonds, with different structures based on high resolution multinuclear NMR data, NMR spectroscopy ¹³C, ²⁹Si in solid state as well as obtaining quantitative values of ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger different stereodynamic processes have been developed. Fundamental results were obtained due to the study of permutation isomerization of derivatives of pentacoordinated silicon, germanium and tin atoms. Studies on the establishment of the permutation mechanism in bischelate hexacoordinated complexes were also carried out in this work. The mechanism proceeds according

to the irregular scheme and depends on the structure of the coordination unit and the nature of the monodentate electronegative substituent [8–10].

In article [11], it was first shown that in the compounds $N(\text{CH}_2\text{CMe}_2\text{O})(\text{CMe}_2\text{CH}_2\text{O})\text{MX}$ ($\text{M}=\text{Sn}, \text{Ge}$; $\text{X}=\text{Ot-Bu}, \text{OEt}, \text{Br}$), the central atom and nitrogen atom are stereogenic centers. For example, germatrans are the monomer in the solid state, but in the liquid state they have been recorded by NMR spectroscopy at low temperature (-80°C) as two diastereomers.

Despite the fact that there are works devoted to the dynamic rigidity of systems with a hypervalent germanium atom, the relevance of the research remains unchanged. This is especially true for germatrans with a six-coordinated germanium atom, which has not been studied in the field of stereochemical rigidity.

2 Results and Discussion

2.1 ^1H and ^{13}C NMR Spectra of 1-Aminoacyloxygermatran (1) and Simplest Signal Assignments

The main goal of this work is to identify the signals in the ^1H and ^{13}C NMR spectra of 1-aminoacyloxygermatran (**1**), which have been recently synthesized in our laboratory for the first time by two following stages (Fig. 2) through intermediate product (1a).

Several assignments of individual signals in both spectra can be made based on the known criteria for their chemical shifts and multiplet structure. In the case of compound (**1**), two doublet signals at 0.93 and 0.99 ppm with scalar constant of 7.0 Hz and an intensity of 3H each of them can be easily assigned to the protons of methyl groups 18a and 18b, respectively. There is no doubt that the signal at 2.22 ppm with a complex multiplet structure (dq—doublet of quartets) and intensity 1H belongs to the H18 proton. It is unlikely that in this spectrum, which was recorded in D_2O , it will be possible to detect signals of mobile protons of the $-\text{N}^{17}\text{aH}_2$ or $-\text{O}^{5c}\text{H}$ groups, but the signal of the C^{17}H proton, which should have a scalar interaction with the C^{18}H proton, of course, on this basis, will be detected in the corresponding region of the ^1H NMR spectrum. Similarly, the signal of the carbonyl group $\text{C}^{16}=\text{O}$ at 174.26 ppm can be easily found in the ^{13}C NMR spectrum or signals of C^{18a} and C^{18b} methyl groups at

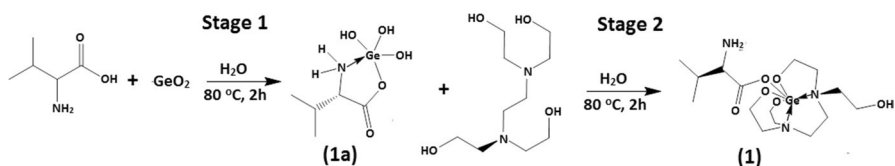


Fig. 2 The scheme of two-stage synthesis of 1-aminoacyloxygermatran (**1**)

17.56 and 17.90 ppm, respectively, as well as a $C^{18}H$ signal at 29.03 ppm (see Fig. S1 and S2 in supplementary information).

2.2 Application of 2D NMR Methods for Complete Signal Assignment

All other signals belonging to the protons of the three ethane fragments $-O-CH_2-$, $-CH_2-N-$, as well as the fragments $-N^5-C^6H_2-C^7H^2-N^8-$ and $-N^5-C^{5a}H_2-C^{5b}H_2-OH$, are situated in two separate regions of the NMR 1H spectrum of the compound (**1**) and create two groups of overlapping signals in the regions of 2.86–3.35 ppm and 3.53–3.96 ppm (Fig. 3) difficult for identification.

Thus, the spectral analysis of two complex regions of proton spectra requires additional information on the spatial and scalar interactions between the protons of all ethane fragments, which can be only obtained using two-dimensional correlation NMR methods. At the same time, the 11 signals of ^{13}C nuclei corresponding to the indicated ethane fragments are in a narrow range of 51–61 ppm and do not overlap (Fig. S2).

It should be noted that the integration of the proton signals of $-O-CH_2-$ and $-CH_2-N-$ groups shows a more uniform distribution of the signals of 9 protons in the range of 3.53–3.96 ppm than of 12 protons in the range of 2.86–3.35 ppm. Particularly overloaded and complex is the region 3.03–3.25 ppm, which contains multiplet signals of approximately six protons. Therefore, the results of the J -COSY [12] experiment have played an extremely important role in the spectral analysis, which made it possible to decompose all overlapping signals into separate multiplets (Fig. 4), which are numbered using letters of the alphabet.

Due to the high resolution along the F1 coordinate in the spectral region of $-O-CH_2-$ protons, one can easily distinguish three multiplet signals at 3.76 (**d**), 3.66 (**f**) and 3.57 (**h**) ppm, which have almost the same structure “**ddd**” (doublet of doublets): $J(\mathbf{d})=5.3, 11.1, 12.1$ Hz, $J(\mathbf{f})=6.1, 10.8, 10.8$ Hz, $J(\mathbf{h})=6.6, 8.6, 10.8$ Hz. In this case, the sum of all constants (i.e., the multiplet width) for signals “**d**”, “**f**” and “**h**” is 28.5, 27.7, 26.0 Hz, respectively. This decrease in the sum of constants for these signals is marked in Fig. 4 by horizontal lines (relative to signal “**d**” at 3.76 ppm) and double vertical arrows.

Three other multiplet signals at 3.86 (**b**), 3.80 (**c**) and 3.68 (**e**) ppm also have the “**ddd**” structure, but a different set of scalar constants: $J(\mathbf{b})=1.5, 7.2, 11.1$ Hz,

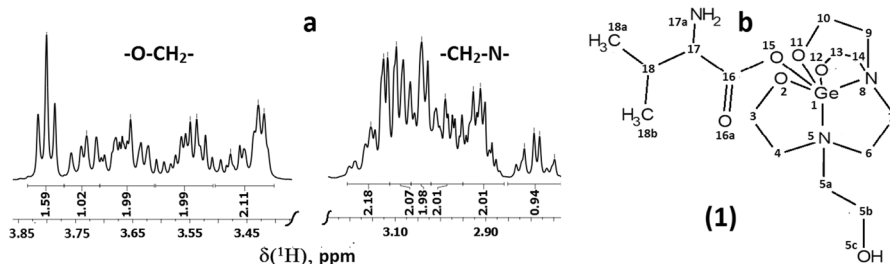


Fig. 3 **a** Fragments of NMR 1H spectrum in D_2O and **b** numbering of compound (**1**)

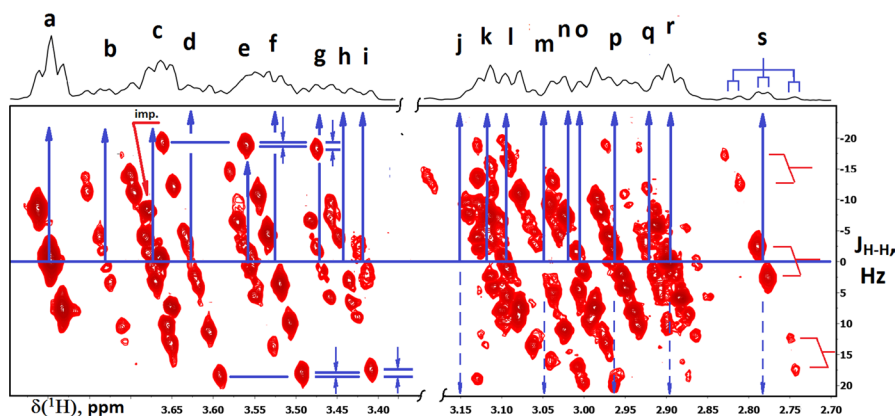


Fig. 4 Fragments of J-COSY spectrum of 1-aminoacyloxygermatran (**1**) in D₂O

$J(\mathbf{c})=2.0, 7.3, 10.8$ Hz, $J(\mathbf{e})=3.5, 7.1, 10.8$ Hz. Therefore, the sum of all constants for signals “**b**”, “**c**” and “**e**” is only 20.2, 20.2, 21.4 Hz, respectively. These results provide the basis for establishing either the protons of the indicated groups of signals belong to pseudo-axial or pseudo-equatorial protons. It is easily determined based on the Karplus dependence of vicinal constants on the dihedral angle [13–15], which leads to the following set of constants for the protons of the ethane fragment in rigid cyclic structures: The sum of the constants (i.e., the multiplet width) for the equatorial proton is always less than for axial. Thus, the signals are at 3.76 (**d**), 3.66 (**f**) and 3.57 (**h**) ppm that belong to pseudo-axial protons, and the signals at 3.86 (**b**), 3.80 (**e**) and 3.68 (**e**) ppm to pseudo-equatorial ones.

In addition, the triplet signal “**a**” at 3.92 ppm can be assigned to protons of the $-C^{5b}H_2-$ group, whose scalar constants with neighboring $-C^{5a}H_2-$ protons are averaged up to 5.7 Hz due to free rotation around $C^{5a}-C^{5b}$ bond. Finally, the last ninth signal in the considered region 3.53–3.96 ppm is a doublet signal “**i**” at 3.54 ppm with constant ${}^3J_{H-H}=4.6$ Hz, which belongs to the H17 proton. This is easily confirmed by the same splitting of the H18 signal at 2.22 ppm: Since the full width of this multiplet is 46 Hz (see Fig. S1 in SI) and the constant of this proton with the methyl group is 7.0 Hz (measured on doublet signals at 0.99 and 0.93 ppm), the value of the vicinal constant ${}^3J_{H18-H17}$ can be determined as the difference between the total width of the multiplet and the sum of all splitting from six protons of two methyl groups 18a and 18b: ${}^3J_{H18-H17}=46 - 2 \cdot 7 \cdot 3 = 46 - 42 = 4$ Hz.

These three pairs of axial and equatorial protons can be related to each other in two independent ways: by observing scalar interactions between geminal protons (i.e., through ${}^2J_{H-H}$), or through strong spatial interactions between these protons, since the cross-relaxation rate between geminal protons ($r_{ax-eq}=1.78$ Å) for such pairs of protons will be maximum in NOESY spectrum. Therefore, the next necessary step in identifying the proton signals of compound (**1**) is the analysis of the COSY [16] and NOESY spectra [17–19] at time mixing of 0.5 s (Fig. 5a, b, respectively).

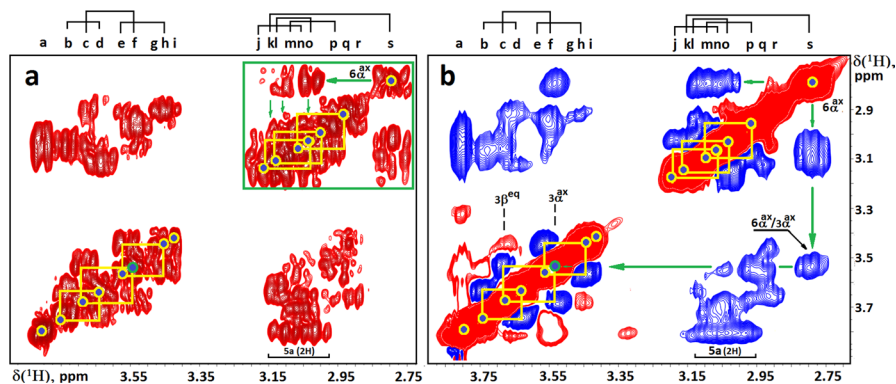


Fig. 5 Fragments of COSY (a) and NOESY (b) spectra of 1-aminoacyloxygermatran (**1**) at mixing time 0.5 s. Signals of geminal proton pairs are shown by yellow rectangles, and most important through space interaction $6\alpha x/3\alpha x$ by green arrows

Comparison of the cross peaks between geminal protons in the COSY and NOESY spectra gives the same result, which confirms the following pair interactions in two independent ways: “b-d”, “c-f” and “h-e.” In Fig. 5, they are shown with the help of yellow rectangles, in which the corresponding protons are located at the ends of one of the diagonals (indicated by yellow circles), and on the other the centers of cross peaks between these protons. These pairs are especially well seen in the NOESY spectrum (Fig. 5b) as intense negative cross peaks (blue color) near the diagonal with a positive (red color) signal orientation. These pairwise interactions are also shown by connecting black lines at the top of the 2D spectra.

In addition to cross peaks between $-O-CH_2-$ protons, the same spectra show cross-peaks between vicinal protons for all ethane fragments of $-N-CH_2-CH_2-O-$ compound (**1**), as well as between geminal protons $-N-CH_2-$ located in the region of 2.86–3.35 ppm. In this case, the same nature of the arrangement of cross peaks associated with scalar (${}^{2,3}J_{H-H}$) and spatial (NOE) interactions is generally retained. This makes it possible to determine three pairs of geminal protons $-N-H_2-$ based on the already known pairs: “b-d”, “c-f” and “h-e” using the cross peaks of the COSY and NOESY spectra located between the two regions 3.53–3.96 ppm and 2.86–3.35 ppm. The only exception to the coincidence of COSY and NOESY cross peaks for compound (**1**) is the fragment $-N^5-C^6H_2-C^7H_2-N^8-$, all four protons of which have signals in the same region. Therefore, the detection of a signal from at least one of them makes it possible to unambiguously assign all other protons. The main criterion for this can be the detection of a NOE cross peak between vicinal protons in the absence of a cross peak in the same place of the COSY spectrum, since the scalar interaction between protons of different ethane fragments is impossible or extremely small.

Careful comparison of cross peaks in two different spectra in Fig. 5 makes it possible to detect the spatial interaction between protons “s” (2.91 ppm) and “f” (3.66 ppm). Based on the multiplicity of the proton signal “s” (dt, $J(s)=5.4, 11.1, 11.1$ Hz), it is axial like proton “f” and is located in position 6 or 7 of compound

(1). Therefore, to determine the unknown proton “f,” it must be found in the nearest environment of protons H6ax (or H7ax) axial proton of the neighboring ethane fragment -O-CHax-, which is located as close as possible to one of them (i.e., to H6ax or H7ax). Optimization of the geometry of the molecule (1) using the molecular mechanics method (MM2) gave an unambiguous answer: Only the H3 $\alpha^{(ax)}$ (s) proton, which is at a distance of 2.86 Å from the proton, can be such a proton H6 $\alpha^{(ax)}$ (f) (Fig. S8). Only the geminal proton H6 $\beta^{(eq)}$ ($r_{6ax-6eq} = 1.78$ Å), the proton H7 $\alpha^{(eq)}$ ($r_{6ax-7eq} = 2.34$ Å) and the proton H4 $\alpha^{(eq)}$ ($r_{6ax-4eq} = 2.47$ Å) are slightly closer to the proton “f,” while all other protons are at a distance more than 3.0 Å (for example, $r_{6ax-7ax} = 3.05$ Å, $r_{6ax-4ax} = 3.71$ Å), but the most important thing is that none of the listed protons, except for H3 $\alpha^{(ax)}$ (s), can have signals in the range of 3.53–3.96 ppm. Therefore, the second sufficiently intense proton cross-peak H6 $\alpha^{(ax)}$ (s) includes all other spatial interactions of this proton (see Fig. S8). This simultaneously indicates the position of the H6 $\beta^{(eq)}$, H7 $\alpha^{(eq)}$, and H4 $\beta^{(ax)}$ protons in the ^1H NMR spectrum in the range of 3.12–3.28 ppm.

Another way to obtain independent information about the position of proton signals is the use of HMBC [20] and HMQC [21] heteronuclear correlation spectra (Fig. 6a, b, respectively), which also allow us to make justified assignments of signals in the ^{13}C NMR spectrum of compound (1).

The most informative of these spectra is undoubtedly HMQC, which is the decomposition of the proton spectrum in terms of the chemical shifts of the carbon nuclei associated with them. Compared to the *J*-COSY spectrum, the sequential arrangement of protons in this spectrum is completely preserved, but the pairs of protons of the O-CH₂- and N-CH₂- groups are clearly visible, and even the multiplicity of some signals, on the basis of which one can conclude that they belong to axial or to equatorial protons. Since this issue for the O-CH₂- groups was already considered when discussing the *J*-COSY spectrum, we will make the same conclusions using the HMQC method for the proton pairs of N-CH₂- groups, where signals are in the region of 2.84–3.34 ppm, that is more difficult to analyze. First of all, it should be noted that in this heteronuclear spectrum, one can easily determine the total number of such protons—there are 12 of them at 6 carbon atoms. In the case of using the *J*-COSY method, only 10 such protons were found, which were designated by letters of the alphabet from “j” to “s.” Therefore, two proton signals

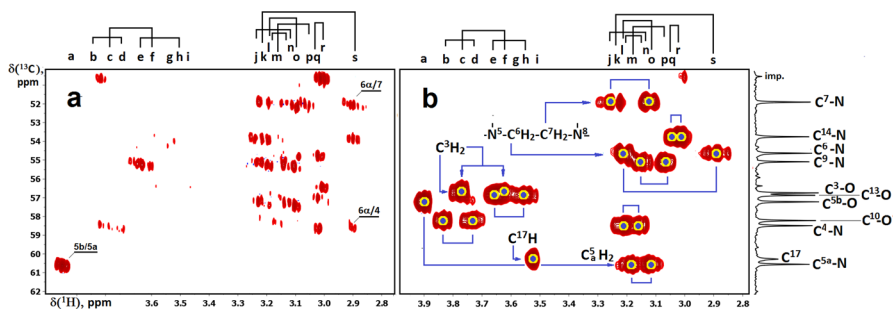


Fig. 6 Fragments of HMBC (a) and HMQC (b) spectra of 1-aminoacyloxygermatran (1)

were missed in the J -COSY spectrum (see Fig. 4), which probably had exactly the same chemical shift with some other protons and simply overlapped with them. The HMQC spectrum shows that this could happen in the area where the “j”- “m” signals are located, in which, according to the heteronuclear experiment, there are not four, but six multiplet signals. The multiplet structures of the signals for the geminal proton pair at 3.15 and 3.02 ppm “j”- “n” (C^7H_2) are a triplet and doublet, respectively, and the multiplet structures of the pair at 3.25 and 2.91 ppm “l”- “s” (C^6H_2), on the contrary, are a doublet and triplet, respectively. Consequently, the sequence of arrangement of the axial and equatorial protons in the ethane fragment $-N^5-C^6H_2-C^7H_2-N^8-$ is opposite.

Compared to HMQC, the HMBC spectrum looks less informative both because of an increase in the number of cross peaks (especially in the region of $N-CH_2$ -protons) and due to the simultaneous registration of interactions through the direct constant $^1J_{C-H}$. Therefore, the exact identification of most cross-peaks is difficult. Nevertheless, marked in Fig. 6a, cross peaks 5b/5a, 6 α /7 and 6 α /4 are important evidence in the identification of carbon signals C^{5a} , C^7 and C^4 , respectively. The results obtained for the identification of signals in the 1H and ^{13}C NMR spectra are shown in Table 1.

Table 1 1H and ^{13}C chemical shifts (δ , ppm) of the 1-aminoacyloxygermatran (**1**) in D_2O

$N^{\#}$ *	1H	$\delta(^1H)$, ppm	$\delta(^{13}C)$, ppm	Signal index	$N^{\#}$ *	1H	$\delta(^1H)$, ppm	$\delta(^{13}C)$, ppm	Signal index
3 (O)	$\alpha(ax)$	3.66	56.79	f	13 (O)	$\alpha(eq)$	3.68	56.91	e
	$\beta(eq)$	3.80		c		$\beta(ax)$	3.57		h
4 (N)	$\alpha(eq)$	3.25	58.52	k**	14 (N)	$\alpha(ax)$	3.04	53.82	q
	$\beta(ax)$	3.18		m**		$\beta(eq)$	3.02		r
5a (N)	5a`	3.13	60.57	o	16	–	–	174.26	–
	5a``	3.22		l		–	–		–
5b (O)	5b`	3.92	57.26	a	17	–	3.54	60.30	–
	5b``	3.92		a		–	–		–
6 (N)	$\alpha(ax)$	2.91	54.70	s	18	–	2.22	29.03	–
	$\beta(eq)$	3.25		k**		–	–		–
7 (N)	$\alpha(eq)$	3.15	51.98	n	18a	–	0.93	17.56	–
	$\beta(ax)$	3.28		J		–	–		–
9 (N)	$\alpha(ax)$	3.18	55.15	m**	18b	–	0.99	17.90	–
	$\beta(eq)$	3.09		p		–	–		–
10 (O)	$\alpha(eq)$	3.86	58.25	b	–	–	–	–	–
	$\beta(ax)$	3.76		d		–	–		–

* – Carbon number and neighboring atom in brackets

** – Identical chemical shift and overlapping of signal pairs 4 $\alpha^{(eq)}$, 6 $\beta^{(eq)}$ и 4 $\beta^{(ax)}$, 9 $\alpha^{(ax)}$

3 Conclusion

The set of NMR methods (*J*-COSY, COSY, NOESY, HMQC and HMBC) was used in this work to identify the signals of 20 protons and 11 carbons in the ^1H and ^{13}C spectra of a previously unknown and recently synthesized compound—1-aminoacyloxygermatran (**1**). A distinctive feature of the proton spectrum of this compound is the close location and, accordingly, overlapping of the signals of $-\text{N}-\text{CH}_2-$ and $-\text{O}-\text{CH}_2-$ groups in two narrow (less than 0.5 ppm) regions of 2.86–3.35 and 3.53–3.96 ppm. The position of these signals and their multiplet structure (including the measurement of geminal and vicinal constants) were established mainly using the *J*-COSY method. The spatial orientation of the corresponding protons in the ethane fragments (i.e., belonging to pseudo-axial or pseudo-equatorial protons) and their α - or β -orientation relative to the main axis of the molecule (**1**) were determined by analyzing the NOESY spectra at different mixing times ($\tau_m = 0.4, 0.5, 0.8$ and 1.2 s) and a qualitative comparison of these data with the results of geometry optimization of the 1-aminoacyloxygermatran (**1**) molecule by the MM2 molecular mechanics method. When establishing the protons that make up the $-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}-$ and $-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-$ ethane fragments, and their belonging to various five-membered cycles, including the germanium atom (Ge), it was used, although in different least, the totality of all obtained experimental and calculated data. It should be noted that the results of assigning the signals of carbon-13 nuclei are a direct consequence of the analysis of the proton spectrum, and the use of the HMQC and HMBC correlation methods is associated only with the formal binding of the signals of the ^{13}C NMR spectrum to the already established signals of the proton spectrum. This approach provided accurate identification of 11 carbon signals in the range of less than 10 ppm, even in the case of a minimal difference in their chemical shifts of 0.12 ppm, observed for C^3 and C^{13} atoms.

Undoubtedly, the complete and reliable sets of ^1H and ^{13}C nuclear signals obtained as a result of the work are the first and necessary step in a comprehensive study of a new and promising compound (**1**), especially in that part of it that is associated with the potential dynamic mobility of 1-aminoacyloxygermatran and, accordingly, with its biochemical properties. The EXSY-NOESY spectrum [22] in Fig. 5b clearly shows positive (i.e., identical in sign with the diagonal ones) exchange cross-peaks (red color) between the protons of three different $-\text{O}-\text{CH}_2-$ groups, which indicate a slow (in the NMR time scale) dynamic rearrangement of the molecule (**1**). So, as a result of this NMR study, protons exchanging with each other have become known, we can proceed to the second more important part of the entire study—to analyze the nature of the dynamic processes of 1-aminoacyloxygermatran (**1**) in aqueous solution and quantify their thermodynamic and kinetic characteristics. But this is the topic of future works and publications. As an announcement, the four figures (Fig. S9–S12) present only preliminary information that is a direct consequence of this study: dynamic proton exchange in 1-aminoacyloxygermatran (**1**) based on EXSY-NOESY spectrum data (Fig. S9), two-position conformational exchange as one of the

possible options for describing the rearrangement process (Fig. S10) and the final scheme of this work (Fig. S11).

The same dynamic processes were found in the study of similar organic germanium compounds and summarized recently in a collection of reviews (edited by Vladimir Ya. Lee) on the study of the synthesis, properties and application of organometallic derivatives of germanium [23]. Publishing of this collection of reviews demonstrates a profound interest to this field of synthesis, various research of structure and properties of organogermanium compounds including their dynamics in liquid.

4 Materials and Methods

All 1D and 2D NMR spectra of compound (**1**) in D₂O were acquired on JEOL ECX400A NMR spectrometer (400 MHz for ¹H nuclei and 100 MHz for ¹³C nuclei) with inverse probe equipped with a z-gradient. Chemical shifts are relative to residual signals of D₂O (4.79 ppm for ¹H) [24]. All measurements were carried out without sample spinning at 295 K. Initial time-domain NMR signals (FID) were processed in MestReNova program [25]. Routine 1D data were apodized with 0.5 Hz exponential functions, while 2D-data were treated with 90-degree sine squared (t1) and 90-degree sine bell (t2) functions prior to Fourier transform. Usual acquisition parameters for phase-sensitive 2D-NOESY spectra of compound (**1**) were 1024 t2 points, 200–256 t1 points, 3.6 kHz sweep width and 0.3 s t2 acquisition time. 2D-NOESY spectra were recorded at different relaxation delays 1–5 s and varied mixing times 0.4, 0.5, 0.8 and 1.2 s. The best result for compound (**1**) was at relaxation delay D1 = 5.0 s and $\tau_m = 0.5$ s. 2D-NOESY spectra were obtained without a zero-quantum coherence elimination, and processing procedures did not include baseplane correction and decreasing t1-noise. Non-overlapping cross-peaks, including low-intensity ones, were integrated by the rectangle “boxing” method, which gives more reliable results compared to the ellipsoid, especially in the case of a strong t2 noise band. The optimization of the geometry of the studied molecule (**1**) was done by the molecular mechanics method MM2 in the Chem3D Pro program [26].

Reagents for synthesis compounds (**1a**) and (**1**) were purchased from Thermo Scientific (THEED 99%) and “Vekton” (Russia), (germanium(IV) oxide and L-valine ($\geq 97\%$)) and used without purification. Only 18 M Ω •cm deionized water (Milli-Q® Water Purification System) was used for the synthesis of complexes (**1a**), (**1**) and preparation of aqueous solutions. Germanium L-valinate (**1a**) was obtained (stage 1 in Fig. 2) by adding an aqueous solution (20 ml) of L-valine (4.2 mmol, 0.49 g) and an aqueous suspension (70 ml) of germanium dioxide (4.2 mmol, 0.44 g) [27]. 1-aminoacyloxygermatran (**1**) was obtained (stage 2 in Fig. 2) by adding an aqueous solution (5 ml) of THEED (0.8 mmol, 0.20 g) to an aqueous suspension (10 ml) of germanium L-valinate (0.8 mmol, 0.20 g) with constant stirring. After complete dissolution of germanium L-valinate, the reaction mixture was heated (up to 80°C) with constant stirring for 2 h. After the reaction was completed, the solution was left in the open air to slowly evaporate

the solvent. The reaction product was isolated as a white powder, washed with ethanol and dried in air. The product yield was 81.4% (0.43 g).

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00723-023-01593-0>.

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Author Contributions DL synthesized 1-aminoacyloxygermatran and together with TK wrote text of introduction. RB recorded all NMR spectra. SS planned NMR experiments and analyzed their results to get complete signal assignments in ^1H and ^{13}C spectra of studied compound. SS also wrote text of sections 2 and 3 including the preparing all spectral figures for these sections and for supplementary information. All authors discussed results and reviewed the manuscript.

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Data Availability All of the material is owned by the authors and/or no permissions are required.

Declarations

Conflict of interest The authors have no competing interests as defined by Springer or other interests that might be perceived to influence the results and/or discussion reported in this paper.

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