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Aromaticity or non aromaticity in germanazenes? Theoretical studies on germanazenes, the *N*-cyano analogs and their carbodiimide isomers

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Abstract

Theoretical studies of germanazene rings [$(Ge_{II}–NR)_{2,3}$; R = H, Me, CN, Ph] have been performed at the DFT/B3LYP level. The fully optimized geometrical structures display four or six-membered planar rings of alternating germanium and nitrogen, in good agreement with the available X-ray experimental data. The hypothetical molecule $(GeN–H)_2$ presents only a small distortion from planarity. Although the planar conformation could indicate some degree of delocalization, the stabilization energy – estimated using the concept of homodesmotic reactions – indicates very little or no aromatic character in these molecules. The easy experimental formation of these germanazenes can be explained by di- (or tri-)merisation of the transient monomeric germylene-imine Ge═NR in its triplet state. When R = CN, in conformity with the experimental results, the most stable species is the isomeric carbodiimide form $(Ge{-}N{=}C{=}N)_n$, a result which is easily explained by the maximum spin density on the terminal nitrogen in the calculated monomer.

Keywords: Germanazenes; Aromaticity; DFT calculations

1. Introduction

Within the germanium(IV) series, cyclogermazanes (Fig. 1(a), R = H, alkyl, aryl; $n = 2, 3, 4$) are well known stable compounds, the size of the ring (n value) being dependent on the size of the substituents both on nitrogen and the metal [1–3]. On the other hand, while Mes_2GeR_2 (R = —C≡N) is stable [4] and does not show any evidence of bonding between nitrogen and the metal, the cyanamide analogs of cyclogermazanes $(Mes_2GeNR)_n$ (Fig. 1(a), R = —C≡N) cannot be isolated. Preparative reactions always lead to the carbodiimide isomers [5] (Fig. 1(b)). The same fact was also observed within the series of acyclic compounds [6–8] where $R_3GeN{=}C{=}NGeR_3$ is obtained instead of the expected digermylamine $(R_3Ge)_2N–CN$. Although monogermylated compounds are observed in solution under an

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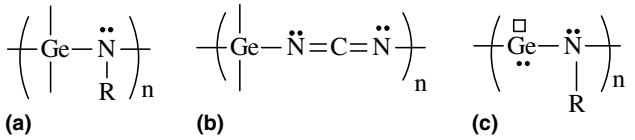


Fig. 1. Germanazanes and germanazenes.

equilibrium between the cyanamide $R_3Ge{-}NH{-}C{\equiv}N$ and the carbodiimide forms [7,8], the compound eventually isolated is the carbodiimide $R_3GeN{=}C{=}NH$.

Within the germanium(II) series, the germanazenes (Fig. 1(c), R = aryl, $n = 3$, 2) [9–11] analogs of the cyclogermazanes, possess planar rings and are unexpectedly stable compounds. One of the hypotheses given for such a stability was a possible aromaticity in such rings [9]. If these compounds obey to the Hückel rule with $(4n+2)$ electrons delocalized in the ring, within the germylene cyanamide/carbodiimide series we should find the cyanamide form (Fig. 1(c), R = —C≡N) more stable than the carbodiimide form $(-Ge_{II}-N{=}C{=}N-)_n$ which is not the case [7,12]. Therefore, the question of the stabilization observed for germanazenes arises again. Actually there are two questions we shall attempt to answer in this paper: what is the reason for the particular stability of germanazenes and why are the carbodiimide isomers more stable than the cyanamides?

To answer these questions, we performed ab initio DFT calculations on Ge_{II} molecules $(GeN–R)_n$ with R = H, Me, CN, Ph, and $n = 2$, 3. We also calculated some smaller molecules containing Ge–N single or double bonds which are necessary to enable a determination of homodesmotic [13] reaction energies usually employed as indicators of aromaticity in hydrocarbons [14–23] and inorganic analogues of benzene [24,25].

2. Computational details

The theoretical treatment of the different systems included in this work was performed by using the DFT/B3LYP approach implemented in the GAUSSIAN 98 series of programs [26]. The B3LYP non-local hybrid functional [27] has been found to be quite reliable in describing potential energy surfaces (PES) of carbodiimidogermylenes [12].

Standard pseudopotentials developed in Toulouse were used to describe the atomic cores of carbon, nitrogen, and germanium [28]. A double-zeta plus polarization valence basis set was employed for each atom. A set of pure 5d functions were used for C, N and Ge (d-type function exponents were 0.80, 0.95 and 0.25, respectively). For hydrogen, a standard (4s) primitive basis contracted to [2s] was used. A p-type polarization function (exponent 0.90) was added for the hydrogen atoms.

The geometries of the different species under consideration were optimized using analytic gradients. The harmonic vibrational frequencies of the different stationary points of the PES were calculated analytically at the same level of theory in order to identify the local minima as well as to estimate the corresponding zero-point vibrational energy (ZPE). The nature of the metal-nitrogen interaction was analyzed using natural bond orbital (NBO) calculations [29].

3. Results and discussion

All isomers identified have been found to be true local minima on their respective PES. Geometrical parameters of the optimized structures for the dimers $(GeN–R)_2$ (Fig. 2) and the trimers $(GeN–R)_3$ (Fig. 3) are given in Tables 1 and 2, respectively.

In the case of the dimers, we observed an overall good agreement between the B3LYP optimized results (Table 1) for $(GeN–Ph)_2$ and the X-ray average values obtained for $(GeN–C_6H_2–2,4,6\text{-}{}^tBu_3)_2$ [11]. The Ge_2N_2 ring in $(GeN–Ph)_2$ is planar with four Ge–N bonds of equal length, about 4% longer than in $(GeN–C_6H_2–2,4,6\text{-}{}^tBu_3)_2$. Such a difference can be attributed to the fact that calculations are related to isolated molecules in the gas phase while RX structures [11] refer to crystals with possible intra-molecular interactions. Moreover our calculation was performed on a model molecule with a non-substituted aromatic ring. For the other calculated molecules (Table 1), they also display a four-membered GeNGeN ring which is planar (R = CN) or almost planar (R = Me). The less sterically hindered $(GeN–H)_2$ represents a particular case with a slight distortion from planarity (Ge1–N1–Ge2–N2 dihedral angle of 11.4°). We can note that the N1–C1 and N2–C2 bonds are significantly shorter in the case of the Ph or CN substituents than in the case of Me. This can probably be attributed to a conjugation between the nitrogen

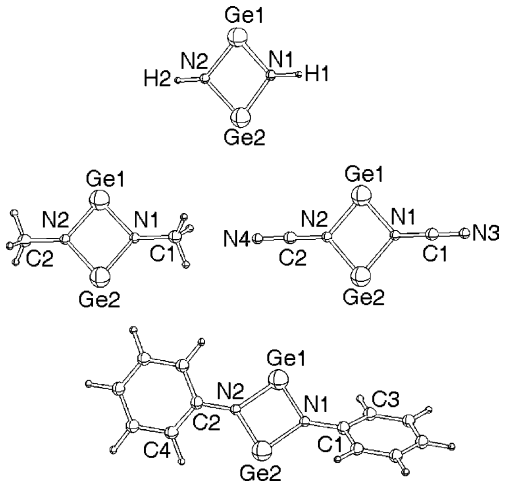


Fig. 2. DFT/B3LYP-optimized geometries of $(GeN–R)_2$ with R = H, Me, CN, Ph.

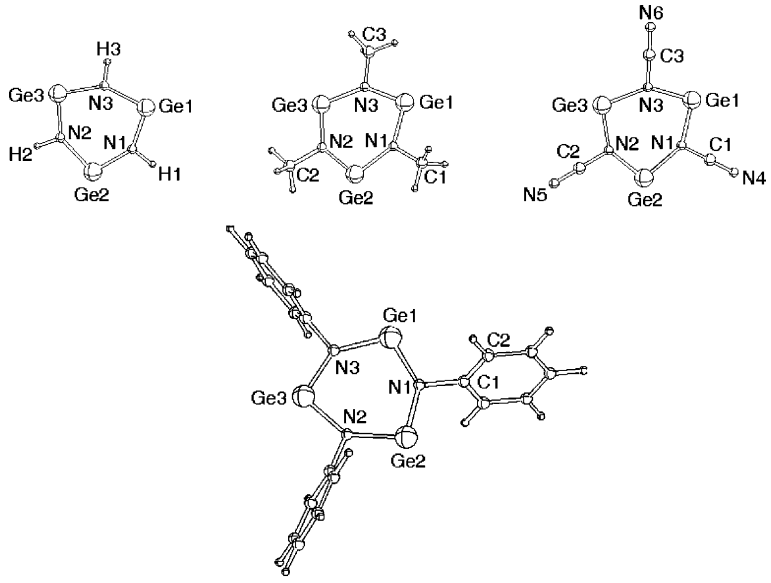


Fig. 3. DFT/B3LYP-optimized geometries of $(GeN–R)_3$ with R = H, Me, CN, Ph.

Table 1
Selected geometrical parameters (Å and °) for the $(GeN–R)_2$ cyclic dimers[a] with R = H, Me, CN, Ph, optimized at the DFT/B3LYP level

Geometrical parameters	$(GeN–H)_2$ C_{2v}	$(GeN–CH_3)_2$ C_2	$(GeN–CN)_2$ D_{2h}	$(GeN–C_6H_5)_2$ C_2	$[Ge–N\text{-}2,4,6\text{-}Bu_3C_6H_2]_2$ X-ray average values[b]
Ge1–N1	1.906	1.922	1.946	1.925	1.855 (3)
Ge2–N1	1.906	1.897	1.946	1.925	1.844 (3)
N1–X	1.022	1.457	1.336	1.407	1.438 (4)
Ge1–N1–Ge2	98.5	98.2	100.9	99.0	93.7 (1)
N1–Ge1–N2	80.3	81.7	79.1	81.0	86.3 (1)
Ge1–N1–X	129.2	131.3	129.5	130.5	136.1 (2)
Ge2–N1–X	129.2	130.5	129.5	130.5	130.2 (2)
Ge1–N1–Ge2–N2	11.4	1.1	0.0	0.0	0.0

X represents the atom directly linked to N1.
[a] See Fig. 2 for labeling of the atoms.
[b] Ref. [11].

Table 2
Selected geometrical parameters (Å and °) for the $(GeN–R)_3$ cyclic trimers[a] with R = H, Me, CN, Ph, optimized at the DFT/B3LYP level

Geometrical parameters	$(GeN–H)_3$ D_{3h}	$(GeN–CH_3)_3$ C_3	$(GeN–CN)_3$ D_{3h}	$(GeN–C_6H_5)_3$ C_3	$[Ge–N(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$ X-ray average values[b]
Ge1–N1	1.893	1.893	1.951	1.918	1.859 (2)
Ge2–N1	1.893	1.910	1.951	1.918	1.859 (2)
N1–X	1.027	1.492	1.358	1.445	1.452 (5)
Ge1–N1–Ge2	140.5	136.3	141.1	137.7	138.0 (2)
N1–Ge1–N2	99.5	103.7	98.9	102.3	101.8 (1)
Ge1–N1–X	109.8	112.1	109.4	111.1	110.9 ± 1.3
Ge2–N1–X	109.8	111.6	109.4	111.1	110.9 ± 1.3
Ge1–N1–Ge2–N2	0.0	0.8	0.0	0.6	0.0

X represents the atom directly linked to N1.
[a] See Fig. 3 for labeling of the atoms.
[b] Ref. [9].

lone pair and the π system of the aromatic or nitrile groups.

Similar remarks can be made about the trimers $(GeN–R)_3$ (Fig. 3, Table 2). The B3LYP optimization of $(GeN–Ph)_3$ confirms the planar structure of the Ge_3N_3 ring as already observed by X-ray crystallography in $[GeN(2,6\text{-}^iPr_2C_6H_3)]_3$. [9] There is a good concordance between the theoretical optimized geometrical

parameters (bonds and angles) of $(GeN–Ph)_3$ and the X-ray average values obtained for $[GeN(2,6\text{-}^{i}Pr_2C_6H_3)]_3$ [9]. All molecules in Table 2 possess planar six-membered rings, even when R = H.

For aromatic substituents on nitrogen, the X-ray results display dihedral angles of about 90° between the planar aromatic group on nitrogen and the Ge_nN_n ring ($n = 2$, 89.6° [11]; $n = 3$, 86.2° [9]) while our B3LYP optimized calculations give the following dihedral angles: Ge1–N1–C1–C3 = 30.5° (Fig. 2) and Ge1–N1–C1–C2 = 103° (Fig. 3). Such a difference could be attributed to the steric hindrance of the *ortho* substituents on the phenyl groups in the isolated crystallized rings [9,11]. To make sure of this hypothesis, the variation of the B3LYP electronic energy with the dihedral angle Ge1–N1–C1–C2 in $(GeN–Ph)_3$ was calculated and is reported in Fig. 4. This diagram shows that there is practically no significant change in energy for angle values between 60° and 120°. Both the experimental RX value (86.2°) and the B3LYP optimized value (103°) calculated in $(GeN–Ph)_3$ are within that range. We can conclude that the bulky substituents on the phenyl groups are not responsible for the almost 90° value of the dihedral angle between the Ge_3 N_3 plane and the aryl planes. Therefore, the π systems of the phenyl groups cannot participate in a possible aromaticity of the germanazene ring.

In both Tables 1 and 2 the calculated Ge–N bond lengths in $(GeN–R)_n$ are slightly longer than the crystallographic ones. For the sake of comparison, we optimized the geometries of some simple molecules containing Ge–N bonds: $H_3Ge_{IV}–NH_2$, $HGe_{II}–NH_2$, $Ge_{II}(NH_2)_2$ (See Fig. 5).

For Ge_{II} molecules (Fig. 5(b) and (c)), the nitrogen bonded to germanium is always planar and the $Ge_{II}–N$ bond length is shorter than the $Ge_{IV}–N$ bond, showing a very weak interaction between the vacant 4p orbital of Ge_{II} and the nitrogen lone pair. However, in the calculated $(Ge_{II}N)_n$ systems, the ring strain leads to longer Ge–N bonds, in the range or slightly longer than

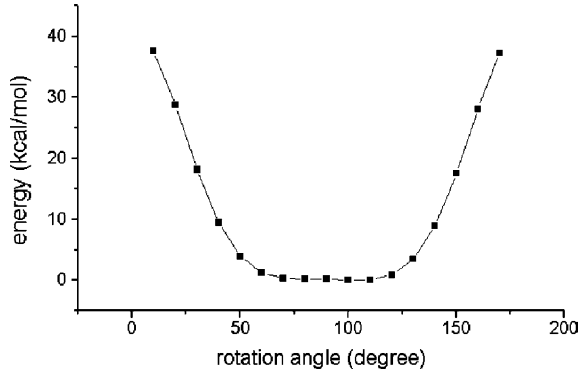


Fig. 4. Variation of the electronic energy of $(GeN–Ph)_3$ with the dihedral angle between the Ge_3N_3 ring and the phenyl plane calculated at the DFT/B3LYP level of theory.

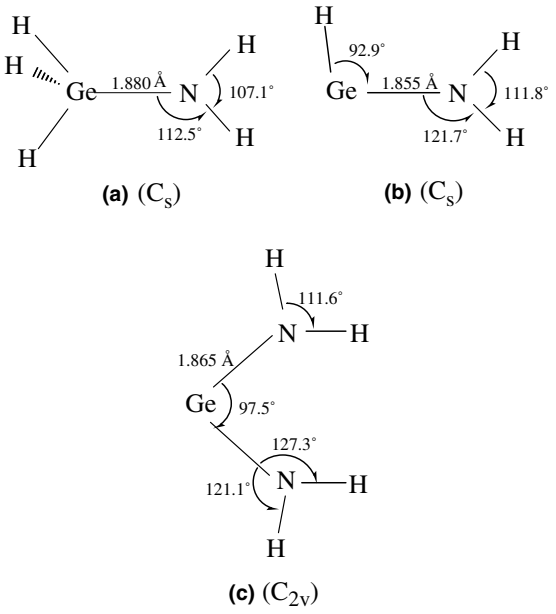


Fig. 5. DFT/B3LYP-optimized geometries of $H_3Ge–NH_2$, $HGe–NH_2$ and $Ge(NH_2)_2$ in their ground state.

the $Ge_{IV}–N$ σ bond (see Fig. 5(a)) (1.880 Å) calculated at the same level of theory.

The most important feature in the germanazene molecules is that all nitrogen atoms are planar which has been known for a long time in some simple silyl or germyl amines [1,3,30,31]. Therefore, the geometry of these $(GeN–R)_n$ molecules could allow a delocalization of the lone pair on nitrogen to the empty p orbital of Ge_{II} (Fig. 6). Since four ($n = 2$) or six ($n = 3$) electrons can be involved in the process, some degree of aromaticity could arise.

Some orbitals related to $(GeN–Ph)_3$ are represented in Fig. 7. They display the expected orientation, but there is no evidence for π interactions between the germanium vacant orbitals and the nitrogen lone pairs. The LUMO orbital of *e* symmetry is mainly constituted by the antibonding combinations of the vacant orbitals on germanium atoms. The HOMO orbital, also of *e* symmetry, is constituted by the lone pairs on germanium atoms, clearly antibonding with the nitrogen orbitals. The HOMO − 1 orbital belongs to a series of five orbitals describing the π systems of the phenyl groups. The HOMO-6 orbital of *a* symmetry shows the three lone pairs on the nitrogens and no contribution from the

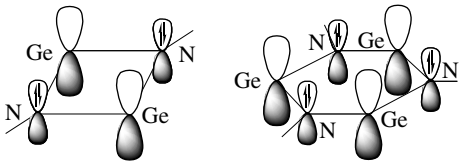


Fig. 6. Possible aromaticity of the $(Ge_{II}N)_n$ rings ($n = 2$, 3).

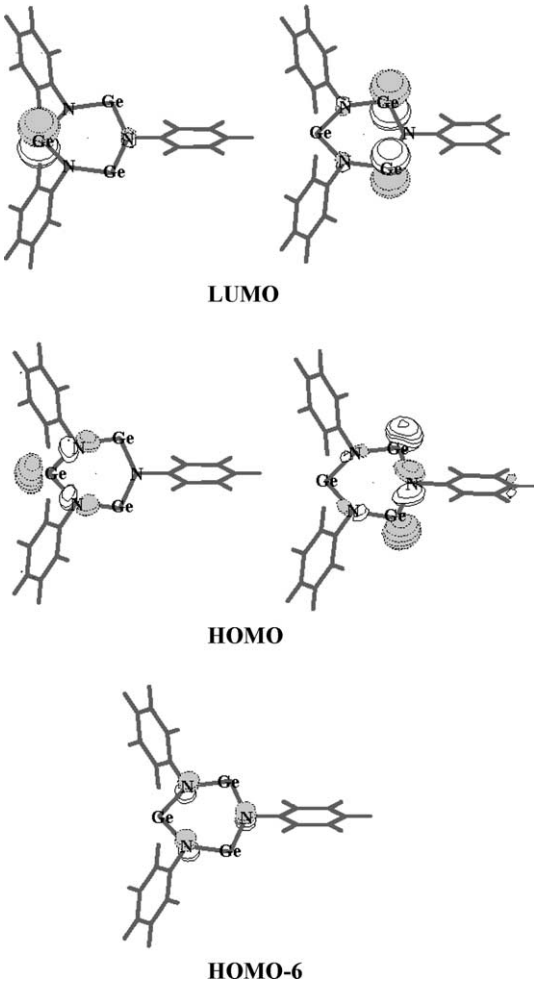
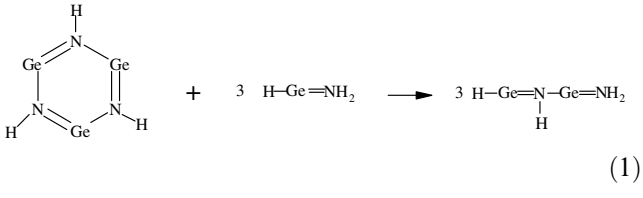
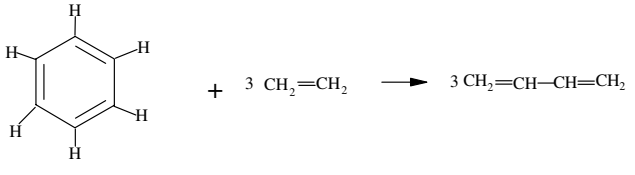


Fig. 7. Molecular orbital pictures for $(GeN–Ph)_3$ species.

germanium orbitals. Therefore, examination of the orbitals does not give an argument for an aromaticity of the germanazene rings.



(1)



(2)

Homodesmotic reactions in which there is an equal number of atoms, with one or two attached hydrogens, on both reaction sides, were used to evidence aromaticity in heteropolar analogues of benzene [25]. We optimized, at the same level of calculation, the molecules involved in the homodesmotic reaction (Eq. (1)) according to the model reaction for benzene [25] (Eq. (2)).

The homodesmotic reaction energy ΔE for Eq. (1) was found to be 4.4 kcal/mol, very far from the value obtained for benzene (21.2 kcal/mol) calculated from experimental heats of formation at 0 K [25]. On the other hand, the ΔE value obtained for germanazene is very close to that calculated at the MP4SDQ level for $Al_2N_3H_6$ analogue (1.9 kcal/mol) [25], which is on the antiaromatic side of the scale. Therefore, if there is any aromaticity in the $(GeN–R)_n$, it is on a very low scale.

After the study of the dimers and trimers $(GeN–R)_n$, we turned our attention towards the GeN–R monomers, postulated in the formation of germanazenes [11], in the hope of finding a clue explaining the easy formation and stabilization of these germanazenes (see Fig. 8).

The optimized geometrical parameters of the monomers for the singlet and triplet states are listed in Table 3. The singlet states are always more stable than the triplet states. The singlet–triplet energy gaps in GeN–R with R = H, Me, CN, Ph are 58.5, 52.9, 45.6 and 41.9 kcal/mol, respectively. All the singlet states adopt a linear conformation with germanium-nitrogen bond lengths corresponding to a double bond: :Ge=N–R. By contrast, the triplet states, for which there is no possible conjugation with the substituents on nitrogen (R = H, Me), are bent with an angle close to 140°, in the range of the angles around nitrogen in $(GeN–R)_3$ (110–140°, see Table 2). When a conjugation between the nitrogen and the substituents is possible (R = CN, Ph), the germanium-nitrogen bond lengths increase and the N–C bond lengths shorten indicating some degree of double bonding between nitrogen and its

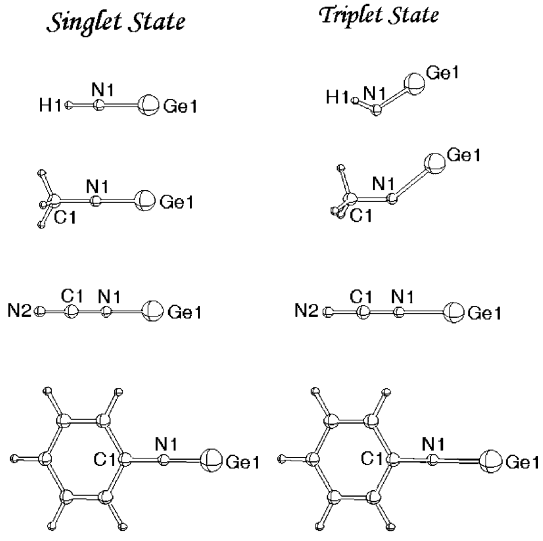


Fig. 8. DFT/B3LYP-optimized geometries of the singlet and triplet states of the GeN–R fragment with R = H, Me, CN, Ph.

Table 3
Selected geometrical parameters (Å and °) for the Ge–N–R monomers[a] with R = H, Me, CN, Ph, optimized at the DFT/B3LYP level

Geometrical parameters	GeN–H	GeN–CH_3	GeN–CN	GeN–C_6H_5
Singlet state				
Ge1–N1	1.686	1.693	1.717	1.705
N1–X	1.017	1.427	1.301	1.375
Ge1–N1–X	180.0	180.0	180.0	180.0
Triplet state				
Ge1–N1	1.881	1.882	1.917	1.845
N1–X	1.033	1.420	1.236	1.301
Ge1–N1–X	134.9	139.9	180.0	180.0

X represents the atom directly linked to N1.
[a] See Fig. 8 for labeling of the atoms.

substituent. Then, GeN–Ph and GeN—C≡N are linear. The spin density analysis in the triplet states indicates, without ambiguity, that germanium is the bearer of a single electron. The density values are 1.03, 1.00, 0.95 and 0.92 for R = H, Me, CN, Ph, respectively. In the first two cases (R = H, Me), nitrogen bears the other single electron, the spin density at nitrogen being 0.98 and 0.93, respectively. For the last two cases (R = CN, Ph), there is a delocalization of that single electron on to the substituent on nitrogen, confirming some degree of conjugation. The spin density is only 0.53 and 0.43, respectively, for the nitrogen directly linked to germanium. Note than in the case of :Ge=N–C≡N, the terminal nitrogen displays a spin density of 0.73.

In the case of the GeN–H and GeN–Me triplet states, both the bent geometry and the NBO natural charges on germanium and nitrogen (Table 4) explain that approaching two monomers (Fig. 9) would lead to a stable molecule.

Table 5 gives the free energies of formation of $(GeN–R)_n$ from triplet state monomers. The calculated values are in good agreement with the measured heat of formation for a Ge–N bond (60–70 kcal/mol) [1,3].

Table 4
NBO natural charges for GeN–R species (R = H, Me, CN, Ph) in their triplet state

Atom	GeN–H	GeN–CH_3	GeN–CN	GeN–C_6H_5
Ge	+0.51	+0.47	+0.67	+0.52
N	−0.85	−0.68	−0.86	−0.85

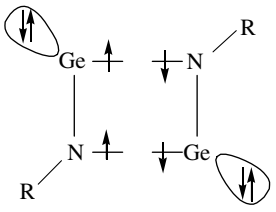


Fig. 9. Schematic illustration for the formation of $(GeN–R)_2$ from two GeN–R fragments in their triplet state.

Table 5
Free energies ($\Delta_f G$) for the formation of $(GeN–R)_n$, with R = H, Me, CN, Ph and $n = 2, 3$, from triplet state monomers

$\Delta_f G$ (kcal/mol)	$(GeN–R)_2$	$(GeN–R)_3$
GeN–H	−154.5	−255.3
GeN–CH_3	−132.6	−208.7
GeN–CN	−124.2	−188.4
GeN–C_6H_5	−106.5	−163.0

However, the values for the free energy of formation for $(GeN–Ph)_3$ and $(GeN—C≡N)_3$ are apparently smaller than for $(GeN–H)_3$ and $(GeN–Me)_3$. That can be easily explained by the fact that the more stable triplet states for monomers GeN–Ph and GeN—C≡N are linear. Such a geometry does not favor the formation of the germanazene ring. To obtain $(GeN–Ph)_3$, it is necessary to destroy the conjugation between the lone pair on nitrogen and the phenyl group in order to reach the bent structure which could lead to cyclization into germanazene. Of course the energy consumed is easily compensated by the system reaching trimerization. Therefore, we calculated the energy of the monomer (GeN–Ph) in the triplet state, but in the bent geometry suitable for the germanazene formation. The difference of energy between linear and bent triplet state for GeN–Ph is calculated to be 14.3 kcal/mol. Therefore, the free energy of formation of $(GeN–Ph)_3$ is of the same order ($3 \times 14.3 + 163 = 205.9$ kcal/mol) as the free energy calculated for $(GeN–Me)_3$ (208.7 kcal/mol, see Table 5).

In the cyclogermanazene $(GeN–Ph)_3$, the single electron on nitrogen in the triplet state is now involved in the σ bond with germanium and therefore the aromatic ring can rotate and take the position required by its stericity (see Fig. 4).

Finally, we briefly come back to the germanazene ring with R = CN. In the case of $Ge^{0.95}$=$N^{0.53}$—C≡$N^{0.73}$, the spin density, maximum (0.73) on the terminal nitrogen, explains the difficulty of formation of $(Ge–N–C≡N)_3$ and why when trying the synthesis of *N*-cyanamide compounds, we always obtain the

carbodiimide forms (—Ge—N═C═N—)$_n$ [7,12]. Fig. 10 gives the B3LYP optimized geometries for the carbodiimide forms for $n=2$, 3 and some selected geometrical parameters are listed in Table 6. The dimer is planar, but the trimer allows a non-planar conformation.

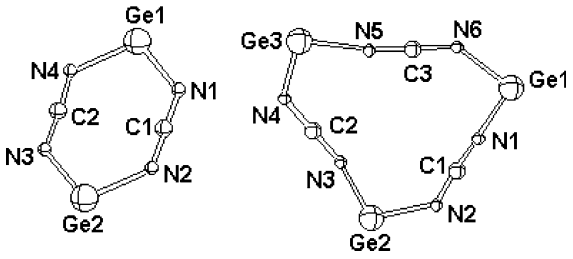


Fig. 10. DFT/B3LYP-optimized geometries of (Ge—N═C═N—)$_n$ with $n=2$, 3.

Table 6
Selected geometrical parameters (Å and °) for the (Ge—N═C═N—)$_n$ carbodiimide cyclic dimers and trimers[a] optimized at the DFT/B3LYP level

$n=2$		$n=3$	
Ge1–N1	1.930	Ge1–N1	1.910
Ge1–N4	1.929	Ge1–N6	1.892
		Ge2–N2	1.889
		Ge2–N3	1.910
		Ge3–N4	1.896
		Ge3–N5	1.909
N1–C1	1.233	N1–C1	1.212
N2–C1	1.234	N2–C1	1.240
		N3–C2	1.212
		N4–C2	1.243
		N5–C3	1.212
		N6–C3	1.240
Ge1–N1–C1	128.8	Ge1–N1–C1	180.0
Ge2–N2–C1	128.0	Ge1–N6–C3	134.1
		Ge2–N2–C1	133.1
		Ge2–N3–C2	166.6
		Ge3–N4–C2	127.7
		Ge3–N5–C3	170.3
N1–Ge1–N4	100.9	N1–Ge1–N6	99.6
		N2–Ge2–N3	98.3
		N4–Ge3–N5	99.2
N1–C1–N2	177.7	N1–C1–N2	176.6
		N3–C2–N4	179.3
		N5–C3–N6	177.9
Ge1–N1–C1–N2	1.4	Ge1–N1–C1–N2	155.2
		Ge1–N6–C3–N5	−173.3
		Ge2–N2–C1–N1	−166.2
		Ge2–N3–C2–N4	11.8
		Ge3–N4–C2–N3	174.0
		Ge3–N5–C3–N6	−5.1

[a] See Fig. 10 for labeling of the atoms.

The carbodiimide form is always more stable than the *N*-cyanamide, by 13.8 kcal/mol ($n=2$) and 28.2 kcal/mol ($n=3$). Note that we also found non planar rings for the X-ray structures of (Mes$_2$GeN═C═N)$_n$ ($n=3$, 4) [5] and that our previous calculations showed that the carbodiimide form was always more stable than the cyanamide form in linear polymers [12].

4. Conclusion

In this work, we have investigated some germanazene rings with different substituents on nitrogens. Our computational results have shown that except for the hypothetical molecule (GeN–H)$_2$, the fully optimized structures consist of planar four- or six-membered rings of alternating germanium and nitrogen atoms. Where available, the DFT/B3LYP calculated geometrical parameters are in good agreement with the experimental values obtained by X-ray crystallography. The planar conformation adopted by the molecules indicates that some degree of delocalization could be present in the (Ge$_{II}$N)$_n$ ring system. The stabilization energy due to this delocalization process is estimated using the concept of homodesmotic reaction. The value calculated for the (GeN–H)$_3$ germanazene (4.4 kcal/mol) indicates very little or no aromatic character in the molecule. No other argument in favor of a significant aromaticity of the germanazene ring can be put forward.

When R = —C≡N, the carbodiimide isomer (Ge–N═C═N)$_n$ is more stable than the nitrile form (GeN–CN)$_n$ in concordance with the experimental results.

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