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Hexacoordinate germanium compounds with BIS-TRIS and amino acid ligands

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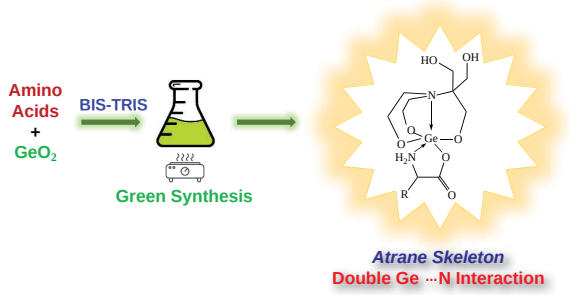
New germanium-containing compounds of the atrane family have been synthesized by reacting germanium glycinate, L-α-alaninate and L-valinate with [bis(2-hydroxyethyl)-amino][tris(hydroxymethyl)]methane (BIS-TRIS) and explored by FT-IR, NMR spectroscopy, thermal and elemental analysis. The fully local meta-GGA correlation functional (M06-L) was applied to investigate their equilibrium geometries. The derivatives of BIS-TRIS and triethanolamine have been investigated by computational screening *via* ADMET and PASS software.



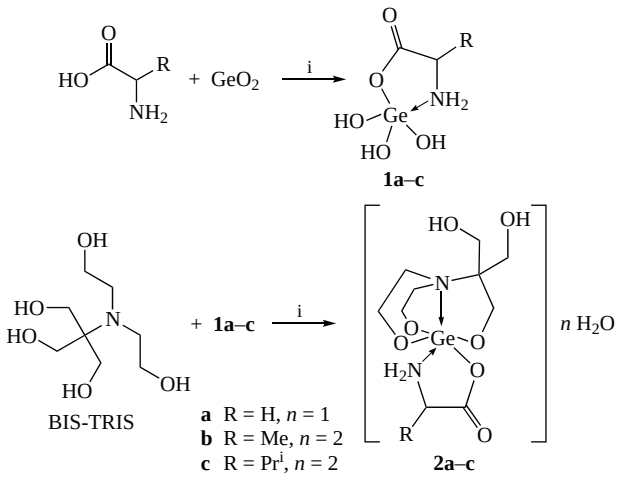
Keywords: germatranes, triethanolamine, BIS-TRIS, 1-germatranol hydrate, amino acids, M06-L DFT method.

In recent years, research on hypercoordinate silicon and germanium compounds has gained great interest in chemistry and materials science due to their unusual biological activity and structural diversity.[1–6] Alkanolamine derivatives with penta-coordinated Si and Ge atoms containing a transannular N→M bond called atranes (silatranes and germatranes)[7] are used in medicine, pharmaceuticals and agriculture as immuno-modulators, adaptogens, antimicrobial, anticancer agents and plant growth regulators.[1,7–14] The germatrane cycle is significantly more resistant to hydrolytic cleavage than the silatrane one, which makes it possible to use germatranes as a transport agent for biologically active fragments in living cells.[7,15] At the moment, a wide range of germatranes containing organic substituents at the germanium atom are known.[5,15–24] Among them, 1-acyloxygermatranes $RC(O)OGe(OCH_2CH_2)_3N$ should be especially distinguished since carboxylic group exerts a significant effect on their biological activity. The first representative of 1-acyloxygermatranes was obtained by the reaction of 1-methoxygermatrane with 98% acetic acid and its anhydride.[25] The treatment of 1-germatranol hydrate with carboxylic acid in xylene or isoamyl alcohol also led to 1-acyloxygermatranes,[26] while in cases of dicarboxylic acids mono- and dicarboxy-substituted 1-germatranes were formed.[27]

The reactions of 1-germatranol hydrate with amino acids are scarcely investigated. Earlier,[24] we studied the reaction of glycine, α- and β-alanines as well as L-valine with 1-germatranol hydrate and detected two conformers of nearly equal energies for the products with the α-amino acids. The comformers differed in the way of the amino acid moiety arrangement toward the germanium atom. In the more stable ('remote') isomers the NH_2 group was far away from Ge, while in slightly less stable ('close') ones these groups were coordinated to Ge. This priority of stabilities of 'remote' molecules was explained by the stabilizing factor of the C–N and C=O bonds in a *cis*-position. This energy preference cannot be overcome by stabilizing interactions of the NH_2 groups and germanium in 'close' structures.

[Bis(2-hydroxyethyl)amino][tris(hydroxymethyl)]methane (BIS-TRIS), a hydroxyalkylamine similar in structure to triethanolamine but containing five hydroxyalkyl groups, is widely used as a buffering agent in biochemistry.[28–30] Its treatment with carboxylic acids leads to the formation of Good's buffer ionic liquids, which are highly effective buffers in ^{68}Ga-radiolabeling reactions.[31] Molecule of BIS-TRIS contains six donor atoms (N and five O atoms) and is also used in the synthesis of metal–organic framework structures as a chelating agent.[32–35]

In this study, we replaced triethanolamine (TEA), popular in the synthesis of silatranes and germatranes, with BIS-TRIS to study the equilibrium geometries of the interaction products with germanium glycinate, L-α-alaninate and L-valinate (Scheme 1). The first step involved the preparation of germanium salts with amino acids, namely, germanium glycinate **1a**, L-α-alaninate **1b**,



Scheme 1 *Reagents and conditions*: i, H_2O, 90 °C, 2 h.

† Deceased.

and L-valinate **1c**. At the second step, the resulting salts **1a–c** were treated with BIS-TRIS to produce atranes **2a–c** formed as hydrates. Their structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy. A common feature of their ^{1}H NMR spectra is that the CH_2O proton signals for two hydroxyethyl groups of BIS-TRIS appear as separate multiplets in the region of 2.9–3.0 and 3.4–3.6 ppm. Protons for CH_2N groups resonate as multiplets in the region of 3.6–3.9 ppm. The broad singlet at 3.78–3.79 ppm corresponds to six protons of three hydroxymethyl groups.

The IR spectra of compounds **2a–c** are similar to each other and close to that of classical germatranes with the TEA moiety.[24,36,37] In particular, the 3500–3100 cm^{-1} region is characterized by intense and broadened bands associated with stretching vibrations for the ν(OH) of BIS-TRIS and ν(NH_2) groups of the amino acids. Relatively weak bands between 2700 and 2000 cm^{-1} belong to the symmetric stretching of the NH_2 group.[38–40] The bands in the region 1683–1588 cm^{-1} relate to the stretching vibrations for ν(COO) and δ(NH_2) groups of the amino acid fragment. The group of bands in the region 1526–1206 cm^{-1} is associated with bending vibrations of δ(C–H), ρ(C–H) and w(C–H) groups. In this region (1330–1300 cm^{-1}) the second stretching band ν(COO) also appears. Intense bands in the region of 1100–1080 cm^{-1} refer to stretching vibrations of ν(C–O) bonds. Note, however, the strong band of C–O stretching at 1089 cm^{-1} that belongs to CH_2O moiety absent in {GlyGe(TEA)}. Stretching vibrations of Ge–O bonds appear as bands in the region of 750–630 (ν_{as}) and 590–540 (ν_{as}) cm^{-1}. A more detailed assignment of IR bands is presented in Tables S1, S2 (see Online Supplementary Materials).

The thermal behavior of compounds **2a–c** was studied in the temperature range 40–900 °C. Decomposition of compound **2a** begins even before 100 °C. The DSC curve (Figure S19) shows an endothermic effect at 87 °C likely related to water loss. It should be noted that this is characteristic of germanium compounds with hydroxyalkylamines.[23,24] The DSC curve also exhibits endothermic effects at 169, 207 and 250 °C, as well as strong exothermic effects peaking at 368–403 (broad peak) and 543 °C. The thermal behavior of compounds **2b** and **2c** (Figures S20 and S21) is slightly different from that of **2a**. The onset of thermal decomposition occurs after 160 ºC. The thermal decomposition process can be divided into three steps. The first step is accompanied by a series of endothermic effects on the DSC curve at 171, 198 and 239 °C (**2b**), as well as at 195 and 235 °C (**2c**). In the second step, a strong exothermic effect was recorded on the DSC curve with a maximum at 354 (**2b**) and 352 °C (**2c**), associated with the combustion of the organic residue. The second exothermic effect was observed at the third step at 589 (**2b**) and 611 °C (**2c**), associated with the combustion of the carbonized residue. The thermal degradation product at 900 °C corresponds to germanium(IV) oxide.

Equilibrium geometries **2a–c** (Figure 1) were estimated by the M06-L DFT method[41] which, as our experience shows, provides best agreement of experimental and theoretical Ge–O bond lengths among other DFT methods.[23] It should be noted that two conformations were considered here depending on the intramolecular interaction of Ge···NH_2. However, a number of conformers are possible that differ in the position of the free hydroxymethyl groups of BIS-TRIS and the amino acid fragment. In addition, germatrane moiety conformations are also possible.[5,42]

We compared the results obtained for BIS-TRIS complexes **2a–c** with those for the complex of 1-germatranol hydrate with glycine {GlyGe(TEA)} estimated at the M06L/aug-cc-pVDZ level. The geometry of the complex does not differ substantially from that calculated earlier by the B3LYP method.[24] However, the energy difference between 'close' and 'remote' conformers becomes smaller and 'close' structure is even slightly more stable (Table 1) than the 'remote' one [see Figure 1(*a*)]. In the case of the BIS-TRIS derivative, the 'close' conformer **2a** becomes *ca.* 2 kcal mol^{-1} more stable than 'remote' (see Table 1). Correspondingly, the intramolecular atrane Ge···N bond lengths become longer in **2a** (by 0.033 Å) compared to {GlyGe(TEA)}, while those between Ge and NH_2 groups of amino residues become by 0.100 Å significantly shorter in **2a**. The effect of

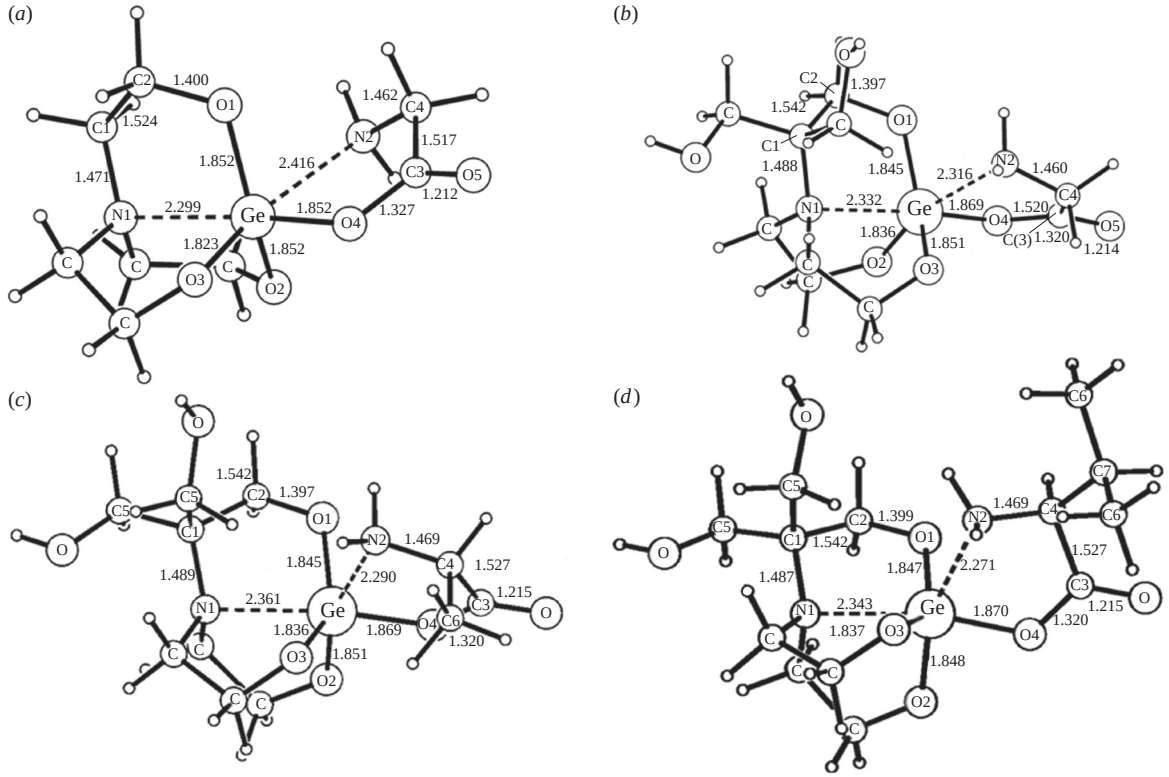


Figure 1 Equilibrium structures of (*a*) {GlyGe(TEA)}, (*b*) compound **2a**, (*c*) compound **2b**, and (*d*) compound **2c** estimated at the M06L/aug-cc-pVDZ level (bond lengths are in Å).

Table 1 Relative total electronic energies (E_e), zero-point-vibrational-energy corrected ($E_0 = E_e + ZPVE$) in kcal mol^{-1} of different conformers of {GlyGe(TEA)} and compounds **2a–c** with respect to the most stable conformers of each species.

Compound	Conformer	M06L/Aug-CC-pVDZ		
		E(hartree)	ΔE_e	ΔE_0
{GlyGe(TEA)}	close	–2877.11486	0	0
	remote	–2877.11456	0.2	0.1
2a	close	–3106.17758	0	0
	remote	–3106.17459	1.9	1.7
2b	close	–3145.49233	0	0
	remote	–3145.48488	4.7	4.1
2c	close	–3224.11791	0	0
	remote	–3224.11243	3.4	3.6

CH_2OH groups is also revealed in the redistribution of Ge–O bond lengths, *i.e*. the Ge–O(1) bond lengths become shorter, while the Ge···O bond [O(4) from the amino acid] is slightly longer in **2a** [see Figure 1(*b*)].

The analysis of the atomic polar tensor (APT) charges (q)[43] of one of the germatrane branches and the amino group residue was additionally performed (Table 2). On going from {GlyGe(TEA)} to **2a**, the positive charge at the quaternary carbon atom C(1) increases substantially. This polarization continues by the increase of positive charge at carbon atom C(2), negative charge at oxygen atom O(1), and small increase of positive charge at germanium atom. These changes make Ge–O bonds weaker thus decreasing interactions between intramolecular Ge···N(1) bonding orbitals and vacant antibonding Ge–O orbitals that is a factor which stabilizes the Ge···N(1) bond. The increase of polarity of Ge···N(2) bonding along with the increase in flexibility of the amino group due to the substantial increase in the Ge–O(4) bonding makes the Ge···N(2) bond stronger in **2a** compared to {GlyGe(TEA)}. The replacement of glycine residue by L-α-alanine **2b** and L-valine **2c** leads to the substantial shortening of Ge···N(2) bonds [see Figure 1(*c*),(*d*)]. As a result, in the series **2a** → **2c**, the interaction Ge···N(2) is enhanced. At the same time, atrane intramolecular Ge···N(1) bonds change nonmonotonically.

The ADME properties of the synthesized germanium-containing derivatives of BIS-TRIS **2a–c**, 1-germatranol hydrate and {GlyGe(TEA)} were *in silico* evaluated. As can be seen from Table 3, all tested compounds fully meet the criteria of the Lipinski's rule of five: the molecular weight < 500 Da, number of H-bond donors < 5, number of H-bond acceptors < 10, and an octanol–water partition coefficient (log*P*) < 5. TPSAs for the synthesized derivatives were observed in the range of 60.39–123.71 Å^2 and are well below the limit of 160 Å^2. Regardless of composition, the compounds were classified as very soluble in water. In the absorption aspect, only TEA derivatives were predicted to have the high gastrointestinal absorption, compounds **2a–c** exhibit low gastrointestinal absorption properties (Table 4). At the same time, all compounds were nonpermeable to the blood–brain barrier and have low values of skin permeability coefficient (logK_p) in the range of –10.24 to –8.68 cm s^{-1}. The bioavailability score for all germanium compounds was 0.55, that is more than 50% of the administered drug will reach the systemic circulation. The synthesis of these derivatives of TEA and BIS-TRIS was not difficult, the synthetic accessibility score was < 6.

PASS analysis was applied to evaluate the biological activity spectrum of 1-germatranol hydrate, {GlyGe(TEA)}, and

Table 2 APT charges (q) of one of the germatrane branches and the amino group residue in complexes {GlyGe(TEA)} and **2a–c**.

Compound	Conformer	q N1	q C1	q C2	q O1	q Ge	q O4	q N2
{GlyGe(TEA)}	close	–0.60	0.18	0.34	–0.88	2.45	–1.05	–0.20
	remote	–0.60	0.20	0.35	–0.90	2.34	–1.13	–0.16
2a	close	–0.60	0.24	0.42	–0.92	2.48	–1.05	–0.50
	remote	–0.60	0.24	0.40	–0.89	2.32	–1.11	–0.42
2b	close	–0.60	0.24	0.32	–0.92	2.48	–1.03	–0.22
	remote	–0.60	0.24	0.37	–0.90	2,35	–1.16	–0.43
2c	close	–0.60	0.24	0.32	–0.92	2.52	–1.06	–0.21
	remote	–0.60	0.24	0.40	–0.89	2.35	–1.14	–0.16

Table 3 ADME physicochemical properties of 1-germatranol hydrate, {GlyGe(TEA)} and compounds **2a–c**.[a]

Compound	MW/g mol^{-1}	log*P*	TPSA/Å^2	HBA	HBD	RB	Lipinski's rule (Vio)
$[HOGe(TEA)]H_2O$	253.83	–1.34	60.39	6	2	0	Yes (0)
{GlyGe(TEA)}	292.86	–1.49	83.25	7	1	3	Yes (0)
2a	352.92	–2.38	123.71	9	3	5	Yes (0)
2b	366.94	–2.12	123.71	9	3	5	Yes (0)
2c	394.99	–1.58	123.71	9	3	6	Yes (0)

[a] MW is molecular weight; log*P* is an octanol–water partition coefficient; TPSA is topological polar surface area; HBA is number of H-bond acceptors; HBD is number of H-bond donors; RB is number of rotatable bonds; Vio is number of Lipinski's rule violations.

Table 4 ADME pharmacokinetic properties of 1-germatranol hydrate, {GlyGe(TEA)} and compounds **2a–c**.[a]

Compound	log*S* (ESOL), class	logK_p/cm s^{-1}	GIA	BBB	BAS	SA
$[HOGe(TEA)]H_2O$	–0.68, very soluble	–8.68	High	No	0.55	4.83
{GlyGe(TEA)}	–0.80, very soluble	–8.82	High	No	0.55	4.96
2a	–0.11, very soluble	–10.24	Low	No	0.55	5.41
2b	–0.45, very soluble	–10.04	Low	No	0.55	5.65
2c	–1.16, very soluble	–9.53	Low	No	0.55	5.70

[a] log*S* is water solubility; logK_p is skin permeation; GIA is gastrointestinal absorption; BBB is blood brain barrier permeant; BAS is bioavailability score; SA is synthetic accessibility.

BIS-TRIS derivatives **2a**–**c** (see Online Supplementary Materials, Table S3). 1-Germatranol hydrate was predicted to have a broad biological activity profile (more than 7 activities with a probability >0.7). These results for 1-germatranol hydrate confirm the experimental data. Thus, 1-germatranol hydrate is a low-toxic substance, may stimulate the immune system (synthesis of immunoglobulins IgG, IgGA, IgGM, and also enhances the synthesis of Ie E), may have an antihypoxic, hemoglobin-protective and antioxidant effect, *etc*.[44,45] The transition from 1-germatranol hydrate to derivatives with amino acid substituents leads to a significant change in the spectrum of biological activity. Thus, {GlyGe(TEA)} and compounds **2a**–**c** are predicted to be effective in phobic disorders treatment and have antihypoxic activity. Apoptosis agonist with a high probability (>0.88) was predicted only for BIS-TRIS derivatives **2a**–**c**.

Thus, all investigated compounds can be considered as prospective drug-like molecules that meet the bioavailability criteria. The transition from derivatives of TEA to BIS-TRIS leads to a deterioration in adsorption in the gastrointestinal tract system and a significant change in the biological activity profile. Only germanium-containing derivatives of BIS-TRIS are predicted to be potential apoptosis agonists and may potentially be used in cancer treatment.

In conclusion, new germanium-containing derivatives with BIS-TRIS and amino acid moieties have been synthesized by the reaction of BIS-TRIS with germanium glycinate, L-α-alaninate, and L-valinate. The thermal decomposition of the synthesized compounds depends on the amino acid substituent and occurs in the temperature range of 87–160 °C. Replacement of triethanolamine with BIS-TRIS in the germatrane skeleton leads to a weakening of intramolecular atrane Ge···N bonding. At the same time, the Ge···NH_2 binding, on the contrary, was increased. On going from glycinate to L-valinate, the substantial strengthening of bonding between germanium and the nitrogen atom of amino groups was observed. ADME analysis revealed that all tested germanium-containing compounds of triethanolamine and BIS-TRIS can be considered as prospective drug-like molecules that meet the bioavailability criteria. BIS-TRIS derivatives are predicted to be potential apoptosis agonists and may potentially be used in cancer treatment.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.003.

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