



Density Functional Study of Intramolecular Proton Transfer and Vibrational Frequencies of Hydroxyaminogermanone

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ABSTRACT

The electronic structure and reactivity of hydroxyaminogermanone conformers were studied in the gas phase by density functional theory. Seven minimum structures (1-7) and six transition states (TSs) were located. The global isomeric structure was 2 at the B3LYP/6-311++G (d,p) level of theory. The natural bond orbital (NBO) analysis reveals that there is a strong interaction $n_{O2} \rightarrow \sigma_{N3-Ge1}^*$ in the most studied compounds, for example, the second order energy for 3 is 14.05 kcal/mol. The 3d orbitals of germanium have little importance in bonding for the molecules. The charge density values strongly support the assumption that bonding between Germanium atom and Oxygen, nitrogen atoms are ionic, whereas N-H and O-H bonds are maintained the covalent bond nature. The computed harmonic frequencies results were in good agreement with available experimentally reported values. The shift in N-H and O-H towards the lower frequency attributed to the intramolecular hydrogen bonding. The calculated vibrational frequencies for symmetrical and asymmetrical stretching modes of GeH_2 are located at 1975 and 1955 cm^{-1} respectively.

Keywords: Hydroxyaminogermanone; Tautomers; Natural bond orbital; stability

INTRODUCTION

The hydroxamic acids play an important role in analytical and biological chemistry, and have been used in the detection and quantitative determination of metals [1-3]. A number of experiments and theoretical calculations have been performed on the simplest hydroxamic acid (formhydroxamic acid) but it is still not known with certainty which of the conformers is present in the gas and solution phases [4-7]. The stabilization energies associated with the dimerization of thioformhydroxamic acid and formhydroxamic acid tautomers and their correlation to proton affinities and deprotonation enthalpies have been considered [8]. The structure and the gas-phase acidities of formhydroxamic acid and silaformhydroxamic acid derivatives have been examined; sila-substitution produces an appreciable shift of the corresponding harmonic vibration frequencies of the formhydroxamic acid [9]. Previously, we are investigated the sila and thio- derivative of formhydroxamic acid in the same manner [10,11]. The molecular structure of hydroxyphosphinecarbothialdehyde has been studied in the gas phase and the interconversion of few isomeric tautomers of the molecule via intramolecular hydrogen transfer has been investigated by density functional theory [12]. Recently, the potential energy surface, the global isomeric structures and the TSs of intramolecular proton transfer of (hydroxphosphino)silanethione is investigated [13]. The structure and reactivity of hydroxyaminosilanethione conformers were studied in the gas phase by density functional theory [14]. The existence of nitrogen-germanium analogues of hydroxamic acids have not been proved experimentally and therefore no structural details are available, and no theoretical calculations have been carried on this structure. The aim of this study is to provide a consistent and reliable set of structures for the hydroxyaminogermanone using B3LYP/6-311++G (d,p) level. Additional interests are the molecular geometries, activation barriers, natural bond orbital

analysis and how these properties change upon isosteric substitution of carbon atom in formohydroxamic acid molecule by germanium.

EXPERIMENTAL SECTION

Computational Details

The calculations investigated the relative stabilities of the various isomeric forms of hydroxyaminogermanone. The study included the analysis of the reaction paths leading from one structure to another. The DFT calculations were performed with the B3LYP three parameter density functional, which includes Becke's gradient exchange correction [15] and the Lee–Yang–Parr correlation functional [16,17]. The geometries of all conformers and TSs were fully optimized at the B3LYP/6-311++G (d,p) level of theory. This was followed by harmonic frequency calculations at same level. The intrinsic reaction coordination (IRC) [18] calculations were performed for all of the TSs to verify that the located TSs actually connected the correct starting and ending structures. The vibrational frequencies were scaled by a factor of 0.9614 [19]. The zero-point vibrational energy (ZPVE) corrections calculated at the B3LYP/6-311++G (d,p) level are used directly without scaling because empirically it appears that the ZPVE corrections at such a level of theory is in good agreement with the experimental values [20,21]. Natural bond orbital analysis was then performed by the NBO 3.1 program [22] included in GAUSSIAN 03 package of programs at B3LYP/6-311++G(d,p) level of theory. The orbitals interaction can be quantitatively described in terms of the NBO approach that is expressed by means of the second-order perturbation interaction energy ($E^{(2)}$) [23,24]. The analysis of electron charge density ($\rho(r)$) and Laplacian ($\nabla^2\rho(r)$) of the charge density at all bond critical points (BCPs) have been calculated at B3LYP/6-311++G(d,p) level of theory using quantum theory atoms in molecules (QTAIM) of Bader [25]. The calculations were performed using Gaussian03 program [26].

RESULTS AND DISCUSSION

The Geometries

There are eight electronic structural types of hydroxyaminogermanone, three keto forms (1,3,7,8), four enol forms (2,4,5,6) and there are six TSs (TS₁₋₂ to TS₆₋₇) for the proton transfer process between two pair of isomers. TS₄₋₅ is the transition structure in which the proton transfer is not involved, this transition structure (TS₄₋₅) is involved in the transformation of the 4 structure (E-(hydroxyimino)germanol) to the 5 structure (Z-(hydroxyimino)germanol). Therefore, eight minima structures and six corresponding transition structures are presented in Figure 1. The structural parameters from the full optimized geometry of the structures are given in Table 1. Five minima structures (1,4,5,7,8) possessed the intramolecular hydrogen bonding (N-HO). The optimized structures at B3LYP/6-311++G (d,p) level of theory gave a good value for the bond distances in comparison with the available experimental data for related compounds [27-32].

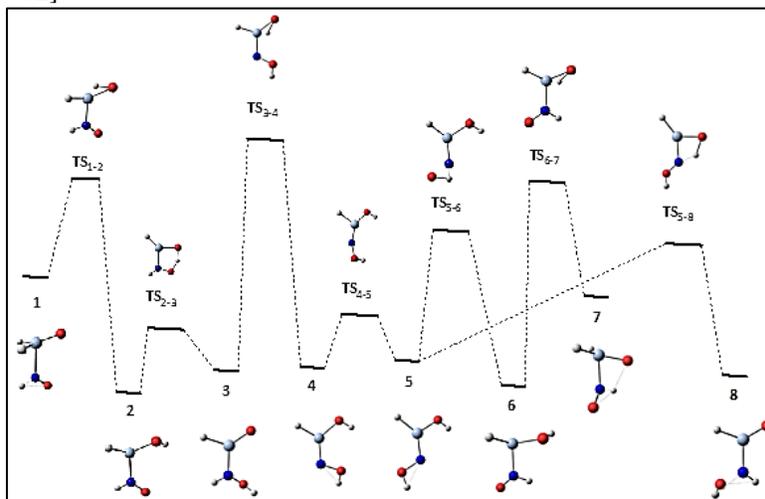


Figure 1: Potential energy surfaces describing the intramolecular proton transfer

Table 1: Geometrical parameters of the molecules, bond length (Å), bond order (in parentheses) and bond angle (°) at B3LYP/6-311++G(d,p) level

System	Ge-O	Ge=O	Ge-N	Ge-N	N-O	Ge-H	N-H	O-H	Ge-O
1	-	1.655	2.309	-	1.19	1.552	1.057	-	3.18
	-	-1.32	-0.26	-	-1.99	-0.84	-0.83	-	-0.04
2	1.811	-	1.966	-	1.229	1.567	1.045	0.963	2.909
	-0.69	-	-0.8	-	-1.6	-0.84	-0.81	-0.77	-0.33
3	-	1.645	1.827	-	1.414	1.536	1.015	0.966	2.82
	-	-1.39	-0.81	-	-1.01	-0.85	-0.83	-0.77	-0.04
4	1.787	-	-	1.744	1.424	1.517	-	0.965	2.647
	-0.7	-	-	-1.5	-1.02	-0.91	-	-0.76	-0.12
5	1.78	-	-	1.748	1.424	1.529	-	0.965	2.651
	-0.71	-	-	-1.47	-1.03	-0.87	-	-0.76	-0.12
6	1.838	-	1.978	-	1.224	1.566	1.045	0.962	2.928
	-0.65	-	-0.77	-	-1.65	-0.84	-0.81	-0.78	-0.31
7	-	1.697	2.097	-	1.205	1.537	1.047	-	2.987
	-	-1.03	-0.42	-	-1.8	-0.87	-0.8	-	-0.05
8	-	1.647	1.832	-	1.424	1.531	1.015	0.966	2.773
	-	-1.38	-0.79	-	-1	-0.87	-0.83	-0.77	-0.04
Exp.	1.828 ^a	1.725 ^b	2.103 ^c	1.889 ^c	1.388 ^d	1.569 ^e	0.91 ^d	0.86 ^d	-

Note: a [27], b [28], c [29], d [30], e [31], and N=O =1.24 [32]

Charge Distribution and Dipole Moment

Natural atomic charges for the minimum structures and the dipole moments obtained with B3LYP/6-311++G(d,p) method are given in Table 2. It can be seen in Table 2 that the atoms O, N and H attached to the Germanium atom acquired negative charges, whereas the Ge and the remaining hydrogen are positively charged. Natural population analysis indicated that charge distribution of all tautomeric forms of hydroxyaminogermanone shows that the oxygen, nitrogen and atoms have more negative charges, whereas their hydrogen atoms have positive charges. The result suggests that the atoms bonded to oxygen or nitrogen atoms are electron donor, and it also indicates that the charge transfers from hydrogen to oxygen or nitrogen. In addition, the oxygen attached to germanium atom takes the most negative charge in all compounds and due to that it will most effectively interact with electrophiles. The results of dipole moments showed that 1, 3 and 8 had the largest dipole moments in the gas phase. The dipole moment of 4 was the lowest (0.74 D). It is notable that dipole moments are significantly related to the nature of compounds, the increase in dipole moment of the 1 is at least nine times more than that of the 4 form. As the result, the latter molecule has become to be less favored than the former.

Table 2: Natural atomic charges of the molecules at B3LYP/6-311++G(d,P) level

System	qGe	qO1	qN	qO2	qH _{Ge}	qH _{O1}	qH _N	qH _{O2}	μ
1	1.34	-1.07	-0.03	-0.15	-0.19	-	0.3	-	6.74
2	0.97	-1.02	-0.25	-0.32	-0.18	0.47	0.32	-	2.41
3	1.67	-1.04	-0.72	-0.55	-0.19	-	0.37	0.46	4.86
4	1.45	-1.01	-0.66	-0.59	-0.14	0.49	-	0.47	0.74
5	1.46	-1.01	-0.67	-0.57	-0.15	0.49	0.37	0.46	0.93
6	0.91	-1.04	-0.21	-0.29	-0.17	0.47	0.33	-	1.92
7	1.33	-1	-0.11	-0.24	-0.17	-	0.35	-	3.29
8	1.67	-1.05	-0.73	-0.56	-0.18	-	0.38	0.46	4.37

Energy Analysis

The energy profile is schematically plotted in Figure 1. It is clear that the highest energy is TS₃₋₄, which is equal to 75.75 kcal/mol above the global isomeric structure 2, is involved in the rate-determining step. The relative energies are listed in Table 3. The 2 isomer is located as a global minimum on the reaction coordinates at all levels of calculations, and the energy values are reported related to 2 in the hydroxyaminogermanone isomers. TS₃₋₄ possessed

the highest energy (85.01 kcal/mol) in the reaction coordinates and was involved in the rate-determining step. The TS energies are affected by the ring strain because the TS₁₋₂ with a five-membered ring structure possessed the lowest energy (18.64 kcal/mol). The TS₁₋₂ and TS₆₋₇ possessed the highest energies (72.19, and 70.71 kcal/mol) respectively, therefore, the three-membered ring structures involving germanium atom have been found as having the highest TSs energies. The 1 and 7 have the highest energies which are (38.41 and 31.59 kcal/mol) above the global minimum 2. The stability order for the local minimum isomers are 6>8>3>4>5>7>1. The transformation of 4 to 5 involves a rotation about the Ge=N double bond. This step involves unexpected barrier of 78.04 kcal/mol via TS₄₋₅. This barrier value is in accord with previously reported results for formohydroxamic acid [33]. Judging from the transition barrier of the intramolecular proton transfer it seems that the 3-TS₃₋₄-4 is the slowest reaction step and it is endothermic with an energy barrier equal to 78.04 kcal/mol whereas the 4-TS₄₋₅-5 is the fastest reaction step and again it is endothermic with an energy barrier equal to 16.32 kcal/mol. There are three exothermic steps 1-TS₁₋₂-2, 5-TS₅₋₆-6 and 7-TS₇₋₈-8 with enthalpies of activation equal to -38.41, -9.41 and -25.89 kcal/mol respectively. The energy difference among the isomers is no greater than 39.35 kcal/mol. The transformation of 3 to 8 involves first a proton transfer (O→N) leading to 4 via TS₃₋₄, secondly a Ge-N rotation leading to 5 isomer via TS₄₋₅, thirdly a proton transfer (O→N) leading to 8 via TS₅₋₈. Therefore, the reaction coordinate occurs via a pathway (3→4→5→8) that has an overall activation barrier of 78.04 kcal/mol. The interconversion between 8 (Keto-analogous) and 5 (enol-analogous) isomer via TS₅₋₈, this step involves a barrier of 49.70 kcal/mol.

Table 3: The total energy, ZPVE in Hartree, relative energy and activation energy, in (kcalmol-1) and HOMO-LUMO gap in eV

	Energy	Energy+ZPVE	ZPVE	ΔE	E [‡]	H-L g
1	-2283.9418	-2283.90802	0.0337	38.4		1.9
TS₁₋₂	-2283.887	-2283.85419	0.0328	72.2	33.8	1.99
2	-2284.0075	-2283.96923	0.0383	0		2.81
TS₂₋₃	-2283.9751	-2283.93952	0.0356	18.6	18.6	2.92
3	-2283.998	-2283.95812	0.0399	6.97		5.55
TS₃₋₄	-2283.867	-2283.83376	0.0332	85	78	2.2
4	-2283.9941	-2283.95566	0.0384	8.52		4.17
TS₄₋₅	-2283.9677	-2283.92965	0.0381	24.8	16.3	3.45
5	-2283.9908	-2283.95273	0.0381	10.4		4.03
TS₅₋₆	-2283.9163	-2283.88377	0.0326	53.6	43.3	2.98
6	-2284.0061	-2283.96773	0.0383	0.94		2.63
TS₆₋₇	-2283.8894	-2283.85654	0.0328	70.7	69.8	1.98
7	-2283.9546	-2283.91889	0.0357	31.6		3.26
TS₅₋₈	-2283.9245	-2283.89002	0.0345	49.7	39.4	4.14
8	-2284.0002	-2283.96014	0.0401	5.7		5.54

NBO Analysis

The electron delocalization resulting between different orbitals can be investigated by NBO. Natural atomic hybrid (NHOs) and the polarization coefficients of the molecules are given in Table 4. Important second order delocalization energies E⁽²⁾ that are representatives of the extent of electron delocalization are given in Table 5. According to the simple bond orbital picture, a NBO is defined as an orbital formed from natural atomic orbitals. Therefore, for a localized σ-bond between atoms A and B, the NBO is defined as:

$$\sigma_{AB} = C_A h_A + C_B h_B$$

Table 4: Calculated natural atomic hybrid (NHOs) and the polarization coefficient for the molecules with B3LYP/6-311++G(d,p), polarization coefficient (in parentheses)

Molecules	Ge1-O2		Bond Lengths	Bond Order
	Ge1	O2	Ge1-O2	Ge1-O2
1	sp ^{2.59} d ^{0.03} (0.4707)	sp ^{4.58} (0.8823)	1.655	1.32
	sp ^{5.74} d ^{0.08} (0.4200)	sp ^{17.79} d ^{0.01} (0.9075)		
2	sp ^{2.82} d ^{0.06} (0.4243)	sp ^{3.01} (0.9055)	1.811	0.69
3	sp ^{18.0} d ^{0.30} (0.4146)	sp ^{53.66} d ^{0.04} (0.9100)	1.645	1.39
4	sp ^{2.86} d ^{0.02} (0.4278)	sp ^{3.06} (0.9039)	1.787	0.7
5	sp ^{2.76} d ^{0.02} (0.4288)	sp ^{2.95} (0.9034)	1.78	0.5

6	-	-	1.838	0.65
7	sp ^{2.14} d ^{0.01} (0.4867)	sp ^{3.62} (0.8736)	1.697	1.03
8	Sp ^{13.47} d ^{0.22} (0.4173)	Sp ^{32.47} d ^{0.02} (0.9088)	1.647	1.38
	Sp ^{1.86} d ^{0.01} (0.4879)	Sp ^{4.52} (0.8729)		
Ge1-N3			Ge1-N3	Ge1-N3
	Ge1	N3		
1	-	-	2.309	0.26
2	sp ^{2.72} d ^{0.02} (0.4442)	sp ^{1.88} (0.8959)	1.966	0.8
3	sp ^{2.67} d ^{0.02} (0.4542)	sp ^{2.06} (0.8909)	1.827	0.81
4	sp ^{4.77} d ^{0.03} (0.5582)	sp ^{28.21} d ^{0.03} (0.8297)	1.744	1.5
	sp ^{3.20} d ^{0.02} (0.4956)	sp ^{4.13} (0.8685)		
5	sp ^{3.81} d ^{0.02} (0.5668)	sp ^{22.01} d ^{0.02} (0.8238)	1.748	1.47
	sp ^{3.73} d ^{0.03} (0.4918)	sp ^{4.36} (0.8707)		
6	-	-	1.977	0.77
7	sp ^{6.82} d ^{0.05} (0.3711)	sp ^{1.65} (0.9286)	2.097	0.42
8	sp ^{2.65} d ^{0.02} (0.4552)	sp ^{2.22} (0.8904)	1.832	0.79

Table 5: Second order delocalization energies ($E^{(2)}$) of the molecules with B3LYP/6-311++G(d,p), all values are in kcal/mol

	1	2	3	4	5	6	7	8
nO2→σ*Ge1-H	11.4					2.1	10.6	
nN3→σ*Ge1-O2	32.2		15.7	8.84				13.6
nO4→σ*N3-H	20.3	16.16				2.7		
nO2→σ*Ge1-O4		10.68						
nN3→σ*Ge1-O4		219.2						
nO2→σ*Ge1-N3			14.1	7.42	6.22		29.1	14.2
nO4→σGe1-N3				11.7	11.5		15.7	
nN3→σ*Ge1-H					9.53			

Where, h_A and h_B are the natural hybrid centered on atom A and B. The filled natural bond orbitals σ_{AB} of the natural Lewis structure are therefore well adapted to describing covalency effect in molecules. The general transformation to NBOs also leads to orbitals that are unoccupied in the formal Lewis structure and that may thus be used to describe non-covalency effect. The most important of these are the anti-bonds σ_{AB}^* [34]. The inspection of the results represented in Table 4 reveals that the increasing d characters on germanium natural hybrid orbital σ_{Ge-O} and increasing the p characters on oxygen NHO σ_{Ge-O} bond orbitals result in a shortening of the Ge1-O2 bond and as expected increasing the bonds order simultaneously. 2,4 and 5 molecules showed a weak Ge-O interaction without d contribution, whereas 3 and 8 molecules showed a strong Ge-O bond with d contribution. Small and nearly equal values of the calculated d contribution of germanium atom show that 3d orbitals have little importance in bonding for the molecules. The sizes of the polarization coefficients show the importance of the two hybrids in the formation of the bond. In 1 the nitrogen has larger percentage of NBO and gives the larger polarization coefficient because it has higher electronegativity. Similar results are found in all the bonding Ge-N and Ge-O orbitals. 3 and 8 molecules showed the largest polarization coefficients on oxygen atoms (0.9100 and 0.9088) among the compound under consideration. The second order delocalization energies ($E^{(2)}$) for the molecules are given in Table 5. There is a strong interaction $n_{O2} \rightarrow \sigma_{N3-Ge1}^*$ in the most studied compounds. For example, the second order energy for 3 is 14.05 kcal/mol. This interaction reduces the Ge-N bond and elongates the O-N bond length. This is accompanied by an $n_{N3} \rightarrow \sigma_{O2-Ge1}^*$ ($E^{(2)} = 15.69$ kcal/mol), which induces partial π character. The NBO analysis for 2 demonstrated that the $n_{N3} \rightarrow \sigma_{O4-Ge1}^*$ interaction between the nitrogen lone pair and the O4-Ge1 is seen to give the strongest stabilization energy. This is accompanied by an $n_{N3} \rightarrow \sigma_{O4-Ge1}^*$ ($E^{(2)} = 219.23$ kcal/mol). An interaction is noted for 2 compound $n_{O4} \rightarrow \sigma_{N3-Ge1}^*$ the O4 lone pair is seen to be the lowest occupancy (1.9198) and highest energy (-0.3260 a.u.) Lewis NBO and to be primarily delocalized into anti-bonds (σ_{N3-Ge1}^*), this interaction elongates the N=O to 1.23Å and the Wiberg bond index is 1.60 calculated for N=O. Generally, the lone pair of oxygen and nitrogen is involved in a strong hyperconjugative interaction. For example, in 8 there is a strong hyperconjugative interaction $n_{O4} \rightarrow \sigma_{N3-Ge1}^*$ and the weakness in the O-N sigma bond is due to $n_{O4} \rightarrow \sigma_{N3-Ge1}^*$ delocalization and is responsible for the elongation of O-N bond. Another important indicator of the bonding character is the second derivative of the charge density at

the bond critical point, the Laplacian of the charge density $\nabla^2\rho(r)$. If the Laplacian is negative and large in magnitude, atoms are bound covalently. The positive Laplacian indicates electrostatic or ionic bonding. The results of the bond critical point ($\rho(r)$ and $\nabla^2\rho(r)$) are represented in Table 6. The study reveals that for all Ge-O and Ge-N bonds the Laplacian is positive. These values strongly support the assumption that bonding between Germanium atom and Oxygen, nitrogen atoms are ionic. This result which has been supported by the natural atomic charges strongly verify the above ionic bonding since the germanium atoms bear high positive charges, while the oxygen and nitrogen atoms have negative charges Table 2. The Laplacian is negative and large for N-H and O-H bonds, this Laplacian maintained the covalent bond nature. The trend in $\rho(r)$ can be related to the bond lengths since, the trend is N-H > O-H with the shortest bond (O-H) displaying the largest $\rho(r)$ values.

Table 6: The values of the electron density $\rho(r)$ (in parentheses), and the Laplacian of charge density $\nabla^2\rho(r)$ at bond critical points at B3LYP/6-311++G(d,p) level of theory

Molecule	Ge-O2	Ge-N	N-O4	Ge-H	N-H	O2-H	O4-H
1	0.871	0.115	-1.507	-0.014	-1.388	-	-
	-0.189	-0.049	-0.537	-0.131	-0.318		
2	0.492	0.231	-1.114	-0.017	-1.43	-2.445	-
	-0.129	-0.102	-0.487	-0.126	-0.323	-0.362	
3	0.907	0.372	-0.344	0.03	-1.59	-	-2.56
	-0.193	-0.141	-0.304	-0.136	-0.337		-0.368
4	0.543	0.461	-0.295	-0.034	-	-2.452	-2.571
	-0.137	-0.17	-0.294	-0.141		-0.358	-0.369
5	0.563	0.443	-0.296	-0.04	-	-2.451	-2.567
	-0.139	-0.169	-0.294	-0.137		-0.358	-0.369
6	0.44	0.233	-1.168	-0.019	-1.468	-2.443	-
	-0.122	-0.099	-0.494	-0.126	-0.324	-0.364	
7	0.739	0.148	-1.347	-0.022	-1.523		-
	-0.172	-0.077	-0.517	-0.136	-0.322		
8	0.906	0.36	-0.312	-0.039	-1.613	-	-2.562
	-0.192	-0.141	-0.295	-0.138	-0.338		-0.368

Vibrational Frequencies

The calculated vibrational frequencies of optimized structures are reported after correction by scaling factor. In Table 7, the OH frequencies values are in the range of 3633-3719 cm^{-1} . The lowest values for 4,5 and 8 are consistent with the usual OH frequency in the presence of hydrogen bonding. In the next column, NH frequencies have shown that their values lie between 2868 and 3401 cm^{-1} . The OH and NH frequencies are in agreement with reported experimental values of hydroxamic acid [35,36] Again this shift towards the lower frequency attributed to the intramolecular hydrogen bonding in 1. The calculated vibrational frequencies for asymmetrical stretching modes of GeH_2 are observed in 1955 cm^{-1} . The GeH vibrational frequencies are located between 1922-2124 cm^{-1} , which are in conformity with the experimental value [37,38]. The highest Ge-H vibrational frequency (2124 cm^{-1}) is located in structure 4. Finally, the computed vibrational frequencies of N→Ge in 1 is located at 129 cm^{-1} .

Table 7: Selected vibrational frequencies in cm^{-1} of the molecules at B3LYP/6-311++G (d,p) level of theory

Molecule	O-H	N-H	Ge-H	N=O	Ge=O	Ge-O	N-O	N-Ge
1	-	2868	1975 s	1614	888	-	-	129
			1955 as					
2	3711	2992	1925	1410	-	615	-	-
3	3633	3398	2043	-	909	-	1009	-
4	3684	-	2124	-	-	652	941	-
5	3686	-	2040	-	-	657	928	-
6	3719	3007	1922	1434	-	581	-	-
7	-	3004	2042	1534	815	-	-	194
			2030					
8	3633	3401	2063	-	907	-	978	-

CONCLUSION

The present study systematically analyzed the conformation stability of the hydroxyaminogermanone molecule, the activation barrier, NBO, electron density, Laplacian and the infrared spectra. 2 is the global minimum. Natural bond orbital analysis shows that the differences in interaction of the energies are due to lone pair of O and N atoms. For example, in 8 there is a strong hyperconjugative interaction $n_{\text{O}4} \rightarrow \sigma_{\text{N}3-\text{Ge}1}^*$ and the weakness in the O-N sigma bond is due to $n_{\text{O}4} \rightarrow \sigma_{\text{N}3-\text{Ge}1}^*$ delocalization and is responsible for the elongation of O-N bond. The bonding between Germanium atom and Oxygen, nitrogen atoms are ionic, the natural atomic charges values strongly verify the above ionic bonding. The intramolecular hydrogen bonding in 1,4,5,7 and 8 is clearly identified and it is responsible for the O-H and N-H vibrational frequency shift.

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