

# In search of triplet ground state GeCNX germylenes (X = H, F, Cl, and Br): An ab initio and DFT study

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Received 31 May 2005; received in revised form 11 July 2005; accepted 12 July 2005

Available online 19 September 2005

## Abstract

Singlet–triplet energy splittings for 24 GeCNX germylenic reactive intermediates are compared and contrasted at 10 levels of theory: B1LYP/6-311++G\*\*, B3LYP/6-311++G\*\*, MP3/6-311+G\*, MP3/LANL2DZ, MP2/6-311++G\*\*, MP4(SDTQ)/6-311++G\*\*, QCISD(T)/6-311++G\*\*, CCSD(T)/6-311++G\*\*, G1 and G2 (where X = H, F, Cl, and Br). Singlet (s) and/or triplet (t) GeCNX, are confined to the following three structures: 3-X-2-aza-1-germylacyclopropenylidene ( $1_{s-X}$ ,  $1_{t-X}$ ), [(X-imino)methylene]germylene ( $2_{s-X}$ ,  $2_{t-X}$ ), or X-cyanogermylene ( $3_{s-X}$ ,  $3_{t-X}$ ). For every of these three structures the order of singlet–triplet energy separations ( $\Delta E_{s-t,X}$ ), appears as a function of electro-negativity (F > Cl > Br > H). Fascinatingly, two triplet structures  $2_{t-H}$  and  $3_{t-H}$  appear more stable than their corresponding singlet states. Good linear correlations are found between the LUMO–HOMO energy gaps of the singlet germylenes, and their corresponding singlet–triplet energy separations, calculated at B3LYP/6-311++G\*\*. Relative energies of the divalent  $3_{s-X}$  and/or  $3_{t-X}$  structures are plotted as a function of the divalent bond angle  $\angle X\text{-Ge-CN}$ , where the singlet and triplet germylenes GeCNH cross at 134°. Little germanium *d* orbital valence participation is found in the cyclic triplet structures  $1_{t-X}$ . The global minimum, among six GeCNH species, appears to be the singlet cyclic  $1_{s-H}$ . However, the global minima among the other eighteen GeCNX (X≠H) species appear to be the singlet acyclic  $3_{s-X}$ . Among all the calculation methods employed, B3LYP appears as the method of choice.

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**Keywords:** Germylene; Triplet germylene; LUMO; HOMO; GeCNH; GeCNF; GeCNCl; GeCNBr; 3-X-2-aza-1-germylacyclopropenylidene; [(X-imino)methylene]germylene; X-cyanogermylene; Ab initio; DFT

## 1. Introduction

Carbenes are popular intermediates in many organic reactions [1]. However, little is known about these highly reactive species, since their direct spectroscopic observation has not yet proven to be generally accessible [2]. One of the most interesting organic species found in the space is  $C_3H_2$ . It has become the topic of a large number of theoretical researches [3–13]. This is in part

due to the economy of the theoretical work with the small molecules. Two  $C_3H_2$  isomers which are detected in the interstellar medium appear as unsaturated carbenes, including singlet cyclopropenylidene and singlet vinylidene carbene [3]. The former is prepared in the laboratory [4]. The later is isolated in matrices as well as in the gas phase [5,6]. Theoretical studies have shown singlet cyclopropenylidene to be the global minimum on the  $C_3H_2$  surface. Hence, it is more stable than triplet propargylene and singlet vinylidene carbene by about 9 and 14 kcal/mol, respectively. Moreover, singlet cyclopropenylidene is predicted to be 28 kcal/mol more stable than triplet cyclopropenylidene [4]. Both carbenic singlet cyclopropenylidene electrons are predicted to occupy

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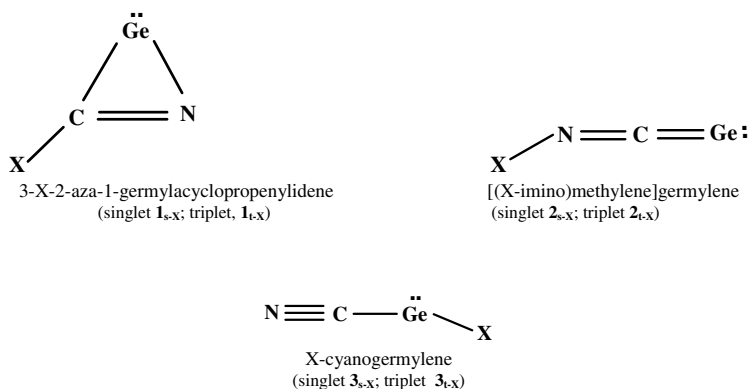


Fig. 1. The three most significant structures considered for singlet (s) and triplet (t) germylenic GeCNX (**1**, **2** and **3**), where X = H, F, Cl, and Br.

the system ( $\sigma^2$ ) in its ground state [9]. Recently, many workers have addressed interesting questions of how the presence of substituents affect the relative stabilities of different  $\text{C}_3\text{H}_2$  isomers. We have already reported how halogens, electron donating, electron withdrawing and/or sterically hindered substituents affect the relative stabilities of different  $\text{C}_3\text{H}_2$  [4,14–16]. Moreover, very recently the query that how the replacement of divalent carbon atom with heavier group 14 elements (Si and Ge) influence the stability and multiplicity of these small species have been reported [17,18]. Finally, the problem of how the replacement of the attached atom to divalent center influence the stability and multiplicity of these small species have been investigated [19–21]. Up to date no attempt is made to account for the effects of halogens on the GeCNH derivatives. Here, we report the results of our theoretical investigation on the singlet (s) and triplet (t) structures of 24 different germylenes of the formula GeCNX (Fig. 1).

## 2. Computational methods

All calculations, in this paper are performed with the GAUSSIAN 98 program package [22]. The fully optimized geometries and energetics are reported for the singlet and triplet GeCNH germylenes as well as their monohalogenated analogues: GeCNF, GeCNCl and GeCNBr. Three skeletal arrangements are employed: 3-X-2-aza-1-germylacyclopropenylidene **1**, [(X-imino)methylene]germylene **2**, and X-cyanogermylene **3**. Standard quantum chemical ab initio and DFT methods used are: B1LYP, B3LYP, MP2, MP3, MP4(SDTQ), QCISD(T), CCSD(T), G1 and G2 levels of theory. For DFT calculations the Beck's hybrid one-parameter and three-parameter functional using the Lee–Yang–Parr correlation including both local and non-local terms as implemented by Adamo and Barone [23,24] with the 6-311++G\*\* basis set are employed. For the second-order Møller–Plesset (MP2) method the 6-

311++G\*\* basis set is used [25]. While, for the third-order Møller–Plesset (MP3) method the 6-311+G\* basis set is employed [26]. The LANL2DZ basis set is also employed for MP3 calculations owing to comparison with the other employed basis sets [27]. In order to improve the energetic forecasts, the MP2/6-311++G\*\* optimized geometries are inputted for single-point calculations at the fourth-order MP(MP4), QCISD(T) and CCSD(T) levels with 6-311++G\*\* basis sets [28–31]. In addition, due to the size of the molecules, higher-level calculations including G1 [32,33] and G2 [34] are carried out, using MP2/6-311++G\*\* optimized geometries. Singlet states are calculated with spin-restricted wave function. Triplet states are calculated using the UMP or UBLYP formalism. To predict the singlet–triplet energy differences more reliably, the spin projected wave functions are employed for triplet states. The harmonic vibrational frequencies and zero point energies (ZPE) for the 24 germylenic species are calculated, for B3LYP optimized structures, at the same level of theory used for their optimization. The vibrational frequencies and ZPE data at the B3LYP are scaled by 0.98 [35,36]. For minimum state structures, only real frequency values (with a positive sign), and for the transition states, only a single imaginary frequency value (with a negative sign) are accepted. The NBO population analysis are accomplished at the B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels [37,38].

## 3. Results and discussion

This section starts with an overview of all the results, followed by their discussion. The singlet (s) and triplet (t) states of GeCNX germylenes: 3-X-2-aza-1-germylacyclopropenylidene (**1**), [(X-imino)methylene]germylene (**2**) and X-cyanogermylene (**3**) are compared and contrasted at: B1LYP/6-311++G\*\*, B3LYP/6-311++G\*\*, MP3/6-311+G\*, MP3/LANL2DZ, MP2/6-311++G\*\*, MP4(SDTQ)/6-311++G\*\*, QCISD(T)/6-311++G\*\*, and CCSD(T)/6-311++G\*\*.

CCSD(T)/6-311++G\*\*, G1 and G2 levels of theory, for X = H, F, Cl and Br (Fig. 1, Table 1). Relative energies of 1–3 are calculated with the every minima set at 0.00 kcal/mol (Table 1). Optimized geometrical parameters of 1 through 3 are reported, using MP2/6-311++G\*\* and B3LYP/6-311++G\*\* levels of theory; where bond lengths are given in angstrom and bond angles in degrees (shown in *italics*, Fig. 2). All optimizations are performed with no imposed constraints, making the starting structures free to transform through optimizations (Fig. 2). For the sake of brevity, geometrical parameters, optimized through methods other than B3LYP/6-311++G\*\* and MP2/6-311++G\*\* are omitted from Fig. 2. Vibrational zero point energy (ZPE) and dipole moments for all 24 germylenic species are calculated at B3LYP/6-311++G\*\* (Tables 1 and 2, respectively). NBO analyses are carried out on atomic charges and bond orders at B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels of theory (Table 3).

In order to study the electronic effects of substituents (X) on the divalent centers, atomic charges on Ge atoms vs. Swain and Lupton constants [39] are plotted for germylenic structures 1–3 (Fig. 3). Harmonic vibrational frequencies are calculated on optimized structures at B3LYP level. This calculation assists to estimate the zero-point vibrational energy (ZPE) correction, and allows assessing the nature of stationary points on their potential energy surfaces. Force constant calculations show that only singlet  $3_{s-H}$  and triplet  $2_{t-Br}$  each has one imaginary frequency and exist as a transition state. To save space, computed harmonic frequencies are omitted but are available upon request.

The energies of HOMO and LUMO orbitals are attained through NBO analyses (at B3LYP level) for both singlet and triplet isomers of GeCNX. Linear correlations are found between the LUMO–HOMO energy gaps of the singlet GeCNX germylenes and their corresponding singlet–triplet energy separations,  $E(s) - E(t)$ , for X = H, F, Cl, and Br (Fig. 4). Evidently, halogens increase the magnitude of LUMO–HOMO energy gaps, in the three germylenic structures 1–3. The magnitude of LUMO–HOMO energy gaps in every 1–3, as a function of substituents X follows the electro-negativity (F > Cl > Br > H). As expected, the highest effect of halogens to increase the magnitude of LUMO–HOMO energy gaps is encountered in the singlet cyanogermylene ( $3_{s-X}$ ) where halogens are directly bonded to the germylenic center (Fig. 1). The linearity trend is:  $3_{s-X}$  ( $R^2 = 0.99$ ) >  $2_{s-X}$  ( $R^2 = 0.98$ ) >  $1_{s-X}$  ( $R^2 = 0.88$ ), where  $R^2$  = correlation coefficient. Three linear curves obtained have the negative slopes. The trend of curve slopes is:  $2_{s-X}$  ( $m = -1.26$ ) >  $1_{s-X}$  ( $m = -0.92$ ) >  $3_{s-X}$  ( $m = -0.78$ ), where  $m$  = slope. One of the significant parameters affecting the  $\Delta E_{s-t}$  and determining the ground state of divalent carbene like species is the magnitude of the divalent bond angle [40]. Therefore, bend-

ing potential energy curves for divalent  $3_{s-X}$  and  $3_{t-X}$  structures are calculated at B3LYP/6-311++G\*\* (Fig. 5). The singlet state  $3_{s-H}$  and triplet state  $3_{t-H}$  cross at the  $\angle HGeC$  divalent angle about  $134^\circ$ . Interestingly, such singlet–triplet cross-points are not found when the hydrogen is replaced by the halogens. Again, this finding indicates the stabilization of the singlet ground states germylenes due to the electro-negativity suggested by Gasspar [40].

Inspection of Table 1 and Fig. 2 reveal some interesting points. First, calculated energetic as well as geometrical parameter results are very dependent on the computational methods and the basis sets employed. However, in the case of Cl-substituted germylenes, GeCNCl, a better consistency is found among different levels employed (Table 1). Second, the energy results obtained at MP3/LANL2DZ are more remote from the results of other calculation methods. Third, the relative energies, calculated at QCISD (T) and CCSD (T) levels, are quite similar to each other, while they appear somewhat different from those of MP4. These differences are more pronounced for triplet species, may be due to the spin-contamination problem which is encountered for MP4(SDTQ) calculations [41,42]. Fourth, the results of higher levels G1 and G2 are rather different from those of MP4(SDTQ), QCISD(T) and/or CCSD(T). Hence, to check the levels of confidence on our results, methods and basis sets, relative energies of the singlet and triplet states of three typical divalent molecules CH<sub>2</sub>, SiH<sub>2</sub> and GeH<sub>2</sub> are calculated at 16 levels including our 10 employed levels (Table 4). Subsequently, the above results are compared and contrasted to the reported CASSCF calculated values for divalent CH<sub>2</sub>, SiH<sub>2</sub> and GeH<sub>2</sub>, which are 10, 20 and 23–24 kcal/mol, respectively [43]. Interestingly, the closest results to the above expensive CASSCF computations are those of B3LYP/6-311++G\*\* (12, 20 and 27 kcal/mol, respectively Table 4). Also, B3LYP appears quite reliable for computing geometrical parameters [17–21,42]. Hence, in the reminder of this discussion, B3LYP/6-311++G\*\* data are preferred over those of other calculation methods.

Considering the above results, two key concerns are discussed below; energetics and the structural properties.

### 3.1. Energetics

#### 3.1.1. Singlet–triplet energy gaps

We begin with the scrutiny of cyclic germylenes. Singlet 3-X-2-aza-gemilacyclopropenylidenes,  $1_{s-X}$ , appear more stable than their corresponding triplet states,  $1_{t-X}$ , due to the angle-strains involved in the latter and the aromatic character anticipated for the former (Table 1). This result is consistent with those reported for analogous carbenic and silylenic singlet and triplet states [14,17]. The B3LYP/6-311++G\*\* calculated order of

Table 1

Comparison of relative energies (kcal/mol) of singlet states of germylenic GeCNX, including  $1_{s-X}$ ,  $2_{s-X}$  and  $3_{s-X}$  as well as their corresponding triplet states  $1_{t-X}$ ,  $2_{t-X}$  and  $3_{t-X}$ , calculated at various levels of theory

Structure	Relative energies (kcal/mol)										VZPE (kcal/mol)
	<sup>a</sup> MP3/ 6-311+G*	<sup>a</sup> MP3/ LanL2DZ	B1LYP/ 6-311++G**	B3LYP/ 6-311++G**	<sup>a</sup> MP2/ 6-311++G**	<sup>a</sup> MP4(SDTQ)/ 6-311++G**	<sup>a</sup> QCISD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ 6-311++G**	<sup>a</sup> G1	<sup>a</sup> G2	
<sup>b</sup> 1 <sub>s-H</sub>	8.44	1.30	0.00 <sup>3</sup>	0.00 <sup>4</sup>	0.00 <sup>5</sup>	0.00 <sup>6</sup>	0.00 <sup>7</sup>	0.00 <sup>8</sup>	10.51	10.53	10.92
<sup>b</sup> 1 <sub>t-H</sub>	20.67	0.00 <sup>2</sup>	23.92	24.56	14.98	14.99	13.67	13.68	32.20	30.80	9.93
2 <sub>s-H</sub>	28.65	10.45	17.23	17.23	23.27	19.71	18.50	18.55	29.81	29.05	10.25
2 <sub>t-H</sub>	23.03	1.65	10.80	11.10	18.00	16.76	14.85	14.96	30.22	28.75	10.03
<sup>b</sup> 3 <sub>s-H</sub>	0.00 <sup>1</sup>	14.54	19.29	76.50	18.40	16.66	16.59	16.65	0.00 <sup>9</sup>	0.00 <sup>10</sup>	8.25
3 <sub>t-H</sub>	30.00	10.71	26.37	27.47	22.10	23.08	20.57	20.63	33.25	32.83	8.40
<sup>b</sup> 1 <sub>s-F</sub>	0.00 <sup>11</sup>	12.38	42.47	41.57	0.00 <sup>15</sup>	0.00 <sup>16</sup>	0.00 <sup>17</sup>	0.00 <sup>18</sup>	0.00 <sup>19</sup>	0.00 <sup>20</sup>	6.60
1 <sub>t-F</sub>	73.29	45.65	79.67	79.30	78.59	78.87	75.60	75.54	145.88	145.66	5.89
2 <sub>s-F</sub>	64.41	51.92	102.39	100.49	68.03	60.72	59.74	60.31	62.15	61.92	5.18
2 <sub>t-F</sub>	81.51	48.42	109.27	110.39	90.35	83.98	78.37	78.72	83.32	81.99	4.75
<sup>b</sup> 3 <sub>s-F</sub>	98.70	89.92	0.00 <sup>13</sup>	0.00 <sup>14</sup>	97.27	92.13	75.25	72.15	76.03	77.31	5.60
<sup>b</sup> 3 <sub>t-F</sub>	12.91	0.00 <sup>12</sup>	58.79	58.99	10.40	13.72	12.09	12.24	99.01	98.67	5.72
1 <sub>s-Cl</sub>	45.43	58.62	44.84	43.83	43.80	43.88	44.34	44.31	44.35	44.79	5.68
1 <sub>t-Cl</sub>	74.88	87.86	76.88	76.46	80.57	80.10	79.46	79.44	85.83	–	5.04
2 <sub>s-Cl</sub>	91.50	79.62	83.26	81.40	92.46	84.71	82.94	83.44	86.01	86.35	4.84
2 <sub>t-Cl</sub>	100.37	118.48	81.88	83.25	91.91	88.49	85.64	85.52	91.71	90.57	4.59
<sup>b</sup> 3 <sub>s-Cl</sub>	0.00 <sup>21</sup>	0.00 <sup>22</sup>	0.00 <sup>23</sup>	0.00 <sup>24</sup>	0.00 <sup>25</sup>	0.00 <sup>26</sup>	0.00 <sup>27</sup>	0.00 <sup>28</sup>	0.00 <sup>29</sup>	0.00 <sup>30</sup>	5.22
3 <sub>t-Cl</sub>	48.12	47.27	51.33	51.60	49.04	50.89	48.39	48.43	51.22	50.57	5.32
<sup>b</sup> 1 <sub>s-Br</sub>	–	9.94	0.00 <sup>33</sup>	44.85	0.00 <sup>35</sup>	0.00 <sup>36</sup>	0.00 <sup>37</sup>	0.00 <sup>38</sup>	0.00 <sup>39</sup>	0.00 <sup>40</sup>	5.34
1 <sub>t-Br</sub>	–	36.99	30.63	76.00	35.75	35.11	33.94	33.94	–	–	4.63
2 <sub>s-Br</sub>	–	23.85	30.46	74.59	38.36	30.24	27.90	28.35	31.45	31.31	4.76
2 <sub>t-Br</sub>	–	13.77	27.23	74.55	51.79	48.06	45.25	45.45	35.23	–	4.48
<sup>b</sup> 3 <sub>s-Br</sub>	–	74.23	69.21	0.00 <sup>34</sup>	71.13	67.65	63.59	63.46	61.50	61.15	5.03
<sup>b</sup> 3 <sub>t-Br</sub>	–	0.00 <sup>32</sup>	2.70	48.82	1.83	3.35	0.10	0.16	4.14	3.06	5.14

The vibrational zero point energies, VZPE (kcal/mol) are calculated at B3LYP/6-311++G\*\* (X = H, F, Cl and Br).

<sup>a</sup> ZPE not included.

<sup>b</sup> The lowest energy minimum is set at 0.00 kcal/mol; the original total energies (hartrees), corresponding to the lowest energy minima, at various levels of theory are: (1) –2168.571419, (2) –96.6607637, (3) –2170.360984, (4) –2170.43007, (5) –2168.560733, (6) –2168.599575, (7) –2168.596992, (8) –2168.596325, (9) –2168.702937, (10) –2168.706128, (11) –2267.643706, (12) –195.6385209, (13) –2269.69071, (14) –2269.775622, (15) –2267.648202, (16) –2267.689853, (17) –2267.684564, (18) –2267.683254, (19) –2267.852183, (20) –2267.854777, (21) –2627.709066, (22) –110.9072652, (23) –2630.055186, (24) –2630.134741, (25) –2627.698231, (26) –2627.747871, (27) –2627.744474, (28) –2627.74376, (29) –2627.920999, (30) –2627.842021, (31) none, (32) –109.0496471, (33) –4743.900958, (34) –4744.058728, (35) –4740.477224, (36) –4740.524889, (37) –4740.520572, (38) –4740.519635, (39) –4740.67726, (40) –4740.686663.

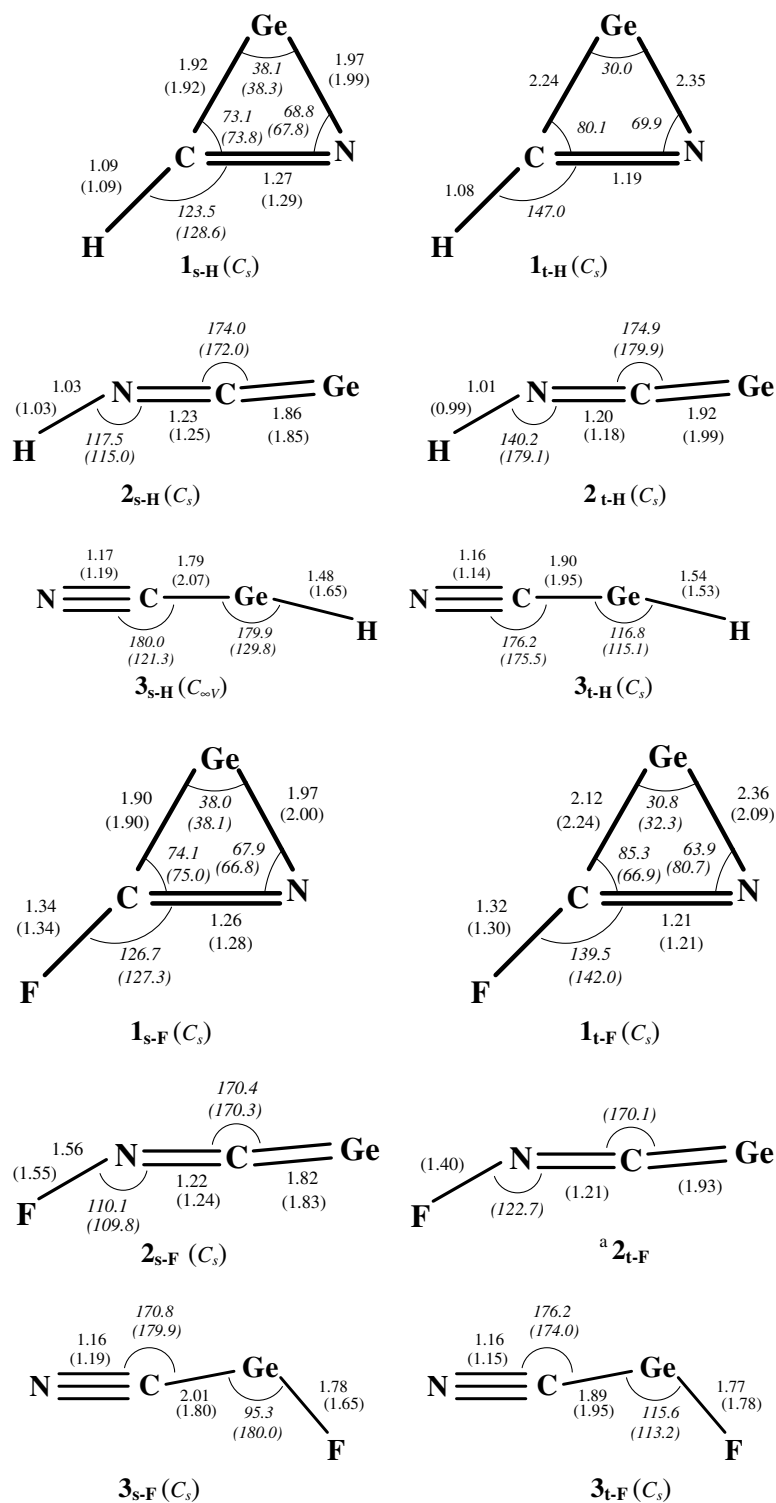


Fig. 2. Geometrical parameters of germylenic GeCNX (X = H, F, Cl, and Br) with bond lengths (Å) and bond angles (°) optimized at B3LYP/6-311++G\*\* and MP2/6-311++G\*\* (in parentheses), along the B3LYP/6-311++G\*\* point groups. (<sup>a</sup> B3LYP optimized geometries ruptured, <sup>b</sup> Both B3LYP and MP2 optimized geometries ruptured.)

singlet–triplet energy gaps ( $\Delta E_{s-t,X}$ ), between **1<sub>s-X</sub>** and **1<sub>t-X</sub>** is:  $\Delta E_{s-t,F}$  (37.73 kcal/mol) >  $\Delta E_{s-t,Cl}$  (32.63 kcal/mol) >  $\Delta E_{s-t,Br}$  (31.15 kcal/mol) >  $\Delta E_{s-t,H}$  (24.56 kcal/mol). Halogens appear to increase the stability of singlet

states, and the magnitude of this stabilization follows the electro-negativity (F > Cl > Br > H). There is a noticeable contrast between  $\Delta E_{s-t,H}$  (24.56 kcal/mol), and  $\Delta E_{s-t,X}$  (31.15–37.73 kcal/mol), with X = F, Cl

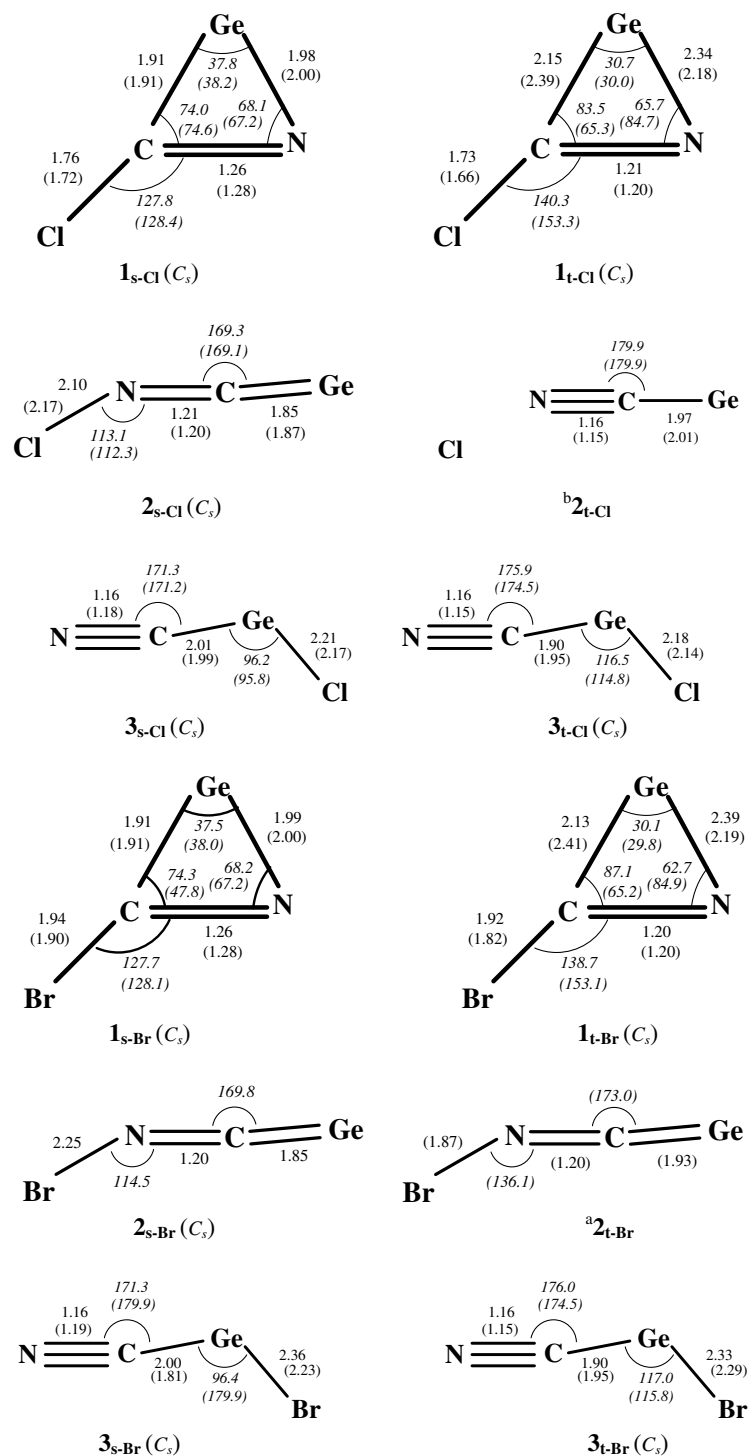


Fig. 2 (continued)

Table 2

B3LYP/6-311++G\*\* calculated dipole moments (Debye) of singlet (s) and triplet (t) states of GeCNX grmylenes in their three structures 1–3 (where X = H, F, Cl and Br)

Structure/dipole moment (D)													
Singlet states (s)	1 <sub>s</sub> -H	1 <sub>s</sub> -F	1 <sub>s</sub> -Cl	1 <sub>s</sub> -Br	2 <sub>s</sub> -H	2 <sub>s</sub> -F	2 <sub>s</sub> -Cl	2 <sub>s</sub> -Br	3 <sub>s</sub> -H	3 <sub>s</sub> -F	3 <sub>s</sub> -Cl	3 <sub>s</sub> -Br	
		2.05	1.32	4.36	3.29	5.68	3.94	3.11	6.67	3.71	3.23	6.36	3.64
Triplet states (t)	1 <sub>t</sub> -H	1 <sub>t</sub> -F	1 <sub>t</sub> -Cl	1 <sub>t</sub> -Br	2 <sub>t</sub> -H	2 <sub>t</sub> -F	2 <sub>t</sub> -Cl	2 <sub>t</sub> -Br	3 <sub>t</sub> -H	3 <sub>t</sub> -F	3 <sub>t</sub> -Cl	3 <sub>t</sub> -Br	
		2.32	2.19	3.88	1.76	5.92	3.11	1.70	5.78	3.12	1.89	5.63	3.28

Table 3

NBO analyses including atomic charges and bond orders of GeCNX (X = H, F, Cl and Br) germylenes confined to three structures, **1–3**, calculated at B3LYP/6-311++G\*\* (first row) and MP2/6-311++G\*\* (second row)

Structure	Species	Atomic charge				Bond order				
		Ge	C	N	X	Ge–C	Ge–N	C–N	C–X	
<b>1</b>	<b>1<sub>s</sub>-H</b>	0.78	–0.33	–0.63	0.19	1.02	1.04	1.82	0.95	
		0.88	–0.36	–0.70	0.18	–	–	–	–	
	<b>1<sub>t</sub>-H</b>	–0.61	–0.12	–0.36	0.09	–	–	–	–	
		–0.02	0.23	–0.44	0.23	0.03	0.33	2.29	0.92	
	<b>1<sub>s</sub>-F</b>	0.87	0.16	–0.69	–0.34	0.92	0.97	1.76	0.87	
		0.98	0.18	–0.76	–0.40	–	–	–	–	
	<b>1<sub>t</sub>-F</b>	0.43	0.32	–0.44	–0.30	0.71	0.58	2.06	0.90	
		0.54	0.51	–0.70	–0.35	0.43	0.64	1.87	0.80	
	<b>1<sub>s</sub>-Cl</b>	0.91	–0.28	–0.64	0.01	–	–	–	–	
		1.01	–0.30	–0.71	0.00	–	–	–	–	
	<b>1<sub>t</sub>-Cl</b>	0.46	–0.13	–0.40	0.08	0.70	0.58	2.13	1.23	
		0.36	0.08	–0.57	0.13	0.57	0.64	2.04	1.29	
	<b>1<sub>s</sub>-Br</b>	0.92	–0.34	–0.64	0.05	–	–	–	–	
		1.02	–0.38	–0.70	0.06	–	–	–	–	
	<b>1<sub>t</sub>-Br</b>	–0.38	–0.17	–0.42	–0.03	0.72	0.54	2.14	1.19	
		0.38	–0.02	–0.57	0.21	0.57	0.63	2.04	1.30	
	<b>2</b>	<b>2<sub>s</sub>-H</b>	0.51	–0.30	–0.57	0.36	1.65	1.87	0.82	
			0.55	–0.28	–0.64	0.37	1.57	1.76	0.80	
<b>2<sub>t</sub>-H</b>		–0.49	–0.22	–0.49	0.20	1.52	1.95	0.76		
		0.08	0.14	–0.69	0.47	1.17	1.79	0.64		
<b>2<sub>s</sub>-F</b>		0.87	–0.52	–0.01	–0.34	1.43	1.97	1.01		
		0.95	–0.56	0.00	–0.39	1.40	1.80	0.99		
<b>2<sub>t</sub>-F</b>		0.67	–0.28	–0.20	–0.19	0.99	2.38	0.51		
		–0.19	–0.38	–0.18	–0.24	1.06	1.81	1.08		
<b>2<sub>s</sub>-Cl</b>		0.87	–0.44	–0.24	–0.19	1.21	2.20	0.82		
		1.01	–0.50	–0.21	–0.30	1.14	2.08	0.82		
<b>2<sub>t</sub>-Cl</b>		–0.12	–0.12	–0.27	–0.49	0.99	2.41	0.33		
		0.67	–0.32	–0.34	0.00	–	–	–		
<b>2<sub>s</sub>-Br</b>		0.83	–0.42	–0.28	–0.13	1.13	2.29	0.70		
		0.99	–0.48	–0.24	–0.27	1.05	2.19	0.68		
<b>2<sub>t</sub>-Br</b>		0.66	–0.28	–0.31	–0.07	0.99	2.41	0.31		
		0.46	–0.11	–0.60	0.24	1.21	1.79	1.17		
<b>3</b>		<b>3<sub>s</sub>-H</b>	3.85	–2.61	–2.24	1.00	–	–	–	
			0.96	–0.28	–0.35	–0.33	–	–	–	
	<b>3<sub>t</sub>-H</b>	0.60	–0.21	–0.29	–0.10	1.06	2.47	1.04		
		0.70	–0.19	–0.34	–0.17	0.90	2.31	1.03		
	<b>3<sub>s</sub>-F</b>	1.24	–0.28	–0.30	–0.67	0.75	2.48	0.84		
		1.23	–0.34	–0.31	–0.58	1.57	2.34	0.83		
	<b>3<sub>t</sub>-F</b>	1.10	–0.24	–0.27	–0.59	1.13	2.50	0.92		
		–0.27	–0.06	–0.29	–0.39	0.93	2.36	0.74		
	<b>3<sub>s</sub>-Cl</b>	0.97	–0.24	–0.31	–0.42	0.77	2.47	1.04		
		1.10	–0.28	–0.32	–0.49	–	–	–		
	<b>3<sub>t</sub>-Cl</b>	0.78	–0.21	–0.27	–0.30	1.10	2.49	1.18		
		0.91	–0.20	–0.32	–0.39	0.92	2.34	1.03		
	<b>3<sub>s</sub>-Br</b>	0.89	–0.25	–0.30	–0.34	0.78	2.47	1.11		
		0.65	–0.24	–0.32	–0.09	1.41	2.35	1.33		
	<b>3<sub>t</sub>-Br</b>	–0.39	–0.13	–0.24	–0.24	1.07	2.48	1.25		
		0.82	–0.20	–0.32	–0.30	–	–	–		

and/or Br. In this context, variations between  $\Delta E_{s-t,X}$  with different halogens (X) is just 6.5 kcal/mol. This low energy difference is expected, since in cyclic **1<sub>s-X</sub>** and **1<sub>t-X</sub>** structures, halogens (X) are not directly attached to the divalent center (Fig. 1).

Between acyclic germylenes, **2** and **3**, the latter is more interesting due to the direct attachment of the halogens to the divalent center along with the presence of C≡N group (Fig. 1). As a result, structure **3** is more affected by halogen substitutions than either **1**

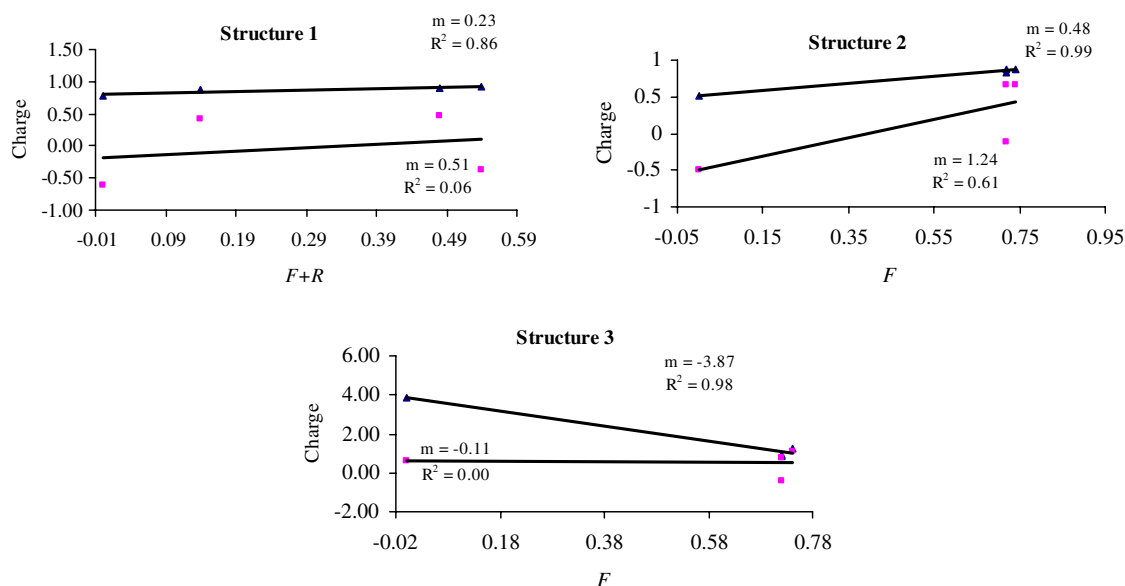


Fig. 3. Plots of atomic charge on the germylenic center vs. polar ( $F$ ), resonance ( $R$ ) as well as sum of polar and resonance effects ( $F+R$ ) (Swain and Lupton constants [39]), for singlet (▲) and triplet (■) states of germylenic  $\text{GeCNX}$ , 1–3, where  $X = \text{H, F, Cl}$  and  $\text{Br}$  (see Table 3). ( $R^2$  = correlation coefficient,  $m$  = slope).

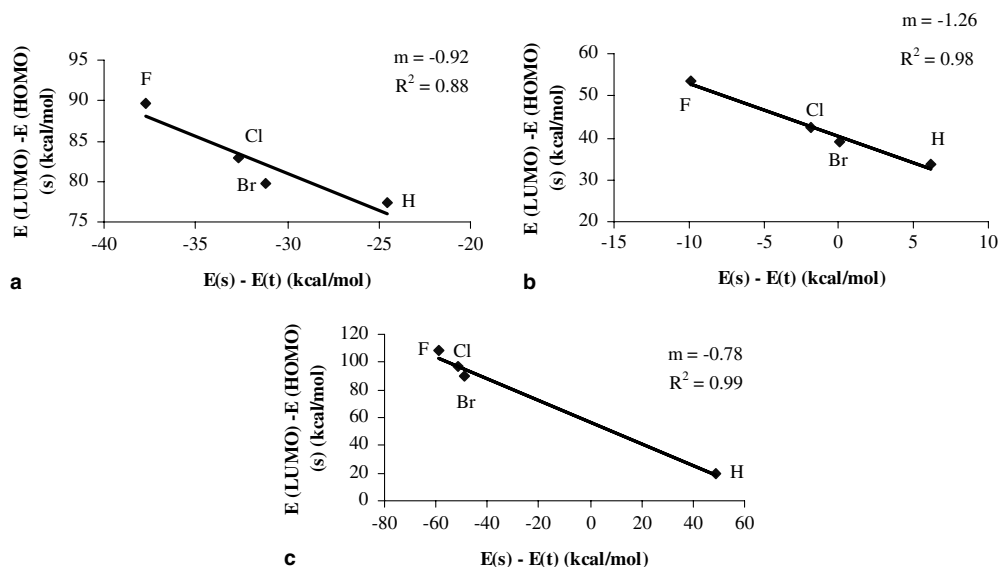


Fig. 4. Correlations between the LUMO–HOMO energy gaps (kcal/mol) of the singlet  $\text{GeCNX}$  germylenes, and their corresponding singlet–triplet energy separations,  $E(s) - E(t)$  (kcal/mol), for  $X = \text{H, F, Cl}$ , and  $\text{Br}$ , calculated at B3LYP/6-311++G\*\* ( $1_{s-X}$ ,  $1_{t-X}$ ;  $2_{s-X}$ ,  $2_{t-X}$  and  $3_{s-X}$ ,  $3_{t-X}$ ; diagrams a–c, respectively) ( $R^2$  = correlation coefficient,  $m$  = slope).

and/or **2**. While singlet states  $3_{s-X}$  appear more stable than their corresponding triplet  $3_{t-X}$ , for  $X = \text{F, Cl}$ , and  $\text{Br}$  (merely at B3LYP) (Table 1), B3LYP/6-311++G\*\* calculations indicate that the minimum triplet  $3_{t-H}$  structure is considerably (49 kcal/mol) more stable than its corresponding singlet transition state  $3_{s-H}$ . This is an interesting finding for those who are interested in the synthesis of the triplet ground state of heavier group 14 carbene-like species [40,43].

The B3LYP/6-311++G\*\* calculated order of  $\Delta E_{s-t,X}$ , between  $3_{s-X}$  and  $3_{t-X}$  follows the electro-negativity:  $\Delta E_{s-t,F}$  (58.99 kcal/mol) >  $\Delta E_{s-t,Cl}$  (51.60 kcal/mol) >  $\Delta E_{s-t,Br}$  (48.82 kcal/mol) (Table 1). Among all the 18 halogenated structures studied in this manuscript, the three singlet states of  $3_{s-X}$  have the lowest energy minima. This is in contrast to carbenes  $\text{C}_3\text{HX}$  and silylenes  $\text{C}_2\text{HSiX}$ , where the global minima are proved to be cyclic structures, which are analogous to  $1_{s-X}$  [14,17]. This clear contrast can be attributed to the nitrogen atom



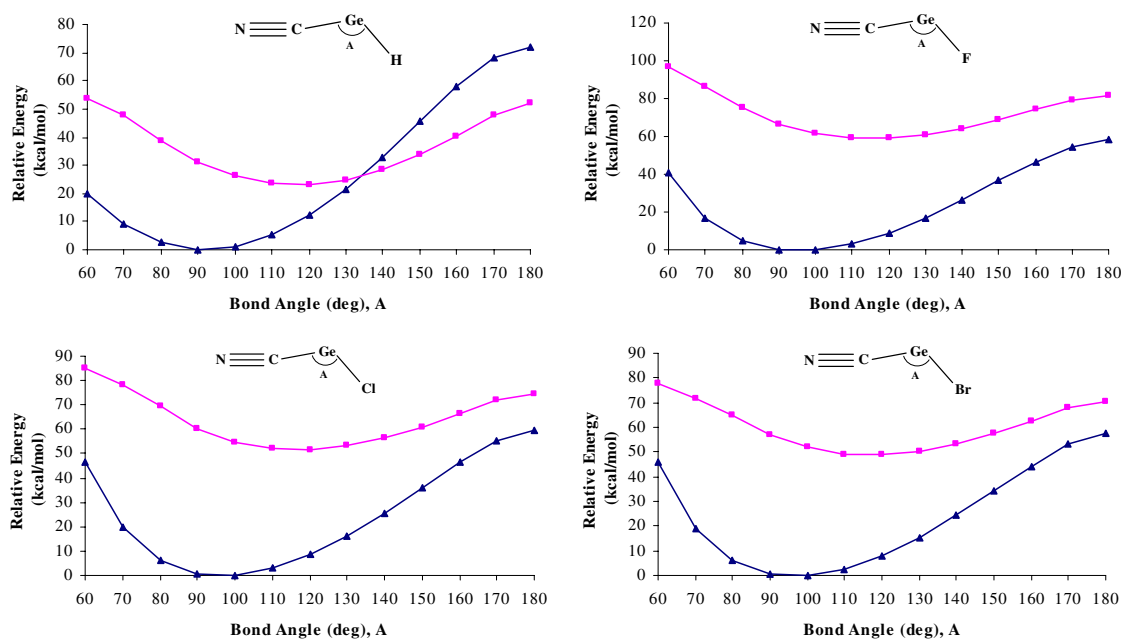


Fig. 5. B3LYP/6-311++G\*\* relative energies (kcal/mol) of the singlet (s, ▲) and triplet (t, ■) states of X-cyanogermylene,  $3_{s-X}$  and  $3_{t-X}$ , species plotted as a function of the divalent bond angle  $\angle X-Ge-CN$  ( $^\circ$ ), where X = H, F, Cl and Br, respectively.

attached to the divalent Ge center, which stabilizes the structure **3** more than the structure **1** due to the formation of cyano group in the former (Fig. 1).

The second acyclic structure considered is [(X-imino)methylene]germylene, **2** (Fig. 1). Singlet  $2_{s-X}$  are more stable than their corresponding triplet  $2_{t-X}$  (for X = F, Cl). Nevertheless, the triplet  $2_{t-H}$  is somewhat (6 kcal/mol at B3LYP) more stable than its corresponding singlet  $2_{s-H}$ , due to the more electropositive character of hydrogen (Table 1). Moreover, triplet transition state  $2_{t-Br}$  and the minimum singlet state  $2_{s-Br}$  are nearly similar in energy at B3LYP level. The order of absolute value of  $\Delta E_{s-t,X}$  between  $2_{s-X}$  and  $2_{t-X}$  calculated at the B3LYP/6-311++G\*\* level is:  $\Delta E_{s-t,F}$  (9.90 kcal/mol) >  $\Delta E_{s-t,H}$  (6.13 kcal/mol) >  $\Delta E_{s-t,Cl}$  (1.85 kcal/mol) >  $\Delta E_{s-t,Br}$  (0.04 kcal/mol).

### 3.1.2. Relative stabilities

All calculation methods designate  $1_{s-H}$  as the lowest energy isomer among GeCNH germynes. The B3LYP/6-311++G\*\* calculated relative stabilities for GeCNH germynes is:  $1_{s-H}$  (0.00 kcal/mol) >  $2_{t-H}$  (11.10 kcal/mol) >  $2_{s-H}$  (17.23 kcal/mol) >  $1_{t-H}$  (24.56 kcal/mol) >  $3_{t-H}$  (27.74 kcal/mol) >  $3_{s-H}$  (76.50 kcal/mol) (Table 1). Interestingly, this is in clear contrast to the relative energies for their SiCNH silylenic analogues, where  $3_{s-H}$  was the most stable structure [21]. One may conclude from this difference that the aromatic three membered ring in GeCNH germynes is more favorable than that in the SiCNH silylenic analogues. Moreover, due to the high electro-positivity of Ge atom in the divalent center, the triplet states  $2_{t-H}$  and  $3_{t-H}$  become rela-

tively more stable than their corresponding singlet states. This phenomenon leads us to choose this system as a candidate for reaching the triplet ground state germynes [40,43]. Another, finding in the above order of stability is the higher stability of the strained three membered  $1_{t-H}$  compared to its reported group 14 analogues [14–21]. The long Ge–C and Ge–N bonds possibly reduce the strain in this non-aromatic ring. The trend of dipole moments, found through B3LYP/6-311++G\*\* calculations, for GeCNH structures is:  $2_{t-H} > 2_{s-H} > 3_{s-H} > 3_{t-H} > 1_{t-H} > 1_{s-H}$  (Table 2). It is not surprising that due to the presence of the polar bonds in these structures the magnitude of dipole moments is rather large. Specially, the higher dipole moments of  $2_{s-H}$  and/or  $2_{t-H}$  could be attributed to the higher significance of the canonical forms where nitrogen lone-pairs participate in forming a triple bond  $N\equiv C$ .

The order of relative stability, calculated at B3LYP/6-311++G\*\* for GeCNF isomers is:  $3_{s-F}$  (0.00 kcal/mol) >  $1_{s-F}$  (41.57 kcal/mol) >  $3_{t-F}$  (58.99 kcal/mol) >  $1_{t-F}$  (79.30 kcal/mol) >  $2_{s-F}$  (100.49 kcal/mol) >  $2_{t-F}$  (110.39 kcal/mol) (Table 1). The global minimum for the GeCNF isomers is found to be  $3_{s-F}$ . Due to the replacement of halogen with the hydrogen this order of stability is different from the above order of GeCNH. Obviously, the  $C\equiv N$  group in singlet  $3_{s-F}$ , has such a great stabilizing effect on the adjacent germylenic center which makes it more stable than  $1_{s-F}$ . However, the higher stability of  $1_{s-F}$  over  $3_{t-F}$  may be attributed to the aromatic character of  $1_{s-F}$ .

The trend of dipole moments in the GeCNF series is:  $2_{s-F} > 3_{s-F} > 2_{t-F} > 1_{t-F} > 3_{t-F} > 1_{s-F}$  (Table 2). Interest-

Table 4  
Relative energies (kcal/mol) for singlet (s) and triplet (t) states of divalent CH<sub>2</sub>, SiH<sub>2</sub> and GeH<sub>2</sub> calculated at 16 levels of theory

Structure	Relative energy (kcal/mol)									
	B1LYP/ 6-31++G**	B1LYP/ 6-311++G**	B3LYP/ 6-31++G**	B3LYP/ 6-311++G**	B3LYP/ 6-311++G**	HF/ 6-31++G**	HF/ 6-311++G**	MP2/ 6-31++G**	MP2/ 6-31++G**	MP2/ 6-311++G**
CH <sub>2</sub> -s	–	12.00	12.30	11.77	–	–	28.45	18.34	17.01	–
CH <sub>2</sub> -t	–	0.00	0.00	0.00	–	–	0.00	0.00	0.00	–
SiH <sub>2</sub> -s	0.00	–	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–
SiH <sub>2</sub> -t	20.14	–	20.31	20.41	4.77	4.69	13.89	14.35	–	–
GeH <sub>2</sub> -s	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–
GeH <sub>2</sub> -t	25.43	26.43	25.79	26.79	8.30	9.32	18.67	18.70	–	–
		<sup>a</sup> MP3/6-31++G**	<sup>a</sup> MP4(SDTQ)/6-311++G**	<sup>a</sup> QCISD(T)/6-311++G**	<sup>a</sup> CCSD(T)/6-311++G**	<sup>a</sup> CCSD(T)/cc-pVTZ	G1	G2		
CH <sub>2</sub> -s	16.32	14.86	13.63	12.12	12.12	10.33	6.22	6.66	–	–
CH <sub>2</sub> -t	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	–
SiH <sub>2</sub> -s	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	–
SiH <sub>2</sub> -t	16.11	16.59	17.56	18.19	18.19	20.03	23.70	23.35	–	–
GeH <sub>2</sub> -s	0.00	0.00	0.00	0.00	0.00	0.00	–	–	–	–
GeH <sub>2</sub> -t	19.04	20.73	21.53	21.899	21.904	22.37	–	–	–	–

<sup>a</sup> ZPE not included.

ingly, all the GeCNF isomers have lower dipole moments than those of the GeCNH. Possibly, fluorine with a high electro-negativity character destabilizes the zwitterionic canonical forms which possess high dipole moments. Hence, the lowest dipole moment is found for **1<sub>s</sub>-F** (1.32D).

B3LYP/6-311++G\*\* calculated order of relative stabilities for GeCNCl is: **3<sub>s</sub>-Cl** (0.00 kcal/mol) > **1<sub>s</sub>-Cl** (44.84 kcal/mol) > **3<sub>t</sub>-Cl** (51.60 kcal/mol) > **1<sub>t</sub>-Cl** (76.46 kcal/mol) > **2<sub>s</sub>-Cl** (81.40 kcal/mol) > **2<sub>t</sub>-Cl** (83.25 kcal/mol) (Table 1). This is exactly the same trend as one finds for GeCNF, but with a shorter range of energy differences between the isomers involved. This may be due to the lower stabilizing effects of chlorine, than the more electro-negative fluorine, on the singlet states of the germylenes. The same justifications for the relative stability trend of GeCNF may be applied to the GeCNCl. The global minimum for the isomeric set of GeCNCl appears to be singlet cyanogermylene, **3<sub>s</sub>-Cl**. The trend of change in dipole moments for GeCNCl isomers is: **3<sub>s</sub>-Cl** > **3<sub>t</sub>-Cl** > **1<sub>s</sub>-Cl** > **1<sub>t</sub>-Cl** > **2<sub>s</sub>-Cl** > **2<sub>t</sub>-Cl** (Table 2).

B3LYP/6-311++G\*\* calculated relative stabilities of GeCNBr are: **3<sub>s</sub>-Br** (0.00 kcal/mol) > **1<sub>s</sub>-Br** (44.85 kcal/mol) > **3<sub>t</sub>-Br** (48.82 kcal/mol) > **2<sub>t</sub>-Br** (74.55 kcal/mol) ≈ **2<sub>s</sub>-Br** (74.59 kcal/mol) > **1<sub>t</sub>-Br** (76.00 kcal/mol) (Table 1). This is nearly the same trend as those found above for GeCNCl, and GeCNF. The transition state **2<sub>t</sub>-Br** is equal in energy with the minimum **2<sub>s</sub>-Br**. Again, the same justifications for the stability order of GeCNF may be applied to the GeCNBr. Once more, the global minimum for the germylenic structures of GeCNBr appears to be singlet **3<sub>s</sub>-Br**. The trend of dipole moments for GeCNBr germylenes is: **2<sub>s</sub>-Br** > **2<sub>t</sub>-Br** > **3<sub>s</sub>-Br** > **1<sub>s</sub>-Br** ≈ **3<sub>t</sub>-Br** > **1<sub>t</sub>-Br** (Table 2).

### 3.2. Structural properties

All the optimized structures are planar with at least C<sub>s</sub> symmetry (Fig. 2). In singlet **1<sub>s</sub>-X** bond lengths change little as a function of substituents, X, since, **1<sub>s</sub>-X** is a relatively stable aromatic structure. Nevertheless, changes of bond lengths in **1<sub>t</sub>-X**, due to the substituents, are more significant (Fig. 2). The order of changes in the Ge–C bond lengths of **1<sub>t</sub>-X** as a function of X is: H (2.24 Å) > Cl (2.15 Å) > Br (2.13 Å) > F (2.12 Å). The Ge–C and Ge–N bond lengths of **1<sub>t</sub>-X** are about 0.25–0.35 Å longer than those of the corresponding **1<sub>s</sub>-X**, whereas the C=N bond lengths of **1<sub>t</sub>-X** are about 0.10 Å shorter than those of the corresponding **1<sub>s</sub>-X**. The divalent angle ∠CGeN of triplet **1<sub>t</sub>-X** is about 7–8° smaller than those of the corresponding **1<sub>s</sub>-X**. This finding is consistent with the other reports on the cyclic carbenes and silylenic analogues but is in contrast to the classic records of many acyclic carbenes and silylenes, where the singlet divalent angle is frequently smaller than those of the corresponding triplet divalent angle

Table 5

NBO calculated hybridizations of singlet ( $1_{s-X}$  and  $3_{s-X}$ ) and triplet states ( $1_{t-X}$  and  $3_{t-X}$ ) of GeCNX germlylenes (X = H, F, Cl and Br)

Structure	Bond		Structure	Bond	
	$\sigma_{\text{Ge-C}}$	$\sigma_{\text{Ge-N}}$		$\sigma_{\text{Ge-C}}$	$\sigma_{\text{Ge-X}}$
$1_{s-H}$	$s^1p^{13.37}d^{0.05}$	$s^1p^{20.77}d^{0.12}$	$3_{s-H}$	$s^1p^{0.42}d^{0.01}$	–
$1_{t-H}$	$s^1p^{31.98}d^{0.23}$	$s^1p^{99.99}d^{1.04}$	$3_{t-H}$	$s^1p^{6.05}d^{0.03}$	$s^1p^{5.87}d^{0.01}$
$1_{s-F}$	$s^1p^{14.93}d^{0.07}$	$s^1p^{19.76}d^{0.15}$	$3_{s-F}$	$s^1p^{13.96}d^{0.12}$	$s^1p^{11.58}d^{0.08}$
$1_{t-F}$	$s^1p^{25.53}d^{0.21}$	$s^1p^{99.99}d^{3.05}$	$3_{t-F}$	$s^1p^{7.02}d^{0.04}$	$s^1p^{8.92}d^{0.05}$
$1_{s-Cl}$	$s^1p^{14.17}d^{0.05}$	$s^1p^{23.25}d^{0.16}$	$3_{s-Cl}$	$s^1p^{12.80}d^{0.12}$	$s^1p^{99.99}d^{0.03}$
$1_{t-Cl}$	$s^1p^{27.14}d^{0.17}$	$s^1p^{99.99}d^{2.48}$	$3_{t-Cl}$	$s^1p^{7.03}d^{0.04}$	$s^1p^{10.55}d^{0.11}$
$1_{s-Br}$	$s^1p^{14.18}d^{0.06}$	$s^1p^{24.04}d^{0.16}$	$3_{s-Br}$	$s^1p^{12.63}d^{0.12}$	$s^1p^{99.99}d^{0.03}$
$1_{t-Br}$	$s^1p^{24.21}d^{0.16}$	$s^1p^{99.99}d^{2.37}$	$3_{t-Br}$	$s^1p^{7.27}d^{0.04}$	$s^1p^{11.79}d^{0.09}$

[14,17,43]. This phenomenon may be rationalized by considering the electronic structures and hybridizations of the atoms which attend in the corresponding bonds to the divalent bond angle  $\angle\text{CGeN}$  [18]. For instance, in the cyclic structures  $1_{s-X}$  and  $1_{t-X}$  the strictly localized natural bond orbitals (NBO) of the  $\sigma$  molecular orbitals have significant  $p$  character for divalent center Ge atom (Table 5). Moreover, the significance of  $p$  orbitals of Ge atom in the  $\sigma_{\text{Ge-N}}$  bond is more than the  $\sigma_{\text{Ge-C}}$ , for the both  $1_{s-X}$  and  $1_{t-X}$  structures. Nevertheless,  $p$  character of Ge in  $1_{t-X}$  is dramatically higher than those of  $1_{s-X}$  which cause to the widening of divalent angle  $\angle\text{CGeN}$  in cyclic singlet states  $1_{s-X}$  compared to the triplet  $1_{t-X}$ . This is in clear contrast to the case of acyclic  $3_{s-X}$  and  $3_{t-X}$ , where divalent Ge atoms in  $3_{s-X}$  structures possess higher  $p$  character than  $3_{t-X}$  (Table 5). Consequently, divalent angle  $\angle\text{CGeX}$  in acyclic singlet states  $3_{s-X}$  is highly smaller than those of the triplet  $3_{t-X}$ . Interestingly, very little germanium  $d$  orbital valence participation is found only for the cyclic triplet structures  $1_{t-X}$  (Table 5). The highest germanium  $d$  orbital valence participation is encountered for  $1_{t-F}$ . The angles  $\angle\text{GeCN}$  of the both  $1_{s-X}$  and  $1_{t-X}$  are considerably larger than the angles  $\angle\text{GeNC}$  (Fig. 2). Moreover, the angles  $\angle\text{GeCN}$  of  $1_{t-X}$  are about 7–13° larger than those of the  $1_{s-X}$ .

Rather small variations of Ge–C bond lengths of  $2_{s-X}$  appears as a function of electro-positivity:  $2_{s-H}$  (1.86 Å) >  $2_{s-Br}$  (1.85 Å)  $\approx$   $2_{s-Cl}$  (1.85 Å) >  $2_{s-F}$  (1.82 Å) (Fig. 2). The cumulenic angle  $\angle\text{GeCN}$  of both  $2_{s-X}$  and  $2_{t-X}$  are somewhat bent and the halogens increase this deviation from linearity. An interesting observation in the optimization of  $2_{t-X}$  structures is the rupture of the starting structure (X = Cl, F, and Br).  $2_{t-Cl}$  ruptures at both MP2 and B3LYP calculations. For  $2_{t-F}$  and  $2_{t-Br}$ , only B3LYP calculations show the rupture. This is in way that the N–X bond undergoes a homolytic bond cleavage which makes N–C bond order increase and halogen atoms attain some negative atomic charge (Table 3).

The changes in C $\equiv$ N bond lengths of both  $3_{s-X}$  and  $3_{t-X}$  are negligible. However, Ge–C bond lengths of singlet  $3_{s-X}$  are about 0.10–0.12 Å shorter than those of triplet  $3_{t-X}$ . Halogens increase the Ge–C bond lengths of  $3_{s-X}$  (about 0.20 Å) but Ge–C bond lengths of  $3_{t-X}$

change little with various halogens. Except for  $3_{s-H}$ , every singlet  $3_{s-X}$  has smaller divalent angle  $\angle\text{CGeX}$  than their corresponding triplet  $3_{t-X}$  where X = F, Cl, and Br (Fig. 2). The singlet  $3_{s-X}$  has larger divalent angle  $\angle\text{CGeX}$  than their corresponding  $3_{t-X}$  even though B3LYP calculations show singlet  $3_{s-X}$  with linear structures and  $C_{\infty V}$  symmetry.

One way to rationalize the variation of charges on the divalent center Ge as a function of substituents, is to draw plots of atomic charges on the Ge against Swain and Lupton constants [39] (Fig. 3, Table 3). These constants are polar ( $F$ ), resonance ( $R$ ) and sum of polar and resonance constants ( $F + R$ ). Among these plots that involving the atomic charges on the Ge atoms of  $1_{s-X}$  vs.  $F + R$  appear to be rather linear (correlation coefficient;  $R^2 = 0.86$ ), assuming comparable weighting factors ( $f \approx r \approx 1$ ). However,  $1_{t-X}$ ,  $2_{s-X}$ ,  $2_{t-X}$ ,  $3_{s-X}$  and  $3_{t-X}$  fail to show such linear relationships between the atomic charges on Ge and  $F + R$ , possibly due to the higher differences between their corresponding empirical sensitivities  $f$  and  $r$ . Instead, the atomic charges on the Ge atoms of  $2_{s-X}$  and  $3_{s-X}$  species, show fairly good linear relationships with polar constant ( $F$ ). Finally, triplet states  $1_{t-X}$ ,  $2_{t-X}$  and  $3_{t-X}$  have no such relationships with none of those constants. These findings indicate the higher importance of polar effects of halogens over their resonance effects in the acyclic  $2_{s-X}$  and  $3_{s-X}$  (Fig. 1). Curves slope ( $m$ ) in the Fig. 3 is a measure of sensitivity of charge on Ge towards  $F$ ,  $R$  and  $F + R$ . The highest magnitude of  $m$  (–3.87) is encountered for the  $3_{s-X}$ , while the lowest magnitude of  $m$  (+0.17) is encountered for the  $1_{s-X}$ .

#### 4. Conclusion

Ab initio and DFT studies on relative stabilities of GeCNH, GeCNF, GeCNCl and GeCNBr germlylenes are carried out at B1LYP/6-311++G\*\*, B3LYP/6-311++G\*\*, MP3/6-311+G\*, MP3/LANL2DZ, MP2/6-311++G\*\*, MP4(SDTQ)/6-311++G\*\*, QCISD(T)/6-311++G\*\*, CCSD(T)/6-311++G\*\*, G1 and G2 levels of theory. All optimized structures are planar with at least  $C_s$  symmetry. The global minimum for all GeCNH

structures appears to be singlet cyclic,  $1_{s-H}$ . Relative stabilities for GeCNH species are:  $1_{s-H} > 2_{t-H} > 2_{s-H} > 1_{t-H} > 3_{t-H} > 3_{s-H}$ . This order is changed when a hydrogen atom is replaced with a halogen. The order of relative stability for the twelve GeCNX germlyenes where X = F and Cl, is:  $3_{s-X} > 1_{s-X} > 3_{t-X} > 1_{t-X} > 2_{s-X} > 2_{t-X}$ . Finally the stability order for five isomers of GeCNBr is:  $3_{s-Br} > 1_{s-Br} > 3_{t-Br} > 2_{s-Br} > 1_{t-Br}$ . The most electro-negative halogen, fluorine, appears to have the highest stabilization effect on its corresponding singlet isomers. This is followed by chlorine and bromine. Triplet germlyenes  $2_{t-H}$  and  $3_{t-H}$  appear more stable than their corresponding singlet states. Among all the calculation methods used, B3LYP appears as the method of choice. Good linear correlations are found between the LUMO–HOMO energy gaps of the singlet germlyenes and their corresponding singlet–triplet energy separations, calculated at B3LYP/6-311++G\*\*. Relative energies of the divalent  $3_{s-X}$  and  $3_{t-X}$  structures as a function of the divalent bond angle  $\angle XGeC$ , are calculated at B3LYP/6-311++G\*\*. Little germanium *d* orbital valence participation in bonds is found. This is only for the cyclic triplet structures  $1_{t-X}$ . Merely, the  $3_{s-H}$  and  $2_{t-Br}$  germlyenes are not real isomers and exist as transition states.

## Acknowledgements

We are grateful to A. Ghaderi (Chemistry Department, Imam Hossein University) for many stimulating and helpful discussions. We thank Dr. Y. Fathollahi and S. Souri (Tarbiat Modares University) for their cordial cooperation.

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