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Vibrational spectra and electronic structure of germatranols $(HO)_{4-n}$ Ge $(OCH_2CH_2)_nNR_{3-n}$ (R = H; n = 1-3) with transannular Ge \cdots N bonding

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ABSTRACT

Series of germatrane compounds with OH functionality and Ge…N transannular bonding, i.e. 1-germatranol (I), 1,1-quasigermatranol (II) and 1,1,1-hypogermatranol (III) with general formula $(HO)_4$ _ $_nGe(OCH_2CH_2)_nNR_3$ _ $_n$ (R = H, Me; n = 1-3) are synthetized and their solid state IR spectra are recorded. Equilibrium structures and vibrational spectra of monomeric and centrosymmetric dimeric species of these compounds are predicted by the DFT B3LYP/aug-cc-pVDZ method. The assignment of the vibrational spectra of I–III was carried out based on theoretical IR spectra scaled with factors obtained earlier for halogermatranes to take account of the substantial and systematic discrepancy between Ge…N interatomic distance of the gas phase and theoretical predictions on the one hand and X-ray solid state data on the other. Dimeric models provide a good agreement between experimental and predicted frequencies, including GeOH bending modes, of I, crystalline state of which is formed by dimers, and slightly worse for II, in which some weaker O–H…O and N–H…O hydrogen bonds are not considered in the dimeric model.

However, this model for **III** is poor since it does not take into account hydrogen bonding of "free" OH and NH_2 groups. Despite the steady decrease of the Ge…N interatomic distance, corresponding frequencies demonstrate the substantial increase on going from **I** to **II** and practically no increase from **II** to **III**.

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1. Introduction

Silatranes and germatranes, that are the molecules with transannular M···N bonding of the general formula XM(OCH₂CH₂)₃N (X = H, Alk, Hal; M = Si, Ge) containing three MOCH₂CH₂N fivemembered cycles were subjects of numerous investigations mainly due to their biological applications [1–4]. Recently, there appeared publications concerning metallatrane analogs containing only two cycles, i.e. ocanes [5–12], and just a few investigations [13,14] were devoted to hypogermatranes containing only one MOCH₂CH₂N cycle. A special interest is involved in derivatives of germatranes containing hydroxyl groups [15–21] due to the ability of hydroxyl groups to form a variety of hydrogen bonds with other proton donors and Lewis acids. The crystal structure of anhydrous 1-germatranol [HOGe(OCH₂CH₂)₃N, **I**] was firstly reported by Voronkov et al. [21]. It consists of centrosymmetrical dimers of germatranol molecules linked by two hydrogen bonds between axial GeOH groups and equatorial oxygen atoms of the GeOCH₂CH₂N cycle.

The building block of the crystal structure of the analogous compound with two hydroxyl groups, i.e. germocane $(HO)_2Ge(OCH_2)_2NH$ (II), has also a dimeric structure [22]. However, this molecule has a diol functionality and in contrast to I forms dimers by two OH groups specific to silanediol dimers [23–25]. These dimers have free hydroxyl groups which may be exploited to link dimers to form ribbon-like networks as in other silanediol structures [23,24]. As





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concerns triol analogs of this class of molecules, i.e. hypogermatranes containing only one GeOCH₂CH₂N cycle (**III**), to the best of our knowledge no data on the structure of this compound exist.

Here we report IR spectra of compounds I-III and optimized quantum chemical structures and predicted vibrational spectra of these molecules in monomeric and dimeric forms. Theoretical results are used for the interpretation of experimental spectra.

2. Experimental and theoretical details

1-Hydroxy-5-aza-2,8,9-oxa-1-germatricycloundecane (1-germatranol, I) 1,1-dihydroxy-5-aza-2,8-dioxa-1-germabicyclooctane (1,1-quasigermatranol, II) 1,11-trihydroxy-5-aza-2-octa-1-germacyclo pentane (1,1,1-hypogermatranol, III) are obtained from GeO₂ and corresponding 2-hydroxyethylamines (HOC₂H₄)_{3 - n}NH_n (n = 0-2) in 1:1 ratio in water media (90 °C) without catalysts [26]. IR spectra were recorded with a Bruker TENSOR 27 spectrometer (split mull technique [27]) and a Varian 3100 FT-IR spectrometer (KBr pellets). These are shown in Figs. 1S, 2S and 3S of supplementary material.

The geometries of all of the molecules have been fully optimized and theoretical vibrational spectra have been calculated by the B3LYP [28,29] hybrid density functional method with the Dunning correlation consistent aug-cc-pVDZ basis set [30,31] as they are implemented in the Gaussian09 [32] suite of programs.

Scaling of the force field was done according to the SQM method [33,34] using the Molvib program [35,36]. For this, the force field matrix expressed in Cartesian coordinates was transferred from the Gaussian output to Molvib, and transformed to natural internal coordinates.

3. Results

Equilibrium structures of monomeric germatranols (I, II, and III) studied are presented in Fig. 1 and corresponding dimeric structures in Fig. 2. The existing X-ray structural data for I and II are compared with our predicted geometry parameters in Tables 1 and 3. In I the dimeric model describes all major intermolecular interactions, however, in dimeric structures II and especially III, the presence of "free" (not involved in hydrogen bonding) hydroxyl groups limits the predictive power of models considered.

The replacement of oxygen atoms of OCH₂CH₂N cycles by more electronegative OH groups results in the steady increase of the positive charge on germanium and shortening of Ge…N transannular bonds. Geometry parameters of OCH₂CH₂N cycles practically do change on going from I to III. Despite this, IR spectra in the 1000–100 cm⁻¹ region differ substantially due to strong mixing of cyclic modes among themselves and with deformation modes of GeOH groups. However, theoretical vibrational spectra allowed us to make an attempt to make a systematic assignment of the vibrational spectra of germatranols. Observed frequencies below 1500 cm⁻¹ (Tables 2, 4 and 5) are compared with theoretical harmonic vibrations. Higher frequencies which include the stretching of the OH and CH bonds are not listed since the values of predicted harmonic frequencies are far from experimental values due to the high anharmonicity of these vibrations. Moreover, samples contain water and its OH stretching bands also blur this region.

One of the most challenging problems in the assignment of vibrational spectra of atranes is the location of the M…N stretching frequencies and attempts to link the values of these frequencies with the strength of the transannular bond [41–45]. However, quantum chemical methods (DFT and MP2) systematically overestimate M…N interatomic distances. This serious disagreement between theoretical M…N distances and those obtained from the solid state diffraction experiment is inherent in all atranes. As was shown by Dillen [40] the only way to remove this discrepancy is to



Fig. 1. Optimized molecular structures and main geometrical parameters (bond distances in Å) of monomeric 1-germatranol (**a**), 1,1-quasigermatranol (**b**) and 1,1,1-hypogermatranol (**c**).

use computational models simulating the crystalline state and including long—range interactions. Due to this difference the predicted frequencies of the vibrations involving M…N stretching are substantially lower than experimental solid state IR frequencies. Ignatyev and Sundius [37] tried to compensate this underestimation of theoretical vibrational frequencies by scaling the corresponding theoretical force constants. Scaling of force constants by the SQM method [33,34] allows us to minimize also some other discrepancies between experimental and predicted frequencies, e.g. CO and MO stretching frequencies. Note, that the assignment of vibrations, especially in the spectral range below 600 cm⁻¹ is rather ambiguous due to the mixture of modes of OCH₂CH₂N cycles.



Fig. 2. Optimized molecular structures and main geometrical parameters (bond distances in Å) of the hydrogen bonded dimers of 1-germatranol (**a**), 1,1-quasigermatranol (**b**) and 1,1,1-hypogermatranol (**c**).

3.1. 1-Germatranol

The equilibrium structure of the 1-germatranol [HOGe(OCH₂) $_3$ N, I] molecule is depicted in Fig. 1a and main geometry parameters obtained in this work are compared with experimental data and the results of previous theoretical predictions in Table 1.

Table 1

Experimental and theoretical geometry parameters (Å,degree) of 1-germatranol [HOGe(OCH_2CH_2)_3N, I].

Geometry	Experiment ^b	M05–2 <i>x</i> /	B3LYP/aug-cc-pVDZ	
parameters ^a		6-11 + G(d,p) dimer ^b	Monomer	Dimer
Ge…N	2.142 (3)	2.381	2.338	2.373
Ge-01	1.779 (3)	1.757	1.791	1.777
Ge-03	1.806 (3)	1.811	1.831	1.843
Ge-07	1.797 (3)	1.787	1.821	1.822
Ge-010	1.787 (3)	1.793	1.815	1.818
O—C, av	1.425(5)		1.414	1.415
C—C, av	1.529(3)		1.534	1.534
N—C, av	1.478(2)		1.472	1.471
N(1)Ge(1)O(4)	178.8(1)		178.8	177.7

^a Notations in Figs. 1 and. 2.

^b Data from ref. [21].

Table 2

Experimental and theoretical vibrational spectra of HOGe(OCH₂CH₂) $_3$ N, [I] (frequencies in cm⁻¹, IR intensity in km mol⁻¹) compared with the scaled theoretical spectrum of FGe(OCH₂CH₂) $_3$ N.

IR	ν (unscaled)		Assignment	ν (scaled) ^b	1-F-germatrane	
	Monomer	Dimer ^a			$\overline{\nu}$ (scaled) ^b	Symm
1482 m	1504 (0)	1503 (0)	δ CH ₂	1484	1484	A
	1500 (2)	1499 (5)	δCH_2	1480	1479	Е
	1497 (2)	1498 (6)	δ CH ₂	1477		
1457 m	1479 (5)	1480 (17)	δCH_2	1459	1460	А
	1478 (6)	1479 (8)	δCH2	1458	1459	Е
	1477 (4)	1479 (7)	δ CH ₂	1457		
1397 w	1395(1)	1397 (6)	δ CH ₂	1376	1375	E
1557 11	1394 (3)	1395 (7)	δ CH2	1375	1070	2
1371 w	1378 (12)	1380 (29)	δ CH ₂	1361	1362	Δ
13/1 ₩	1370(12) 1372(2)	1300(23) 1373(11)	δ CH-	1353	1352	Δ
	1372(2) 1362(1)	1373 (11)	\$ CU	1242	1332	л Е
	1305(1)	1303 (2)	0 СП ₂	1345	1541	E
1070	1361(1)	1362 (1)	0 CH2	1342	1071	F
12/2 111	1296 (13)	1298 (29)	ρCH_2	1275	1271	E
	1294 (13)	1296 (25)	ρCH_2	1273	1000	
	1282 (9)	1282 (20)	ρCH_2	1266	1266	A
	1257(1)	1260(1)	ρCH_2	1241	1239	E
	1256 (1)	1257 (2)	ρCH_2	1240		
	1246 (0)	1248 (1)	ρCH_2	1229	1229	A
1162 m	1183 (2)	1186 (4)	ρCH_2	1164	1161	E
	1181 (3)	1184 (5)	ρCH_2	1162		
1102 s		1133 (289)	δ GeOH			
			(dimer)			
	1129 (135)	1122 (152)	<i>ν</i> OC	1098	1097	А
1065 m	1102 (76)	1101 (159)	νOC	1062	1057	Е
	1101 (72)	1095 (133)	νOC	1062		
	1086 (22)	1086 (58)	ρ CH ₂	1075	1075	А
1042 m	1065 (10)	1066 (23)	Vac NC2	1043	1039	Е
	1063 (9)	1064(17)		1042		
1028 m	1025 (60)	1025 (23)	<i>v</i> CC	1018	1019	А
1020 111	958 (116)	1025 (25)	λ CeOH	972	1015	
	550 (110)		(monomer)	572		
035 m	032 (15)	033 (34)		026	025	F
955 III	932 (13)	933 (34)	<i>v</i> cc	920	925	Ľ
006 m	909 (29)	902 (01) 808 (00)	» СЦ	925 907	000	٨
900 III	090 (30)	898 (99) 877 (2)	ρCH_2	897 865	090	л Г
	875,4)	877(3)	ρCH_2	805	864	E
705	875(2)	877 (4)	ρCH_2	803	750	
/35 m	754(0)	756 (2)	$\nu_{\rm s}$ NC ₃	748	/50	A
6/8 s	686 (150)	/15 (2/2)	v GeO(H)	690		
636 s		638 (235)	τGeOH			
			(dimer)			_
	587 (26)	619 (197)	v_{as} GeO ₃	654	670	E
	581 (37)	600 (22)	v_{as} GeO ₃	642		
613 s	621 (92)	587 (17)	δ NCC	610	601	E
	613 (74)	582 (82)	δ NCC	600		
594 m	588 (29)	571 (133)	δ NCC	597	587	А
569 m	538 (7)	539 (7)	v_s GeO ₃	559	551	А
421w	427 (1)	425 (2)	$\delta_{s} NC_{3}$	454	451	А
			(<i>ν</i> Ge…N)			
	421 (2)	422 (1)	$\delta_{as} NC_3$	418	418	Е
	418(1)	419 (2)	$\delta_{as} NC_3$	415		
332 sh	317 (14)	318 (19)	δ GeOC	317	315	E
320 sh	313 (7)	313 (12)	δ GeOC	314		
310 m	294 (0)	297 (0)	δ GeO ₄	305	313	А
276 m	257 (14)	276 (27)	δΟCC	290	287	Е
260 m	254 (20)	258 (34)	δ OCC	280		
242 m	212 (28)	200 (94)	ν Ge…N	250	271	А
	210(20)	235 (17)	δ GeO₄	223	216	E
182 ch	203 (2)	208 (5)	δ GeO ·	214	210	-
162 m	168 (32)	156(7)		168	144	F
100 111	143 (3)	143(2)	ρ GeO4	147	1-1-1	-
	92(4)	97 (12)	μ GCO4 δ CeOC	105	111	Δ
	72 (75)	57 (12)	τ CeOH	74		<i>.</i> 1
	. 2 (23)		(monomer)	, ,		
			(inononici)			

 $^{\rm a}$ Only IR active $A_{\rm u}$ modes are presented, six inter-monomeric rotational and translational modes with frequencies below 75 cm $^{-1}$ are not shown. $^{\rm b}$ Scale factors from ref. 37: CO: 0.874, CC: 1.024, GeO: 1.167, GeO(H): 1.000,

^b Scale factors from ref. 37: CO: 0.874, CC: 1.024, GeO: 1.167, GeO(H): 1.000, GeOH: 1.000, CN: 0.948, GeOC: 1.000, δ_s : 2.633, δ_{as} : 0.971, ρ: 1.570, OCC: 0.973, HCH: 0.973, CCH: 0.970, NCC: 1.114, GeOC: 1.000, CNC: 0.914.

Table 3 Experimental and theoretical geometry parameters (Å, degrees) of (HO)₂Ge(OCH₂ CH₂)₂NH [II].

Table 4

Experimental and theoretical vibrational spectra of $(HO)_2Ge(OCH_2CH_2)_2NH$, [II] (frequencies in cm⁻¹, IR intensity in km mol⁻¹).

Geometry	Experiment ^b	MP2/	B3LYP/aug-cc-pVDZ	
parameters		6-311++G(d,p) ^b monomer	Monomer	Dimer
Ge…N6	2.1246 (5)	2.207	2.270	2.262
Ge-01	1.7994 (5)	1.799	1.806	1.827
Ge-03	1.8044 (5)	1.813	1.819	1.822
Ge-07	1.7969 (5)	1.823	1.834	1.836
Ge-010	1.7735 (5)	1.805	1.816	1.788
03–C4	1.4288 (8)	1.413	1.415	1.415
07–C8	1.4219 (9)	1.411	1.415	1.415
C4–C5	1.5169 (11)	1.528	1.534	1.535
C8–C9	1.5238 (10)	1.530	1.534	1.535
N6-C5	1.4789 (9)	1.472	1.473	1.472
N6-C9	1.4739 (9)	1.470	1.473	1.472
N6-Ge-O3	84.24 (2)	82.3	81.3	81.5
N6-Ge-07	83.99 (2)	81.9	80.9	80.9
N6-Ge-01	177.53 (2)	176.3	173.7	169.3
N6-Ge-010	85.76 (2)	81.1	81.3	83.3
01-Ge-03	95.44 (2)	101.3	96.5	95.2
01-Ge-07	94.02 (3)	96.1	96.0	93.1
01-Ge-010	96.51 (2)	97.5	103.8	95.2
03-Ge-07	118.15 (3)	116.9	127.6	126.3
03-Ge-010	119.67 (3)	114.7	112.4	113.4

^a Atom notations from Figs. 1 and 2.

^b Data from ref.[22].

Although in contrast to halogermatrane molecules [37] there are no more C_3 symmetry axis in germatranol, the axial GeO1(H) bond (collinear to the Ge…N bond) is the shortest among four GeO bonds (atom notations in Fig. 1). However, its predicted bond length is in a good agreement with the experimental value in contrast to halosilatranes and halogermatranes where theoretical M-Hal bond distances differ substantially from experimental ones [37]. As compared to the equilibrium structure of trimethylgermanol the substitution of methyl groups by electronegative oxygen atoms leads to the substantial shortening of the GeO1(H) bond from 1.830 to 1.791 Å (B3LYP/aug-cc-pVDZ). The reduction of bond length due to the substitution by electronegative elements is well known and usually is attributed to negative hyperconjugation [38,39]. The other effect which may influence the length of the axial GeO1(H) bond is the formation of coaxial Ge…N bonding. In order to separate these two effects we have predicted the structure of HOGe(OMe)₃ at the same theory level. In this molecule the equilibrium bond distance is 1.780 Å. Thus, small increase of the GeO1(H) bond length in germatranol may be attributed to Ge…N bonding. However, the different arrangement of oxygen atoms around germanium in germatranol and trimethoxygermanol may also contribute to this effect. The GeO1(H) bond length is in a good agreement with X-ray experimental data (Table 1). This agreement improves in the equilibrium structure of the dimer (Fig. 2a). Here the length of the proton-donating GeO1 bond decreases, while that of Ge-O3 (containing a proton-accepting oxygen atom) increases. The length of the GeO7 and GeO10 bonds, not involved in interdimeric hydrogen bonding, practically do not change.

The Ge···N theoretical interatomic distances in germatranols are markedly longer than that obtained by X-ray diffraction [21] (Table 1). This difference (ca. 0.2 Å) is of the same order as in XM(OCH₂CH₂)₃N (M = Si, Ge; X = F, Cl) compounds [37]. Note that our B3LYP values are shorter than corresponding M05 – 2x/6-311 + G(d,p) bond lengths of the previous work [21].

Experimental IR frequencies of 1-OH germatrane (I) are compared with predicted frequencies in Table 2. They contain not only theoretical harmonic vibrational frequencies, but also frequencies of HOGe(OCH₂CH₂)₃N, obtained with scaled theoretical force field (scale factors are transferred from ref. [37]) as well as those of

IR	ν (unscaled)		Assignment	ν (scaled) ^D
	Monomer	Dimer ^a		
1484 m	1502 (6)	1502 (13)	δ CNH	1488
	1495 (0)	1495 (0)	δCH_2	1474
	1489 (8)	1489 (14)	δCH_2	1470
1462 w	1479 (11)	1480 (20)	δCH_2	1463
1452 m	1462 (1)	1464 (2)	δCH_2	1447
1366 w	1392 (10)	1391 (24)	δCH_2	1375
	1374 (2)	1373 (3)	δCH_2	1358
	1367 (3)	1366 (7)	δCH_2	1351
1348 sh	1336(1)	1336 (2)	δ CH ₂	1319
1279 m	1306 (6)	1304 (13)	ρCH_2	1290
1262 m	1266(1)	1266 (2)	ρCH_2	1250
1251 w	1256 (3)	1255 (5)	ρCH_2	1241
1228 w	1225(1)	1225 (2)	ρCH_2	1209
1151 m	1167 (2)	1167 (1)	ρCH_2	1151
1115	1124 (45)	1146 (197)	o GeOH _{eq} (dimer)	1100
1115 m	1134 (45)	1136 (86)	νCN	1106
1097 s	1111 (95)	1109 (156)	νOC	1068
1064 vs	1091 (76)	1091 (154)	νOC	1055
1022	1069(1)	1070(1)	ρCH_2	1043
1033 VS	1033 (54)	1032 (130)	\mathcal{V}	1032
1011 c	975 (160)	1004 (216)	6 GeOH _{eq} (monomer)	974
1011 \$	060 (12)	1004 (216)	$\delta GeOH_{ax}$ (differ)	050
022 m	900(13)	022 (25)	v CC	939
933 111	934 (12)	933 (25)	v CC	934
802	926 (69)	925 (240)		910
092 W	891 (4) 877 (5)	890 (4) 877 (5)	v CN	874 850
816 m	837 (3)	832 (53)	ρCH_2	833 972
010111	052 (10)	790 (188)	τ GeOH _{eq} (dimer)	855
699 vs	666 (142)	709 (155)	ν GeO(H) _{eq}	722
666 vs	654 (105)	630 (400)	ν GeO(H) _{ax}	705
637 vs	619 (119)	617 (170)	$v_{as} \text{ GeO}_2$	656
606 vs	593 (24)	594 (39)	δ ΝCC	626
560 m	580 (3)	579 (7)	δ ΝCC	574
	542 (19)	542 (77)	$v_{\rm s} {\rm GeO}_2 (v {\rm Ge} \cdots {\rm N})$	551
458 m	403 (10)	407 (33)	$\nu \text{ Ge} \cdots \text{N}$	458
	420(75)		τ GeOH _{eq} (monomer)	420
414 w	417 (18)	418 (23)	δNC_2	396
	377 (3)	379 (15)	δ GeOC	377
346 m		340 (116)	τ GeOH _{ax} (dimer)	
	305 (35)		τ GeOH _{ax} (monomer)	306
307 m	286 (17)	298 (40)	δGeOC	282
282 m	277 (13)	285 (33)	$\delta \text{ GeO}_2$	279
261 m	0.44 (46)	282 (87)	$\delta \text{GeO}_2(\text{H}) \text{(dimer)}$	050
2.40	241 (46)	220 (7)	$\delta \text{ GeO}_2(\text{H}) (\text{monomer})$	253
248	220 (11)	239(7)	τ GeOH _{eq} (dimer)	226
210	220(11)	214 (2)	τ GeOH _{eq} (monomer)	226
218		214 (2)	$o \text{ GeO}_2(\nu \text{ Ge} \cdots \text{N})$	
	105 (20)		(dimer)	216
	195 (20)		(monomer)	210
208	176(1)	190 (47)	δ GeOC	172
181	157 (4)	173 (8)	ρ GeO ₄	151
-	106 (0)	125 (6)	$\rho \text{ GeO}_4$	105
	80 (0)	87 (3)	δ GeOC	77
	· · /	. ,		

^a Only IR active A_u modes are presented, six intermonomeric rotational and translational modes with frequencies below 75 cm⁻¹ are not shown.

^b Scale factors: CO: 0.874, CC: 1.024, GeO: 1.167, GeOH: 1.000, CN: 0.948, GeOC: 1.000, GeN: 2.663 OGeO: 1.000, OCC: 0.973, HCH: 0.973, CCH: 0.973, NCC: 0.973, GeOC: 1.000, CNC: 0.914, CNH: 1.000, OGeOH: 0.800.

 $FGe(OCH_2CH_2)_3N$ Note, that predicted vibrational frequencies of the XGe(OCH_2CH_2)_3N skeleton for X = OH are very close to those for X = F however, due to the absence of the C₃ axis in the former molecule, degenerate vibrations of the latter molecule are split.

The main contribution of the Ge…N stretching is located in the vibration with the predicted frequency of 212 cm⁻¹ (Table 2). In the dimeric model it lays slightly lower (200 cm⁻¹) in keeping with the small increase of the Ge…N interatomic distance in the dimer

Table 5

Experimental and theoretical vibrational spectra of $(HO)_3Ge(OCH_2CH_2)NH_2$, [III] (frequencies in cm⁻¹, IR intensity in km mol⁻¹).

IR	ν (unscaled)		Assignment	ν (scaled)
	Monomer	Dimer ^a		
1622 m	1630 (34)	1632 (64)	δ NH2	1624
1518 m	1493 (1)	1494 (2)	δ CH ₂	1474
1458 w	1484 (5)	1483 (8)	δ CH ₂	1464
1391 w	1392 (6)	1391 (15)	δ CH ₂	1392
	1365 (1)	1365 (3)	δ CH ₂	1355
1327 w	1306 (3)	1306 (7)	ρ CH ₂	1312
1272 w	1265 (7)	1265 (13)	ρ CH ₂	1256
	1194 (2)	1194 (3)	ρ CH ₂	1191
1145 w		1158 (171)	δ GeO _{eq} H (dimer)	
1070 m	1118 (64)	1118 (130)	ν OC	1090
	1073 (18)	1074 (47)	ν NC	1060
	1020 (250)	992 (372)	δ GeOH free	1026
1015 m	1010 (41)	1014 (250)	δ CNH	1013
	983 (56)	980 (14)	δ CNH	999
	979 (131)		δ GeO _{eq} H (monomer)	979
978 sh		972 (384)	δ GeO _{ax} H (dimer)	979
929 sh	926 (135)		δ GeO _{ax} H (monomer)	926
889 sh	906 (6)	906 (13)	νCC	903
861 sh	875 (3)	875 (2)	ρCH_2	865
782 s		799 (232)	τ GeO _{eq} H (dimer)	
	689 (138)	722 (224)	ν GeO _{eq} (H) (τ NH ₂)	737
	665(26)	671 (94)	$\tau \text{ NH}_2 (\nu \text{ GeO}_{eq} (H))$	703
	650 (102)	650 (80)	ν GeO (H) free	689
587 m	632 (126)	608 (279)	ν GeO _{ax} (H)	649
	594 (14)	591 (108)	$\nu \text{ GeO}_{eq}(C)$	622
560 sh	550 (18)	550 (51)	δ ΝCC	536
	457 (101)		τ GeOH _{eq} (monomer)	455
491 m	440 (76)	440 (175)	τ GeOH free	440
453 m	273 (14)	257 (36)	$\nu \text{ Ge} \cdots \text{N}$	474
358 w	412 (24)	413 (90)	δ GeOC (ν Ge…N)	345
346 w		333 (50)	τ GeO _{eq} H (dimer)	
317 w		300 (75)	τ GeO _{ax} H (dimer)	
279 w		289 (62)	δ GeO ₄ (dimer)	
	292 (9)		τ GeO _{eq} H (monomer)	291
	275 (16)	272 (20)	δ GeO ₄	266
	252 (44)		τ GeO _{ax} H (monomer)	254
247 w	248 (8)	243 (9)	δ GeO ₄	237
	232 (15)		δ GeO ₄ (monomer)	228
227 w	212 (28)	230 (2)	$\tau \text{ NH}_2 (\tau \text{ GeO}_{ax} \text{H})$	196
	153 (4)	182 (8)	ho GeO ₄	153
	125 (0)	140 (11)	ho GeO ₄	128
	71 (1)	91 (7)	δ GeOC	67

^a Only IR active A_u modes are presented, six intermonomeric rotational and translational modes with frequencies below 75 cm⁻¹ are not shown.

^b Scale factors: CO: 0.874, CC: 1.024, GeO: 1.167, GeOH: 1.00, CN: 0.948, GeOC: 1.00, GeN: 2.663, OGeO: 1.00, OCC: 0.973, HCH: 0.973, CCH: 0.973, NCC: 0.973, GeOC: 1.00, CNC: 0.914, CNH: 1.120, HNH: 0.950, OGeOH: 0.800.

(Table 1). The scaling of the theoretical force field of the monomer with factors from ref. [37] brings this frequency to 250 cm^{-1} which is in good agreement with the observed 242 cm^{-1} band (Table 2). Note that, in FGe(OCH₂CH₂)₃N, the scaled theoretical frequency of the analogous vibration is 271 cm⁻¹ (experimental Raman band at 273 cm⁻¹). This difference is in agreement with the shorter equilibrium Ge…N bond length in F-germatrane (2.284 Å [26] vs 2.338 Å).

There are also small differences in the frequencies of these vibrations between the monomeric and dimeric models. However, larger difference may be traced for vibrations with frequencies in 620–570 cm⁻¹ region (assigned as v_{as} GeO₃ and δ NCC in Table 2).

Certainly, the largest difference between frequencies of monomers and dimers may be observed for the vibrations of the GeOH group. In the 1-germatranol monomer δ GeOH and τ GeOH modes have frequencies of 958 and 72 cm⁻¹. In the dimeric model these frequencies rise up to 1133 and 638 cm⁻¹ due to the formation of hydrogen bonds between GeOH groups. Both vibrations have high theoretical IR intensities (Table 2). The τ GeOH mode may be

assigned to the experimental 636 cm⁻¹ band, while the attribution of the GeOH bending is not so straightforward. There are two strong IR bands in the 1050–1100 cm⁻¹ frequency range. One of them is the band assigned to the stretching of the OC bond (1065 cm⁻¹) which frequency does not change from that of 1-F-germatrane [40]. Thus the 1102 cm⁻¹ band may be assigned to hydrogen bonded δ GeOH (Table 2).

3.2. 1,1-Quasigermatranol

The equilibrium structure of the ocane (HO)₂Ge(OCH₂CH₂)₂NH (II) molecule is depicted in Fig. 1b. The length of the axial GeO1(H) bond slightly increases compared to I. Since bond lengths and NBO charges demonstrate that there is no significant redistribution of electron density on going from I to II, this small increase in the GeO1(H) bond length may be assigned to a shorter Ge…N interatomic distance in II. In the equilibrium structure of centrosymmetric dimer of II (Fig. 2b) the Ge…N interatomic distance is slightly shorter than in a monomer and is 0.137 Å longer than that found in the X-ray study [22]. Note, that this difference between theoretical and experimental Ge…N distance in II (Table 3) is smaller than in I (0.231 Å, Table 1). The dimer of II is formed utilizing two OH groups of each monomer: one hydroxyl group acts as a proton donor (GeO10H, Fig. 2b) and the other (GeO1H) as an acceptor. Note, that in the experimental structure GeO10 is the shortest GeO bond. This cannot be rationalized within the monomer model [22]. However, in the dimeric model it shortens substantially in accordance with the experimental data. In the crystal structure [22] dimers are linked by the hydrogen atoms of OH acceptor groups and N-H…O hydrogen bonds to form polymeric chains of dimers. However, these types of hydrogen bonds are substantially weaker than the bonding in a dimer and the vibrational spectrum of the ocane crystal may be described in a first approximation by the dimeric model. In the dimeric model axial GeO(H) bonds in which the oxygen atom acts like a proton acceptor in contrast to the real crystal do not take part in hydrogen bonding between dimers and this may cause some discrepancies between theoretical and experimental geometry parameters and the corresponding vibrational frequencies.

The predicted vibrational spectra of monomers and dimers of **II** are compared with IR experimental data in Table 4. In addition to unscaled IR spectra of the monomer and dimer (only IR active A_u modes are shown) the scaled spectrum of the monomer is presented. Scale factors are those used for **I** (transferred from ref. [37]) with one exception. Due to the different symmetry of the GeO₄ fragment (C_{3v} in **I** and C_{2v} in **II**) the definition of the bending coordinates of the GeO₄ group was changed. Therefore, the axial *ds* coordinates for the reproduction of Ge…N vibrations cannot be employed for **II**. However, the introduction of the redundant GeN coordinate with scale factor 2.633 used for the δ_s coordinate in the non-redundant set of ref. 26 and putting the scale factor for δ_s equal to unity, gives practically the same vibrational frequencies.

The main contribution of the GeN bond stretching is in a vibration at 403 cm⁻¹ in a monomer (407 cm⁻¹ in the dimer). However, scaling of the GeN stretching in a way described above gives 458 cm⁻¹ (Table 4). There exists a band in the experimental IR spectrum with the same frequency which may be assigned to ν Ge…N. All other frequencies of the cage vibrations in the dimer do not differ substantially from those calculated for a monomer.

Large shifts of frequencies are observed for vibrations of the GeOH groups. In addition to the above mentioned high anharmonicity of CH and OH stretching modes, which prevents their comparison with theoretical vibrational frequencies, in **II** the NH stretching band overlaps the OH stretching region. Therefore, in Table 4 (similar to Table 2) only the vibrational bands with frequencies below 1500 cm⁻¹ are presented. The predicted frequency of the axial GeOH group (proton acceptor) deformation is 760 cm⁻¹ with no nearby experimental band. However, in the dimer its value is 1004 cm⁻¹ and it may be assigned to a strong IR band at 1011 cm⁻¹. The dimeric frequency of the deformation of the equatorial GeOH group (proton donor) may be assigned to the IR band at 1151 cm⁻¹ which may overlap the low intensity ρ CH₂ band. The predicted frequencies of τ GeOH, in the dimer are in a fair agreement with their experimental counterparts at 816 and 346 cm⁻¹. However, the assignment of the latter mode (τ GeOH_{ax}) is dubious, since its proton in the crystal is involved in inter-dimeric hydrogen bonds and the absence of these interactions in the dimeric model may cause significant errors in the predicted frequency of the torsional mode.

The substantial discrepancy exists between the frequency of the δ CNH mode in the experimental and theoretical spectra (both monomer and dimer models). It may be the result of the absence of the N–H…O hydrogen bonding in these models. Similar to O–H…O interactions included in the dimeric model, the introduction of these interactions may lead to the increase of the δ CNH frequency.

3.3. 1,1,1-Hypogermatranol

The structure of the triol member of germatranols studied, i.e. hypogermatranol containing only one GeOCH₂CH₂N cycle (III), as well as germanium and silicon analogs with other X substituents. was not determined experimentally. The predicted structure of III is depicted in Fig. 1c. Due to the presence of three hydroxyl groups in the monomer there are different plausible structures of the dimer. They were analyzed for the case of methylsilanetriol in ref. [25]. From four structures which correspond to energy minima two have maximum coordination energy, i.e. the one which utilize for hydrogen bonding only two hydroxyl groups of each molecule, and the other in which all three hydroxyl groups participate in intradimeric bonding [25]. Two distinct types of the corresponding hypogermatranol (III) dimeric forms with almost equal energy were found at the B3LYP/6-31G* level but with the cc-pVDZ basis both converge to the first type (with only two hydroxyl groups involved in hydrogen bonding). This structure, presented in Fig. 2c, is similar to the analogous dimeric form of II, but has completely free (not involved in hydrogen bonding) hydroxyl groups. Thus, similar to dimer II, Fig. 2b, molecule III may form multiple hydrogen bonds not only with protons of hydroxyl groups which oxygen atoms act as proton acceptors (like in II), but also with free (non-bonded) hydroxyl groups. Thus, the solid state structure of III may differ substantially from that of II. The comparison of predicted (monomeric and dimeric forms) and experimental IR spectra of III (Table 5) and especially GeOH deformations may draw some light on the plausible solid state structure, however these conclusions may be quite tentative. Among GeOH bending modes, the highest frequency in the dimeric model belongs to the deformation of the GeOegH group (GeO10 at Fig. 2c), which donates its proton to the hydrogen bond. Its predicted frequency of 1158 cm⁻¹ is in a good agreement with the IR 1145 cm⁻¹ band. In contrast to this vibration, the frequency of which rises from 979 cm^{-1} in a monomer to 1158 cm^{-1} in the dimer, the second hydroxyl group non-bonded in the dimer (GeO7H) practically does not change its frequency. The experimental 1015 cm⁻¹ band may correspond to the predicted value 992 cm⁻¹, but most likely this "free" hydroxyl group (GeO7H in the dimeric model) is involved in hydrogen bonding in solid state and its frequency may lie above 1050 cm⁻¹. The predicted frequencies of the axial GeOaxH group (GeO1-proton acceptor) deformation are 926 cm⁻¹ (monomer) and 972 cm⁻¹ (dimer). The 978 cm^{-1} shoulder of the 1015 cm^{-1} IR band coincides well with the predicted frequency of the dimer; however most probably the frequency of this deformation may lie higher due to the involvement of protons of these groups in inter-dimeric interactions.

Along with axial and "free" hydroxyl group protons hydrogen atoms of N-H groups may take part in inter-dimeric bonding to form polymeric chains. Therefore, the theoretical description of the $700-450 \text{ cm}^{-1}$ frequency range in the dimeric model is rather poor. Only one strong band (491 cm^{-1}) with shoulders at 587, 560, and 453 cm⁻¹ is observed in this range. Theory predicts seven modes with frequencies in this range. Three of them, that are ν GeO_{ax} (GeO1), ν GeO_{eq} (GeO3), and δ NCC, may be assigned to the shoulders at 587 and 560 cm^{-1} with fair agreement between theoretical and experimental frequencies while the main 491 cm⁻¹ band should be assigned to τ GeO7H (free) as theory predicts high IR intensity of this mode. There is a large discrepancy between experimental and theoretical frequencies for this case, but it may be understandable due to the fact the dimeric model does not describe their involvement in inter-dimeric hydrogen bonds. Two from three remaining bands have a large contribution of NH₂ deformations which are inadequately described in the dimeric model and the third belongs to the GeO stretching of "free" GeOH groups which do not participate in hydrogen bonding in the dimeric model.

The spectral features of III in the $1650-1200 \text{ cm}^{-1}$ region may also indicate the involvement of NH₂ group in hydrogen bonding.

There are two vibrations with the substantial contribution of the Ge…N stretching with predicted frequencies of 273 and 412 cm^{-1} for the monomer. However scaling of the Ge…N stretching coordinate by the factor 2.663 (employed for the scaling of theoretical force fields of I and II gives frequencies equal to 474 and 345 cm⁻¹ (Table 5)). They may be assigned to IR bands 453 and 358 cm^{-1} . Thus, modes with the largest contribution of the Ge…N may be assigned in I to the 242 cm⁻¹ IR band, in II to the 458 cm⁻¹ band, and in III to the 453 cm⁻¹ band. Minor, but considerable contribution of this coordinate is in vibrations that may assigned to IR bands with 421 cm⁻¹ (I), 560 cm⁻¹ (II), and 358 cm⁻¹ (III). Thus, although the tendency of the increase of the ν Ge…N frequency on going from I to II may be related with the shortening of the Ge…N interatomic distance be traced, it is not straightforward, since these vibrations are strongly mixed with other vibrations of the $Ge(OCH2CH2)_n$ N cage.

4. Conclusions

- 1. Solid state IR spectra of germatranol compounds $(HO)_{4-n}Ge(OCH_2CH_2)_nNR_{3-n} (R = H; n = 1-3)$ with a transannular Ge…N bonding which contain different number of Ge(OCH_2CH_2)N cycles were recorded. The assignment of the observed bands was carried out with the help of theoretical predicted vibrational frequencies obtained at the B3LYP/aug-cc-pVDZ level of theory. Theoretical force fields scaled with factors obtained earlier for the FGe(OCH_2CH_2)_3N molecule were used to take into account the systematic difference between the gas phase and theoretical M…N distances (M = Si, Ge) on the one hand and X-ray solid state transannular bond lengths on the other.
- 2. Equilibrium structures of germatrane molecules $(OH)_nGe(OCH_2 CH_2)_4 {}_nNH_n {}_1 (n = 1-3)$ exhibit the reduction of a transannular Ge…N interatomic distance with *n*. Vibrations with a greater contribution of the Ge…N stretching coordinate may be assigned to IR bands at 242 (I), 458 (II), and 453 (III) cm⁻¹. Thus, despite the steady decrease of the Ge…N interatomic distance, corresponding frequencies demonstrate the substantial increase on going from I to II and a practically no increase on going from II to III.

- 3. The dimeric form of I revealed by the X-ray diffraction study is an energy minimum on the potential energy surface of [HOGe(OCH₂CH₂)₃]₂. Ongoing from monomer to dimer the length of the proton-donating GeO bond decreases, while that containing a proton-accepting oxygen atom increases.
- 4. The equilibrium structure of the [(HO)₂Ge(OCH₂CH₂)₂NH]₂ dimer is in a good agreement with the structure found in the Xray study, although weaker inter-dimeric OH…O and N…H interactions revealed in solid state are not present in the dimeric model. In contrast to **I**, where the Ge…N transannular distance increases on going from monomer to dimer, in **II** it decreases.
- 5. There is a significant increase of predicted δ GeOH and τ GeOH frequencies on going from monomeric to dimeric models due to formation of hydrogen bonds (from 958 to 1133 cm⁻¹ and from 74 to 638 cm⁻¹ in **I**). These deformation vibrations of hydrogen bonded GeOH groups may be assigned to the experimental IR bands observed at 1102 and 636 cm⁻¹ for 1-germatranol.
- 6. Similar increase of theoretical δ GeOH and τ GeOH frequencies is observed in **II**. For the equatorial GeOH group (proton acceptor) these modes are assigned to 1115 and 816 cm⁻¹ bands, and for the axial (proton donor) group to 1011 and 346 cm⁻¹ IR bands. However, the assignment of the latter mode may be dubious, due to the absence of inter-dimeric hydrogen bonds in our model.
- 7. Only one energy minimum was found at the potential energy surface of the [(HO)₃Ge(OCH₂CH₂)NH₂]₂ dimer, in which two hydroxyl groups of each monomer form hydrogen bonds (one as a proton donor and the other as an acceptor) while the third one remains "free". Substantial deviations of theoretical frequencies from experimental ones may indicate that a dimeric model of **III** is a poor approximation for the description of the solid state experimental spectrum of **III** in contrast to dimeric models of **II** and, especially, **I**. Solid state structure may comprise a three dimensional network formed by strong hydrogen bonds.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.12.036.

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