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# Detours for Reaching at New Germylenes, Silylenes, Carbenes, and Carbenogermylenes through Substituted Cyclopropenylidenes at *Ab initio* and DFT Levels

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**Summary.** Heavier atom containing $X_2SiC_2$, and $X_2GeC_2$ cyclopropenylidenes transform into new silylenes, germylenes, and carbenogermylenes at DFT and *ab initio* levels ($X = H$, CN, $NH_2$, and O*Me*). The number of transformations or rearrangements appear roughly proportional to the covalent radii of the group 14 elements (Ge > Si > C).

**Keywords.** *Ab initio* calculations; Density functional calculations; Germylene; Silylene; Carbenogermylene.

## Introduction

The structures and properties of carbenes and their analogues have been the subject of numerous investigations [1–13]. Specifically, increasing attention has been focused on small unsaturated carbenes, because they often appear as intermediates in organic reactions, as well as their attendance in astrophysical chemistry [14–19]. The first identified, most abundant interstellar cyclic organic compound is singlet cyclopropenylidene [15]. This carbene has been isolated in an argon matrix [20]. Many workers have addressed interesting questions of how the presences of substituents affect the relative stabilities of different $C_3H_2$ isomers. A unified *ab initio* account on the energy surfaces of $C_3H_2$ structures along with their corresponding mono-halogenated isomers has appeared [21]. It reveals that the global minimum for the set of $C_3H_2$ is singlet cyclopropenylidene. Moreover, halogens stabilize the singlet ground states of $C_3H_2$ carbenes. The electronic effects of cyano- (CN), amino- ($NH_2$) and methoxy- (O*Me*) groups on the stability of $C_3H_2$ isomers also indicate that electron donating groups stabilize the singlet carbenes [22].

An important parameter which affects the multiplicity and singlet-triplet energy separations ($\Delta E_{s\text{-}t}$) of particular carbenes is the electronegativity of the directly attached atom to the carbenic center [23]. Considering the great interest of many experimental and theoretical workers on divalent reactive intermediates, and following up on our previous studies on divalent species of group 14 elements [24, 25], we look at the role and characteristics of $C{=}M$ double bonds on the structural parameters of cyclic three-membered ring carbenes: $\alpha$-$M$-substituted $X_2MC_2$ cyclopropenylidenes ($M = C$, Si, and Ge; $X = H$, CN, $NH_2$, and O*Me*) (Fig. 1).

## Results and Discussion

In order to increase confidence on our results, the singlet (s) and triplet (t) states of cyclopropenylidenes $X_2MC_2$, including: 2,3-di$X$-cyclopropenylidene ($\mathbf{1}_{s\text{-}X}$ and $\mathbf{1}_{t\text{-}X}$), 2,3-di$X$-2-silacyclopropenylidene ($\mathbf{2}_{s\text{-}X}$

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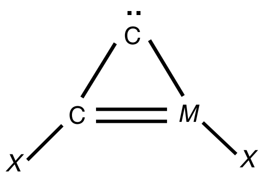


**1** ($\mathbf{1}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$): $M = \text{C}$
**2** ($\mathbf{2}_{\text{s-}X}$ and $\mathbf{2}_{\text{t-}X}$): $M = \text{Si}$
**3** ($\mathbf{3}_{\text{s-}X}$ and $\mathbf{3}_{\text{t-}X}$): $M = \text{Ge}$

**Fig. 1.** General structures for 2,3-di*X*-cyclopropenylidene and its $\alpha$-*M*-substituted analogues, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$–$\mathbf{3}_{\text{t-}X}$, with singlet (s) and triplet (t) states, where $M = \text{C}$, Si, and Ge; while $X = \text{H}$, CN, $NH_2$, and O*Me*

and $\mathbf{2}_{\text{t-}X}$), and 2,3-di*X*-2-germacyclopropenylidene ($\mathbf{3}_{\text{s-}X}$ and $\mathbf{3}_{\text{t-}X}$) are compared and contrasted at eight levels of theory: *HF*/6-311++G$^{**}$, *B*1*LYP*/6-311++G$^{**}$, *B*3*LYP*/6-311++G$^{**}$, *MP*2/6-311++G$^{**}$, *B*3*LYP*/cc-pVTZ, *MP*2/cc-pVTZ, *MP*4(SDTQ)/6-311++G$^{**}$, and QCISD(T)/6-311++G$^{**}$ (where $X = \text{H}$, CN, $NH_2$, and O*Me*) (Fig. 1, Table 1). Except for triplet $^{b}\mathbf{1}_{\text{t-CN}}$ and $^{c}\mathbf{1}_{\text{t-NH}_2}$, which rupture upon optimization, other six structures with $\mathbf{1}_x$ formula conserve their cyclopropylidene form. In contrast, except for triplet $^{a}\mathbf{3}_{\text{t-O}Me}$, which conserves its cyclopropene moiety through optimization, other seven structures tend to rupture. Silicon substituted $\mathbf{2}_x$ run between these two extremes: two structures $^{a}\mathbf{2}_{\text{s-H}}$ and $^{a}\mathbf{2}_{\text{s-CN}}$ rupture upon optimization, while the other six structures conserve their cyclopropene moiety (Fig. 2). Consequently, the number of ruptures appears roughly proportional to the covalent radii and densities of the group 14 elements C, Si, and Ge.

All global minima in each isomeric series are taken as references and set at 0.00 kJ/mol. Other isomers are adjusted accordingly. Again, we have deliberately included data from several different levels of theory, since this may offer an opportunity to compare various levels and to improve the level of confidence in our results. *B*3*LYP*/6-311++G$^{**}$ calculated dipole moments and vibrational zero point energies (*VZPE*) are also presented in Table 1. Force constant calculations show two silicon containing species, $\mathbf{2}_{\text{s-O}Me}$ and $\mathbf{2}_{\text{t-O}Me}$, to be transition states on the potential energy surface (PES) of $(\text{O}Me)_2\text{SiC}_2$ for each possessing one imaginary frequency. On the other hand, $\mathbf{1}_{\text{t-H}}$ appears as a second order saddle point on the PES of $H_2C_3$ with two imaginary frequencies. Harmonic vibrational frequencies pertaining to the four employed substituents (*X*) are calculated at *B*3*LYP*/6-311++G$^{**}$ level of theory (Tables 2–5).

Calculated energetic as well as geometrical parameters are dependent on the computational methods and the basis sets employed (Table 1). This is a reasonable finding for such electron deficient molecules. The energy results obtained at the *HF* level are very remote from the results of other calculation methods. The relative energies calculated at higher levels including *MP*4(SDTQ) and QCISD(T) also appear somewhat different. Extension of basis sets for both *MP*2, as well as *B*3*LYP*, slightly increase the magnitude of calculated relative energies. Finally, attempts failed to optimize structures containing Si ($\mathbf{2}_{\text{s-}X}$ and $\mathbf{2}_{\text{t-}X}$) or Ge ($\mathbf{3}_{\text{s-}X}$ and $\mathbf{3}_{\text{t-}X}$) at the higher levels of theory: *MP*4(SDTQ)/6-311++G$^{**}$, *MP*2-cc-PVTZ, and QCISD(T)/6-311++G$^{**}$ (Table 1). To check the levels of confidence in our results, including methods and basis sets, relative energies of the singlet and triplet states of three typical divalent molecules $CH_2$, $SiH_2$, and $GeH_2$ are calculated at our eight employed levels (Table 6). Subsequently, the above results are compared and contrasted to the reported CASSCF calculated values for divalent $CH_2$, $SiH_2$, and $GeH_2$, which are 41.8, 83.6, and 96.14–100.32 kJ/mol [23]. The closest results to the above experimental and expensive CASSCF computational results are those of *B*3*LYP*/6-311++G$^{**}$ (49.20, 85.31, and 111.98 kJ/mol, Table 6). On the other hand, DFT methods (specially, *B*3*LYP*) based on unrestricted determinants for open-shell systems are not very prone to spin contamination, as a consequence of electron correlation being included in the single-determinantal wave function through the exchange-correlation functional [26, 27]. Moreover, *B*3*LYP* appears quite reliable for computing geometrical parameters [26–28]. In the reminder of the discussion, *B*3*LYP*/6-311++G$^{**}$ data are preferred over those of other calculation methods. Fully optimized geometrical parameters are reported, at *B*3*LYP*/6-311++G$^{**}$ and *MP*2/6-311++G$^{**}$ levels (Fig. 2). NBO analysis, consisting of atomic charges (Table 7), as well as the hybridizations (Table 8), are calculated at *B*3*LYP*/6-311++G$^{**}$.

### *Energetics*

All singlet state isomers appear more stable than their corresponding triplet states (Table 1). The structure

**Table 1.** Relative energies (kJ/mol), including *ZPE* corrections, for singlet (s) and triplet (t) states of carbenic di*X*-substituted cyclopropenylidene and its analogues, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$–$\mathbf{3}_{\text{t-}X}$, ($X = \text{H, CN, NH}_2$, and O*Me*) calculated at various levels of theory; along with the dipole moments (Debye) and vibrational zero point energies (*VZPE*, kJ/mol) calculated at *B*3*LYP*/6-311++G$^{**}$

| Species | Relative energies/kJ mol$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | *HF*/6-311++G$^{**}$ | *B*1*LYP*/6-311++G$^{***}$ | *B*3*LYP*/6-311++G$^{**}$ | [a]*MP*2/6-311++G$^{**}$ | [a]*B*3*LYP*-cc-PVTZ |
| $\mathbf{1}_{\text{s-H}}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{1}_{\text{t-H}}$ | 213.60 | 233.45 | 218.91 | 275.63 | 227.39 |
| $\mathbf{1}_{\text{s-CN}}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{1}_{\text{t-CN}}$ | 110.81 | 244.03 | 238.43 | 312.08 | 248.21 |
| $\mathbf{1}_{\text{s-NH}_2}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{1}_{\text{t-NH}_2}$ | 200.10 | 271.91 | 264.89 | 245.83 | 271.70 |
| $\mathbf{1}_{\text{s-O}Me}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{1}_{\text{t-O}Me}$ | 206.87 | 232.49 | 227.27 | 260.75 | 234.37 |
| $\mathbf{2}_{\text{s-H}}$ | [1]0.00 | 23.20 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{2}_{\text{t-H}}$ | 23.41 | [2]0.00 | 80.38 | 83.18 | 80.92 |
| $\mathbf{2}_{\text{s-CN}}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{2}_{\text{t-CN}}$ | 152.78 | 206.66 | 205.70 | 476.23 | 206.99 |
| $\mathbf{2}_{\text{s-NH}_2}$ | 56.35 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{2}_{\text{t-NH}_2}$ | [1]0.00 | 3.59 | 4.10 | 25.50 | 4.39 |
| $\mathbf{2}_{\text{s-O}Me}$ | 67.55 | 14.00 | 12.25 | [4]0.00 | 14.63 |
| $\mathbf{2}_{\text{t-O}Me}$ | [1]0.00 | [2]0.00 | [3]0.00 | 11.79 | [5]0.00 |
| $\mathbf{3}_{\text{s-H}}$ | 44.64 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{3}_{\text{t-H}}$ | [1]0.00 | 33.40 | 36.58 | 19.77 | 34.23 |
| $\mathbf{3}_{\text{s-CN}}$ | 58.39 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{3}_{\text{t-CN}}$ | [1]0.00 | 165.53 | 19.27 | 237.13 | 165.28 |
| $\mathbf{3}_{\text{s-NH}_2}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{3}_{\text{t-NH}_2}$ | 147.80 | 209.88 | 207.75 | 211.22 | 208.75 |
| $\mathbf{3}_{\text{s-O}Me}$ | [1]0.00 | [2]0.00 | [3]0.00 | [4]0.00 | [5]0.00 |
| $\mathbf{3}_{\text{t-O}Me}$ | 231.99 | 260.50 | 256.03 | 253.94 | 259.49 |

| Species | Relative energies/kJ mol$^{-1}$ | | | Dipole moment/D | *VZPE* / kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| | [a]*MP*2-cc-PVTZ | [a]*MP*4(SDTQ)/6-311++G$^{**}$ | [a]QCISD(T)/6-311++G$^{**}$ | *B*3*LYP*/6-311++G$^{**}$ | *B*3*LYP*/6-311++G$^{**}$ |
| $\mathbf{1}_{\text{s-H}}$ | [6]0.00 | [7]0.00 | [8]0.00 | 14.571 | 84.365 |
| $\mathbf{1}_{\text{t-H}}$ | 275.21 | 265.76 | 249.80 | 6.918 | 68.949 |
| $\mathbf{1}_{\text{s-CN}}$ | [6]0.00 | [7]0.00 | [8]0.00 | 0.414 | 80.277 |
| $\mathbf{1}_{\text{t-CN}}$ | 305.56 | 278.18 | 213.85 | 1.367 | 69.752 |
| $\mathbf{1}_{\text{s-NH}_2}$ | [6]0.00 | [7]0.00 | [8]0.00 | 21.109 | 177.554 |
| $\mathbf{1}_{\text{t-NH}_2}$ | 252.76 | 270.24 | 224.01 | 11.871 | 170.306 |
| $\mathbf{1}_{\text{s-O}Me}$ | [6]0.00 | [7]0.00 | [8]– | 29.477 | 260.063 |
| $\mathbf{1}_{\text{t-O}Me}$ | 275.21 | 265.76 | [8]– | 15.320 | 254.667 |
| $\mathbf{2}_{\text{s-H}}$ | [6]0.00 | [7]0.00 | [8]0.00 | 63.511 | 23.200 |
| $\mathbf{2}_{\text{t-H}}$ | 90.46 | 90.08 | 81.05 | 7.938 | 65.229 |
| $\mathbf{2}_{\text{s-CN}}$ | [6]0.00 | [7]0.00 | [8]– | 13.731 | 68.652 |
| $\mathbf{2}_{\text{t-CN}}$ | [6]– | 27.80 | [8]– | 13.159 | 67.327 |
| $\mathbf{2}_{\text{s-NH}_2}$ | [6]0.00 | [7]– | [8]0.00 | 22.835 | 161.845 |
| $\mathbf{2}_{\text{t-NH}_2}$ | 27.67 | [7]– | 17.14 | 13.226 | 159.877 |
| $\mathbf{2}_{\text{s-O}Me}$ | [6]– | [7]– | [8]– | 30.589 | 244.944 |
| $\mathbf{2}_{\text{t-O}Me}$ | [6]– | [7]– | [8]– | 17.046 | 244.651 |
| $\mathbf{3}_{\text{s-H}}$ | [6]– | [7]0.00 | [8]0.00 | 12.344 | 61.204 |
| $\mathbf{3}_{\text{t-H}}$ | [6]– | 37.75 | 27.50 | 0.665 | 62.520 |
| $\mathbf{3}_{\text{s-CN}}$ | [6]– | [7]0.00 | [8]– | 12.356 | 62.060 |

(*continued*)

**Table 1** (*continued*)

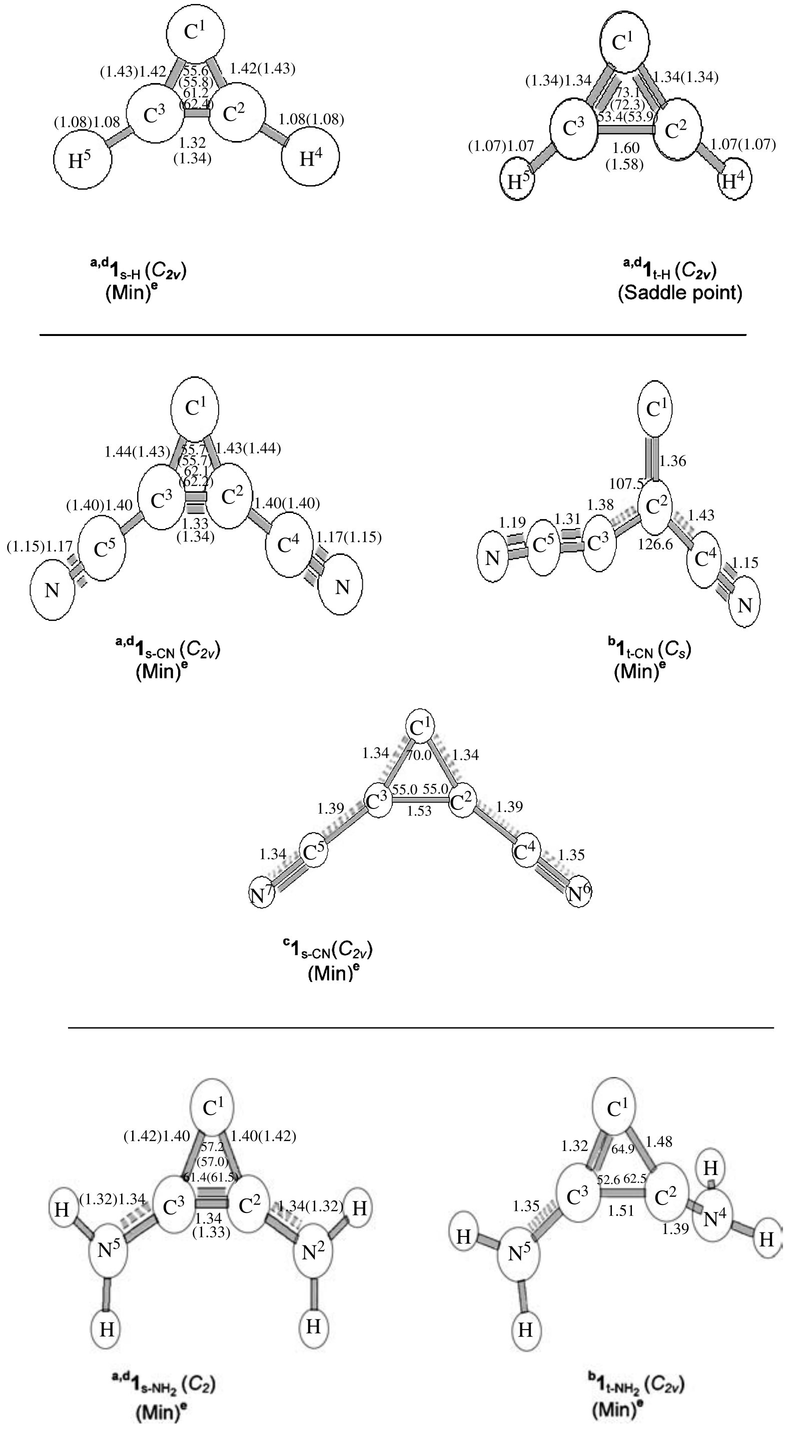
| Species | Relative energies/kJ mol$^{-1}$ | | | Dipole moment/D | *VZPE* kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| | [a]*MP*2-cc-PVTZ | [a]*MP*4(SDTQ)/6-311++G** | [a]QCISD(T)/6-311++G** | *B3LYP*/6-311++G** | *B3LYP*/6-311++G** |
| $\mathbf{3}_{\text{t-CN}}$ | [6]– | 237.47 | [8]– | 13.570 | 66.340 |
| $\mathbf{3}_{\text{s-NH}_2}$ | [6]– | [7]0.00 | [8]– | 11.248 | 160.541 |
| $\mathbf{3}_{\text{t-NH}_2}$ | [6]– | 216.32 | [8]– | 7.248 | 157.599 |
| $\mathbf{3}_{\text{s-O}Me}$ | [6]– | [7]– | [8]– | 11.946 | 243.945 |
| $\mathbf{3}_{\text{t-O}Me}$ | [6]– | [7]– | [8]– | 13.075 | 239.970 |

[a] *ZPE* corrections are not included. [b] The lowest energy minima are set at 0.00 kJ/mol; the original total energies (hartrees) corresponding to the lowest energy minima at various levels of theory: $\mathbf{1}_{\text{s-H}}$: [1] −479.2395724, [2] −482.0617663, [3] −482.3184922, [4] −480.8168791, [5] −482.3588012, [6] −481.0880077, [7] −480.9905384, [8] −480.9906538; $\mathbf{1}_{\text{s-CN}}$: [1] −1246.200317, [2] −1253.070723, [3] −1253.597599, [4] −1250.172092, [5] −1253.6988, [6] −1250.8288, [7] −1250.4809, [8] −1250.428607; $\mathbf{1}_{\text{s-NH}_2}$: [1] −939.5900976, [2] −944.9532332, [3] −945.4250733, [4] −942.6953569, [5] −945.4894666, [6] −943.2446528, [7] −942.9553454, [8] −939.5784149; $\mathbf{1}_{\text{s-O}Me}$: [1] −1431.602583, [2] −1439.409968, [3] −1440.082598, [4] −1436.085696, [5] −1440.205446, −1442.105446, −1441.605446, –; $\mathbf{2}_{\text{s-H}}$: [1] −1528.603154, –, [3] −1533.201669, [4] −1530.077821, [5] −1533.253773, [6] −1530.375475, [7] −1530.271067, [8] −1530.270977; $\mathbf{2}_{\text{s-CN}}$: [1] −2295.890749, [2] −2304.24004, [3] −2304.768966, [4] −2299.730843, [5] −2304.877964, [6] −2300.40498, [7] −2300.05173, [8] –; $\mathbf{2}_{\text{s-NH}_2}$: –, [2] −1995.733023, [3] −1996.20989, [4] −1991.887845, [5] −1996.285397, [6] −1992.46363, [7] −1992.159018, [8] −1992.150038; $\mathbf{2}_{\text{t-O}Me}$: [1] −2481.088422, [2] −2490.307859, [3] −2490.982194, [4] −2490.902184, [5] −2490.507959, –; $\mathbf{3}_{\text{s-H}}$: –, [2] −9004.699509, [3] −9004.9973, [4] −8997.2121, [5] −9005.346406, [6] −8997.414561, [7] −8997.415367; $\mathbf{3}_{\text{s-CN}}$: –, [2] −9775.996326, [3] −9004.9973, [4] −9766.877879, [5] −9776.974147, [6] −9767.191301; $\mathbf{3}_{\text{s-NH}_2}$: [1] −9456.365518, [2] −9467.803424, [3] −9468.313091, [4] −9459.320181, [5] −9468.695078; $\mathbf{3}_{\text{s-O}Me}$: [1] −9948.437459, [2] −9962.333558, [3] −9963.045238, [4] −9952.780072, [5] −9963.488306

of the lowest energy, and presumably the global minimum of the PESs of each $X_2MC_2$ isomeric series emerges as singlet cyclopropenylidene, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$. In fact, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$ structures have a $\sigma^2$ carbenic center which enables them to show aromatic character (Fig. 3). In other words, the intrinsic tendency of carbenes for having triplet ground states is compensated by the aromaticity involved in the singlet three-membered rings [23]. Hence, regardless of electronic effects of the substituents (H, CN, $NH_2$, and O*Me*), every global minimum is a singlet. For singlet and triplet 2,3-di*X*-cyclopropenylidenes, $\mathbf{1}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$, where $X =$ H, CN, $NH_2$, and O*Me*, the *B3LYP*/6-311++G** calculated order of singlet-triplet energy gaps ($\Delta E_{\text{s-t},X}$) is: $\Delta E_{\text{s-t,NH}_2}$ (264.87 kJ/mol) > $\Delta E_{\text{s-t,CN}}$ (238.43 kJ/mol) > $\Delta E_{\text{s-t,O}Me}$ (227.27 kJ/mol) > $\Delta E_{\text{s-t,H}}$ (218.91 kJ/mol) (Table 1). Both electron donating and electron withdrawing substituents appear to somewhat increase the stability of the corresponding singlet states. These results are consistent with those reported for analogous carbenic $C_3HX$ and the related silylenic systems [22, 29].

Again (except for $\mathbf{2}_{\text{s-O}Me}$), singlet 2,3-di*X*-2-silacyclopropenylidene isomers $\mathbf{2}_{\text{s-}X}$ are more stable than their corresponding triplet states $\mathbf{2}_{\text{t-}X}$ (Table 1). The order of energy gaps between $\mathbf{2}_{\text{s-}X}$ and $\mathbf{2}_{\text{t-}X}$ calculated at *B3LYP*/6-311++G** is: $\Delta E_{\text{s-t,CN}}$ (205.70 kJ/mol) > $\Delta E_{\text{s-t,H}}$ (80.38 kJ/mol) > $\Delta E_{\text{s-t,O}Me}$ (12.25 kJ/mol) > $\Delta E_{\text{s-t,NH}_2}$ (4.10 kJ/mol). Finally, all singlet 2,3-di*X*-2-germacyclopropenylidenes $\mathbf{3}_{\text{s-}X}$ are more stable than their corresponding triplet states $\mathbf{3}_{\text{t-}X}$ (Table 1). The *B3LYP*/6-311++G** calculated order of $\Delta E_{\text{s-t},X}$, for $\mathbf{3}_{\text{s-}X}$ and $\mathbf{3}_{\text{t-}X}$ is: $\Delta E_{\text{s-t,O}Me}$ (256.02 kJ/mol) > $\Delta E_{\text{s-t,NH}_2}$ (207.75 kJ/mol) > $\Delta E_{\text{s-t,H}}$ (36.57 kJ/mol) > $\Delta E_{\text{s-t,CN}}$ (19.27 kJ/mol).

The above energy data indicate three points: i) Replacing of carbon with more electropositive atoms (Si and Ge) in the $\alpha$-position to the divalent center of unsubstituted three-membered ring, causes a clear increase in the stability of triplet species $\mathbf{1}_{\text{t-H}}$–$\mathbf{3}_{\text{t-H}}$ compared to their corresponding singlet states $\mathbf{1}_{\text{s-H}}$–$\mathbf{3}_{\text{s-H}}$. This is consistent with the fact that electropositive substituents favor the triplet states, as has been shown previously for silylenes [30]. Moreover, the order of increasing the stability of triplet states as a function of *M* is: C ($\Delta E_{\text{s-t,H}} = 218.91$ kJ/mol) > Si($\Delta E_{\text{s-t,H}} = 80.38$ kJ/mol) > Ge($\Delta E_{\text{s-t,H}} = 36.57$ kJ/mol). This is in agreement with the previously well documented reports for stabilization factors of carbenes and other carbene-like divalent



$^{a,d}\mathbf{1}_{s\text{-}H}$ ($C_{2v}$) (Min)[e]

$^{a,d}\mathbf{1}_{t\text{-}H}$ ($C_{2v}$) (Saddle point)

$^{a,d}\mathbf{1}_{s\text{-}CN}$ ($C_{2v}$) (Min)[e]

$^{b}\mathbf{1}_{t\text{-}CN}$ ($C_s$) (Min)[e]

$^{c}\mathbf{1}_{s\text{-}CN}$($C_{2v}$) (Min)[e]

$^{a,d}\mathbf{1}_{s\text{-}NH_2}$ ($C_2$) (Min)[e]

$^{b}\mathbf{1}_{t\text{-}NH_2}$ ($C_{2v}$) (Min)[e]

**Fig. 2.** Optimized geometrical parameters (see Fig. 1; bond lengths/Å, bond angles/degrees) for singlet (s) and triplet (t) states of 2,3-di*X*-cyclopropenylidene and its *α*-*M*-substituted analogues, $\mathbf{1}_{s\text{-}X}$–$\mathbf{3}_{s\text{-}X}$ and $\mathbf{1}_{t\text{-}X}$–$\mathbf{3}_{t\text{-}X}$, where $M$ = C, Si, and Ge; while $X$ = H, CN, $NH_2$, and O*Me*, at *B3LYP*/6-311++G** and *MP*2/6-311++G** (in parentheses)

[a] The structure encountered at *B3LYP*/6-311++G** and (*MP*2/6-311++G**)

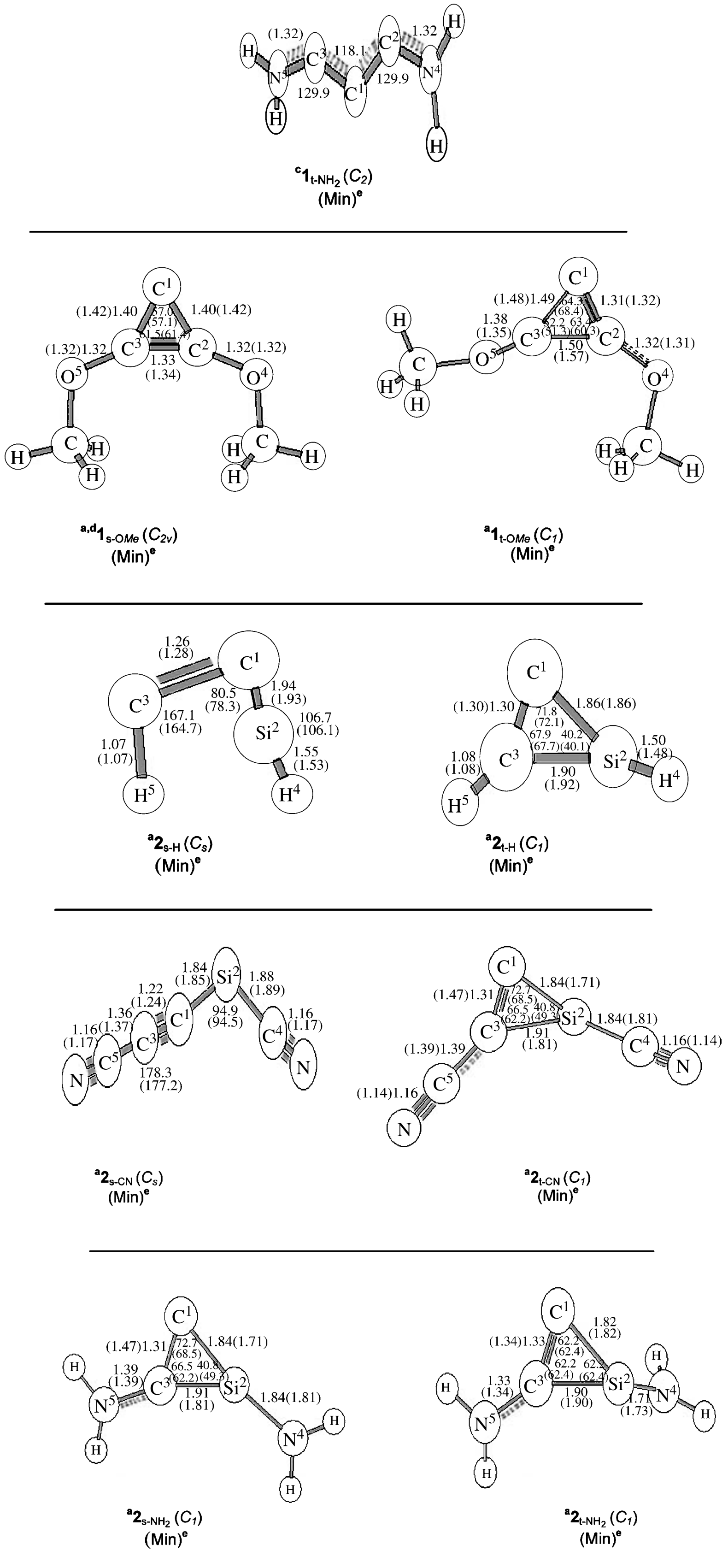
[b] The structure obtained merely through *B3LYP*/6-311++G**

[c] The structure obtained merely through *MP*2/6-311++G**

[d] $\angle C^1C^2C^3$ is equal to $\angle C^1C^3C^2$

[e] Min denotes minimum

[f] TS denotes transition state



$^{c}\mathbf{1}_{t\text{-}NH_2}$ ($C_2$)
(Min)$^{e}$

$^{a,d}\mathbf{1}_{s\text{-}OMe}$ ($C_{2v}$)
(Min)$^{e}$

$^{a}\mathbf{1}_{t\text{-}OMe}$ ($C_1$)
(Min)$^{e}$

$^{a}\mathbf{2}_{s\text{-}H}$ ($C_s$)
(Min)$^{e}$

$^{a}\mathbf{2}_{t\text{-}H}$ ($C_1$)
(Min)$^{e}$

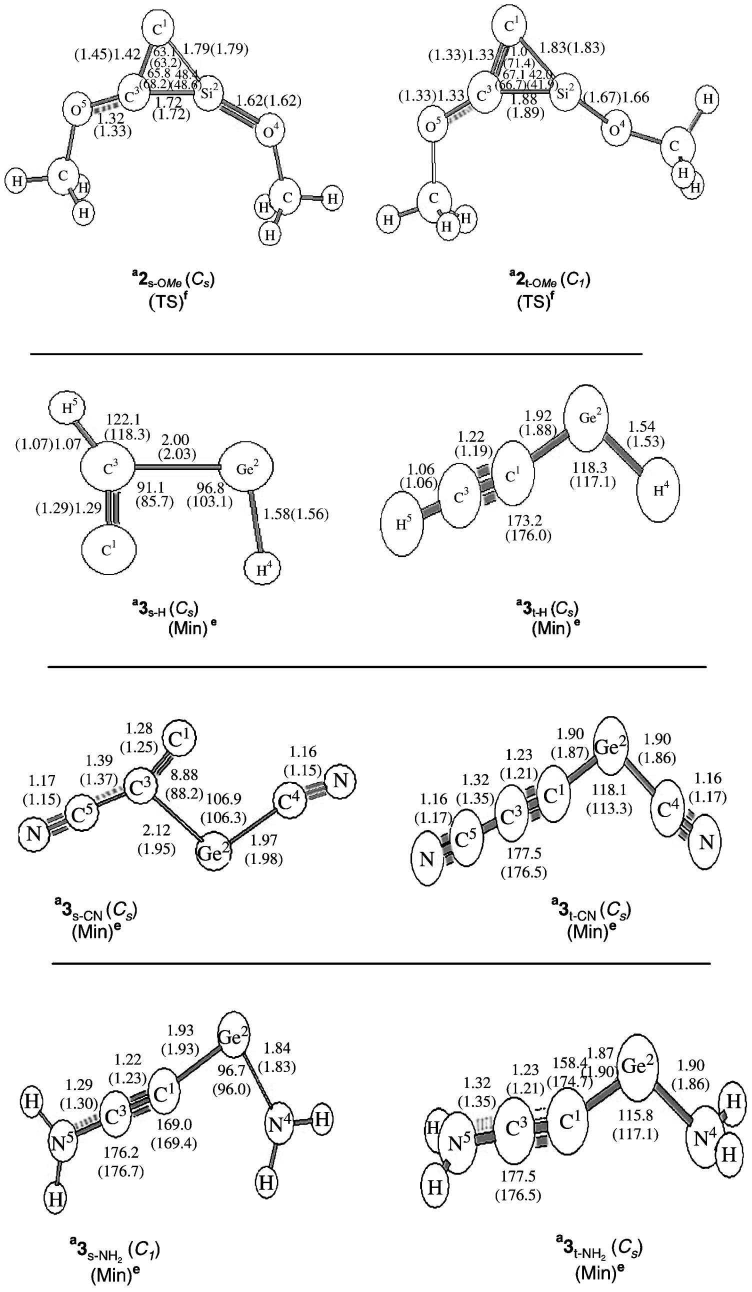
$^{a}\mathbf{2}_{s\text{-}CN}$ ($C_s$)
(Min)$^{e}$

$^{a}\mathbf{2}_{t\text{-}CN}$ ($C_1$)
(Min)$^{e}$

$^{a}\mathbf{2}_{s\text{-}NH_2}$ ($C_1$)
(Min)$^{e}$

$^{a}\mathbf{2}_{t\text{-}NH_2}$ ($C_1$)
(Min)$^{e}$

**Fig. 2** (*continued*)



$^{a}\mathbf{2}_{s\text{-}OMe}$ ($C_s$) (TS)$^{f}$

$^{a}\mathbf{2}_{t\text{-}OMe}$ ($C_1$) (TS)$^{f}$

$^{a}\mathbf{3}_{s\text{-}H}$ ($C_s$) (Min)$^{e}$

$^{a}\mathbf{3}_{t\text{-}H}$ ($C_s$) (Min)$^{e}$

$^{a}\mathbf{3}_{s\text{-}CN}$ ($C_s$) (Min)$^{e}$

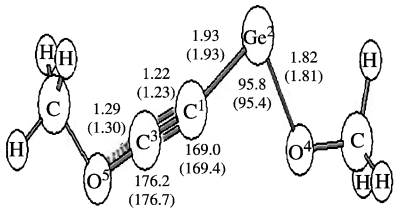
$^{a}\mathbf{3}_{t\text{-}CN}$ ($C_s$) (Min)$^{e}$

$^{a}\mathbf{3}_{s\text{-}NH_2}$ ($C_1$) (Min)$^{e}$

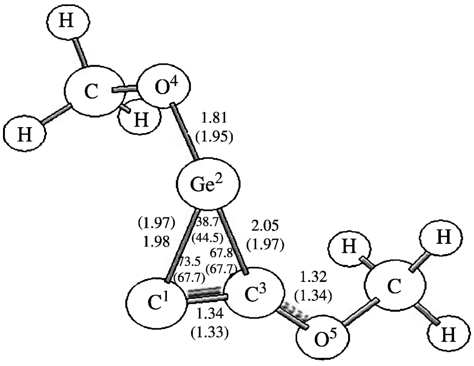
$^{a}\mathbf{3}_{t\text{-}NH_2}$ ($C_s$) (Min)$^{e}$

**Fig. 2** (*continued*)

species [1–13, 21–23, 31, 32]. Interestingly, $\mathbf{1}_{t\text{-}H}$ is only a second order saddle point while other isomers $\mathbf{2}_{t\text{-}H}$ and $\mathbf{3}_{t\text{-}H}$ are real isomers. ii) In the $\mathbf{1}_{s\text{-}CN}$–$\mathbf{3}_{s\text{-}CN}$ and $\mathbf{1}_{t\text{-}CN}$–$\mathbf{3}_{t\text{-}CN}$ series the trends are similar, but the cleavage in going from Si to Ge is higher than that from C to Si. The trend of increase in the stability of triplet states in the $\mathbf{1}_{s\text{-}CN}$–$\mathbf{3}_{s\text{-}CN}$ and $\mathbf{1}_{t\text{-}CN}$–$\mathbf{3}_{t\text{-}CN}$ series is a function of *M*: C ($\mathbf{1}_H$, $\Delta E_{s\text{-}t,CN} = 238.43\,\text{kJ/mol}$) > Si($\mathbf{2}_H$, $\Delta E_{s\text{-}t,CN} = 205.70\,\text{kJ/mol}$) > Ge($\mathbf{3}_H$, $\Delta E_{s\text{-}t,CN} = 19.27\,\text{kJ/mol}$). iii) In the $\mathbf{1}_{s\text{-}NH_2}$–$\mathbf{3}_{s\text{-}NH_2}$, $\mathbf{1}_{t\text{-}NH_2}$–$\mathbf{3}_{t\text{-}NH_2}$, $\mathbf{1}_{s\text{-}OMe}$–$\mathbf{3}_{s\text{-}OMe}$, and $\mathbf{1}_{t\text{-}OMe}$–$\mathbf{3}_{t\text{-}OMe}$ series the trends are incredibly different and gaps in going from C to Ge are small. In contrast, triplet $\mathbf{2}_{t\text{-}OMe}$ (transition state) is surprisingly 12.25 kJ/mol more stable than its corresponding singlet $\mathbf{2}_{s\text{-}OMe}$ (another transition state). This sharp contrast between electronic effects exerted by electron donating and electron withdrawing substituents on carbenes



$^{a}\mathbf{3}_{s\text{-}OMe}$ ($C_1$)
(Min)$^{e}$



$^{a}\mathbf{3}_{t\text{-}OMe}$ ($C_s$)
(Min)$^{e}$

**Fig. 2** (*continued*)

containing Si atoms may be attributed to their less aromatic character than the corresponding cyclopropenylidenes, in one hand, and the smaller size and little relativistic effect of Si compared to Ge, on the other hand, which cause better interactions with the substituents *X* [33]. No significant group 14 element d orbital valence participation is found for any of the scrutinized carbenes **1**–**3** (Table 8). One may wonder why the p-exponents in some cases are tremendously high (like 7.58, 8.58, or even 11.08). Such a phenomenon has been already reported and well explained for Si [34, 35]. High strain in the three-membered rings of $\mathbf{2}_{s\text{-}X}$ and $\mathbf{2}_{t\text{-}X}$ along with the relative radial extensions of the valence p *vs.* s orbitals of Si increase its "hybridization defects" which cause conserving the cyclic skeletons (Fig. 2).

### *Geometries*

Our interest in this area is to provide mainly some insight into the geometry observed for double bonds including heavier congeners of carbon in group 14. We describe our study in a stepwise manner. First, we discuss the geometry of unsubstituent cyclic structures, $\mathbf{1}_{s\text{-}H}$–$\mathbf{3}_{s\text{-}H}$ and $\mathbf{1}_{t\text{-}H}$–$\mathbf{3}_{t\text{-}H}$. Subsequently, effects of substituents for $\mathbf{1}_{s\text{-}X}$–$\mathbf{3}_{s\text{-}X}$ and $\mathbf{1}_{t\text{-}X}$–$\mathbf{3}_{t\text{-}X}$ are presented.

### *Structures of $1_{s\text{-}H}$–$3_{s\text{-}H}$ vs. $1_{t\text{-}H}$–$3_{t\text{-}H}$*

The singlet $\mathbf{1}_{s\text{-}H}$ is a stable cyclic three-membered ring which benefits from aromaticity, and appears planar with a $C_{2v}$ symmetry (Fig. 2). The $C^2{=}C^3$ bond length is typical (1.32 Å), while both $C^1$–$C^3$ and $C^1$–$C^2$ bond lengths are somewhat shorter than those of usual C–C single bonds (1.42 *vs.* 1.54 Å). The triplet $\mathbf{1}_{t\text{-}H}$ with two imaginary frequencies is not a real isomer on the PES of $H_2C_3$. Its optimized structure is planar with a $C_{2v}$ symmetry. The $C^2{=}C^3$ bond length of $\mathbf{1}_{t\text{-}H}$ is considerably lengthened (1.60 Å), showing a single bond while both $C^1$–$C^3$ and $C^1$–$C^2$ bond lengths are shortened to 1.34 Å. Actually, this planar structure is an allene like species. Location of an allenic moiety in a three-membered ring makes it strictly bent (allenic angle $\angle C^2C^1C^3 = 73°$). Due to the great instability of cyclic triplet three-membered ring [36], the two orthogonal p orbitals can interact with the C=C endocyclic $\pi$-bond to generate an allene group. However, this structure is a second order saddle point on the PES of $H_2C_3$. The singlet isomer $\mathbf{1}_{s\text{-}H}$ has higher dipole moment (3.48 D) than the corresponding triplet $\mathbf{1}_{t\text{-}H}$ (1.65 D). The $\mathbf{2}_{s\text{-}H}$ is not a stable cyclic three-membered structure and undergoes a $Si^2{=}C^3$ bond breaking through optimization, forming an acyclic ruptured structure (a minimum). Its optimized structure is a planar ethynylsilylene with a $C_s$ symmetry. This transformation may stem from the fact that a typical C=C double bond is greatly favored relative

**Table 2.** Calculated (*B3LYP*/6-311++G**) harmonic frequencies/cm$^{-1}$ for $C_2MH_2$ species

| Symmetry | $\mathbf{1}_{s\text{-}H}$ | $\mathbf{1}_{t\text{-}H}$ | $\mathbf{2}_{s\text{-}H}$ | $\mathbf{2}_{t\text{-}H}$ | $\mathbf{3}_{s\text{-}H}$ | $\mathbf{3}_{t\text{-}H}$ |
|---|---|---|---|---|---|---|
| $\nu_1$ (a′) | 803.71 | −611.54 | 298.98 | 517.72 | 335.73 | 220.78 |
| $\nu_2$ (a′) | 895.29 | −477.97 | 347.15 | 565.90 | 396.09 | 268.84 |
| $\nu_3$ (a′) | 905.02 | 711.99 | 576.30 | 655.83 | 402.73 | 521.11 |
| $\nu_4$ (a″) | 1001.65 | 783.06 | 747.17 | 661.23 | 552.36 | 598.16 |
| $\nu_5$ (a′) | 1077.19 | 807.52 | 776.54 | 741.32 | 713.00 | 620.99 |
| $\nu_6$ (a′) | 1310.27 | 929.57 | 815.99 | 857.77 | 876.86 | 727.17 |

**Table 3.** Calculated (*B3LYP*/6-311++G**) harmonic frequencies/cm$^{-1}$ for $C_2M(CN_2)_2$ species

| Symmetry | $\mathbf{1}_{\text{s-CN}}$ | $\mathbf{1}_{\text{t-CN}}$ | $\mathbf{2}_{\text{s-CN}}$ | $\mathbf{2}_{\text{t-CN}}$ | $\mathbf{3}_{\text{s-CN}}$ | $\mathbf{3}_{\text{t-CN}}$ |
|---|---|---|---|---|---|---|
| $\nu_1$ (a′) | 102.13 | 80.93 | 57.25 | 68.10 | 38.74 | 49.02 |
| $\nu_2$ (a′) | 192.18 | 87.21 | 92.81 | 143.44 | 58.12 | 109.17 |
| $\nu_3$ (a′) | 258.91 | 182.92 | 161.37 | 168.13 | 117.24 | 144.26 |
| $\nu_4$ (a″) | 260.24 | 253.31 | 207.82 | 231.26 | 196.22 | 272.60 |
| $\nu_5$ (a′) | 483.46 | 268.93 | 291.29 | 320.70 | 214.96 | 276.97 |
| $\nu_6$ (a′) | 508.92 | 440.90 | 301.38 | 351.29 | 218.91 | 321.43 |

**Table 4.** Calculated (*B3LYP*/6-311++G**) harmonic frequencies/cm$^{-1}$ for $C_2M(NH_2)_2$ species

| Symmetry | $\mathbf{1}_{\text{s-NH}_2}$ | $\mathbf{1}_{\text{t-NH}_2}$ | $\mathbf{2}_{\text{s-NH}_2}$ | $\mathbf{2}_{\text{t-NH}_2}$ | $\mathbf{3}_{\text{s-NH}_2}$ | $\mathbf{3}_{\text{t-NH}_2}$ |
|---|---|---|---|---|---|---|
| $\nu_1$ (a′) | 243.46 | 150.11 | 117.71 | 132.37 | 88.15 | 79.04 |
| $\nu_2$ (a′) | 253.03 | 202.99 | 166.60 | 219.64 | 94.62 | 125.13 |
| $\nu_3$ (a′) | 258.97 | 295.85 | 299.71 | 246.72 | 217.72 | 183.78 |
| $\nu_4$ (a″) | 345.60 | 384.86 | 340.11 | 273.59 | 263.22 | 212.19 |
| $\nu_5$ (a′) | 451.49 | 425.34 | 346.80 | 298.93 | 352.28 | 253.16 |
| $\nu_6$ (a′) | 462.55 | 448.22 | 366.58 | 314.56 | 376.66 | 256.57 |

**Table 5.** Calculated (*B3LYP*/6-311++G**) harmonic frequencies/cm$^{-1}$ for $C_2M(OMe)_2$ species

| Symmetry | $\mathbf{1}_{\text{s-O}Me}$ | $\mathbf{1}_{\text{t-O}Me}$ | $\mathbf{2}_{\text{s-O}Me}$ | $\mathbf{2}_{\text{t-O}Me}$ | $\mathbf{3}_{\text{s-O}Me}$ | $\mathbf{3}_{\text{t-O}Me}$ |
|---|---|---|---|---|---|---|
| $\nu_1$ (a′) | 85.70 | 46.80 | −32.45 | −22.36 | 44.02 | 42.43 |
| $\nu_2$ (a′) | 121.44 | 58.45 | 63.88 | 54.46 | 50.63 | 74.24 |
| $\nu_3$ (a′) | 128.78 | 110.31 | 66.91 | 65.06 | 80.33 | 83.70 |
| $\nu_4$ (a″) | 141.17 | 137.02 | 98.36 | 90.23 | 122.71 | 107.34 |
| $\nu_5$ (a′) | 193.43 | 155.90 | 137.08 | 144.54 | 139.22 | 130.17 |
| $\nu_6$ (a′) | 246.55 | 247.56 | 187.66 | 163.73 | 148.21 | 140.25 |

to a C=Si double bond [36–39]. The corresponding triplet isomer $\mathbf{2}_{\text{t-H}}$ (another minimum) adopts the cyclic three-membered ring. This structure is non-planar with a $C_1$ symmetry. The geometry around its Si=C bond appears to be *cis*-bent (dihedral angle $\angle HC^3SiH = -74.9°$). The shortened $C^1$–$C^3$ bond length of $\mathbf{2}_{\text{t-H}}$ (1.30 Å) reveals its double bond character. Conversely, the $C^3$=$Si^2$ emerges rather lengthened (1.90 Å). The $\mathbf{3}_{\text{s-H}}$ is not a stable cyclic three-membered structure and undergoes $Ge^2$=$C^1$ bond breaking through optimization, forming an acyclic ruptured structure (a minimum). This optimized structure is a planar germylene with a $C_s$ symmetry. Here, we come across with a carbenogermylene species which is interesting for being a poly-divalent structure [40, 41]. Again, this transformation may be due to the fact that a typical C=C double bond is greatly favored relative to a C=Ge double bond. Moreover, the tendency for having singlet ground state increases with increase of atomic number in group 14 elements: germylenes > silylenes > carbenes [36]. The triplet isomer $\mathbf{3}_{\text{t-H}}$ is also not a stable cyclic three-membered structure. This carbene undergoes $Ge^2$–$C^3$ bond breaking through optimization creating an acyclic ruptured structure (a minimum). This optimized structure is a planar ethynylgermylene with a $C_s$ symmetry. The triple bond attached to the divalent center makes it highly stabilized. The triplet isomer $\mathbf{3}_{\text{t-H}}$ is a rather non-polar molecule. The divalent angle $\angle C^1GeC^3$ is 118.3°, clearly indicating that the germylenic center has a triplet ground state (Fig. 2) [23, 25].

### *Structures of* $\mathbf{1}_{s\text{-}CN}$*–*$\mathbf{3}_{s\text{-}CN}$ *vs.* $\mathbf{1}_{t\text{-}CN}$*–*$\mathbf{3}_{t\text{-}CN}$

The $\mathbf{1}_{\text{s-CN}}$ (a minimum) has a similar structure to the $\mathbf{1}_{\text{s-H}}$. Its optimized structure is planar with a $C_{2v}$ symmetry (Fig. 2). The carbenic divalent angle

**Table 6.** Relative energies (kJ/mol), including *ZPE* corrections, for singlet (s) and triplet (t) states of $CH_2$, $SiH_2$, and $GeH_2$ molecules calculated at 8 levels of theory

| Structure | Relative energy/kJ mol$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *HF*/6-311++G** | *B1LYP*/6-311++G** | *B3LYP*/6-311++G** | *MP2*/6-311++G** | $^{a}$*MP4*(SDTQ)/6-311++G** | $^{a}$QCISD(T)/6-311++G** | *B3LYP*/cc-PVTZ | *MP2*/cc-PVTZ |
| $CH_2$s | 28.45 | 12.00 | 11.77 | 17.01 | 13.63 | 12.12 | 11.77 | 15.36 |
| $CH_2$t | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $SiH_2$s | 0.00 | – | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $SiH_2$t | 4.69 | – | 20.41 | 14.35 | 17.56 | 18.19 | 20.55 | 16.28 |
| $GeH_2$s | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $GeH_2$t | 9.32 | 26.43 | 26.79 | 18.70 | 21.53 | 21.90 | 26.46 | 19.52 |

[a] *ZPE* Not included

**Table 7.** Calculated NBO atomic charges on di*X*-substituted cyclopropenylidene and its $\alpha$-*M*-substituted analogues, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$–$\mathbf{3}_{\text{t-}X}$, ($M$ = C, Si, and Ge; $X$ = H, CN, NH$_2$, and O*Me*) at *B3LYP*/6-311++G**

| Structure | Species | Atomic charge | | | | |
|---|---|---|---|---|---|---|
| | | C$^1$ | C$^2$ | C$^3$ | $X^4$ | $X^5$ |
| $\mathbf{1}_{\text{s-}X}$ *vs.* $\mathbf{1}_{\text{t-}X}$ | $\mathbf{1}_{\text{s-H}}$ | −0.11 | −0.17 | −0.17 | 0.22 | 0.22 |
| | $\mathbf{1}_{\text{t-H}}$ | −0.21 | −0.53 | −0.53 | 0.13 | 0.13 |
| | $\mathbf{1}_{\text{s-CN}}$ | 0.06 | −0.07 | −0.07 | 0.23 | 0.23 |
| | $\mathbf{1}_{\text{t-CN}}$ | 0.44 | −0.33 | 0.64 | 0.17 | −0.10 |
| | $\mathbf{1}_{\text{s-NH}_2}$ | −0.23 | 0.12 | 0.12 | −0.78 | −0.78 |
| | $\mathbf{1}_{\text{t-NH}_2}$ | −0.10 | 0.08 | 0.11 | −0.83 | −0.79 |
| | $\mathbf{1}_{\text{s-O}Me}$ | −0.16 | 0.24 | 0.24 | −0.51 | −0.51 |
| | $\mathbf{1}_{\text{t-O}Me}$ | −0.04 | 0.23 | 0.18 | −0.50 | −0.57 |
| | | C$^1$ | Si$^2$ | C$^3$ | $X^4$ | $X^5$ |
| $\mathbf{2}_{\text{s-}X}$ *vs.* $\mathbf{2}_{\text{t-}X}$ | $\mathbf{2}_{\text{s-H}}$ | −0.42 | 0.83 | −0.39 | −0.26 | 0.25 |
| | $\mathbf{2}_{\text{t-H}}$ | −0.29 | 0.81 | −0.58 | −0.17 | 0.24 |
| | $\mathbf{2}_{\text{s-CN}}$ | −0.45 | 1.02 | −0.06 | −0.25 | 0.21 |
| | $\mathbf{2}_{\text{t-CN}}$ | −0.42 | 0.04 | −0.31 | −0.12 | 0.13 |
| | $\mathbf{2}_{\text{s-NH}_2}$ | −0.57 | 1.41 | −0.37 | −1.25 | −0.80 |
| | $\mathbf{2}_{\text{t-NH}_2}$ | −0.63 | 0.19 | −0.21 | −0.69 | −0.42 |
| | $\mathbf{2}_{\text{s-O}Me}$ | −0.56 | 1.52 | −0.24 | −0.88 | −0.54 |
| | $\mathbf{2}_{\text{t-O}Me}$ | −0.40 | 1.24 | −0.10 | −0.89 | −0.53 |
| | | C$^1$ | Ge$^2$ | C$^3$ | $X^4$ | $X^5$ |
| $\mathbf{3}_{\text{s-}X}$ *vs.* $\mathbf{3}_{\text{t-}X}$ | $\mathbf{3}_{\text{s-H}}$ | −0.02 | 0.77 | −0.83 | −0.18 | 0.26 |
| | $\mathbf{3}_{\text{t-H}}$ | −0.55 | 0.60 | −0.16 | −0.11 | 0.23 |
| | $\mathbf{3}_{\text{s-CN}}$ | 0.09 | 1.09 | −0.68 | −0.24 | 0.24 |
| | $\mathbf{3}_{\text{t-CN}}$ | −0.24 | 1.20 | 0.12 | −0.08 | 0.06 |
| | $\mathbf{3}_{\text{s-NH}_2}$ | −0.62 | 0.94 | 0.17 | −1.23 | −0.80 |
| | $\mathbf{3}_{\text{t-NH}_2}$ | −0.60 | 0.79 | 0.18 | −1.10 | −0.79 |
| | $\mathbf{3}_{\text{s-O}Me}$ | −0.69 | 1.05 | 0.36 | −0.86 | −0.50 |
| | $\mathbf{3}_{\text{t-O}Me}$ | −0.58 | 0.20 | −0.16 | −0.48 | −0.31 |

$\angle C^2C^1C^3$ is 55.7°. Apparently, the aromatic stabilization of the singlet state cyclic three-membered ring is so important that the two cyano groups exert little affects on the geometry of the molecule. In clear contrast, the corresponding triplet $\mathbf{1}_{\text{t-CN}}$ is not a stable cyclic three-membered structure and undergoes a C$^1$–C$^3$ bond breaking, through optimization, forming an acyclic ruptured structure (a minimum). This optimized structure is planar with a $C_s$ symmetry. A cumulenic moiety including three C=C bonds is formed in the final structure (Fig. 2). Bond lengths of the two cyano groups appear different, denoting that only one of the CN groups takes part in the resonance with the divalent center. The $\mathbf{2}_{\text{s-CN}}$ is not a stable cyclic three-membered structure and undergoes a Si$^2$=C$^3$ bond cleavage, through optimization, generating an acyclic ruptured structure (a minimum). This optimized structure is a planar ethynylsilylene with a $C_s$ symmetry. Bond lengths of two cyano groups are equal (1.16 Å), suggesting that none of the cyano groups takes part in resonance with the divalent center. The silylenic divalent angle $\angle C^1Si^2C^3$ is 94.9°, indicating that the silylenic center has a singlet ground state [23]. In contrast, the triplet isomer $\mathbf{2}_{\text{t-CN}}$ (a minimum) is able to tolerate the cyclic three-membered ring. The geometry around the Si$^2$=C$^3$ bond is distorted to a *trans*-bent arrangement [36]. Hence, this structure is not planar and has a $C_1$ symmetry. The Si$^2$=C$^3$ bond length is lengthened (1.91 Å), while C$^1$–C$^3$ is clearly shortened (1.31 Å). These changes in bond lengths suggest a resonance canonical form which stabilizes the carbenic center (Fig. 3). Here, one encounters "reversed polarity" in the Si=C double bond [37]. Replacing the cyano groups with hydrogen on the rather polarized Si=C C double bond makes reversing the polarity of bond temporarily. Since electron withdrawing effects of cyano groups are more significant for C than Si. Lengthening or diradical character of this double

**Table 8.** The NBO calculated hybridizations for singlet (s) and triplet (t) states of carbenic di*X*-substituted cyclopropenylidene and its $\alpha$-*M*-substituted analogues, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$–$\mathbf{3}_{\text{t-}X}$ ($M$ = C, Si, and Ge; $X$ = H, CN, NH$_2$, and O*Me*), calculated at *B3LYP*/6-311++G**

| Species | Bond | | Species | Bond | | Species | Bond | |
|---|---|---|---|---|---|---|---|---|
| | $^{\sigma}$C$^1$–C$^2$ | $^{\sigma}$C$^1$–C$^3$ | | $^{\sigma}$C$^1$–Si$^2$ | $^{\sigma}$C$^1$–C$^3$ | | $^{\sigma}$C$^1$–Ge$^2$ | $^{\sigma}$C$^1$–C$^3$ |
| $\mathbf{1}_{\text{s-H}}$ | $s^1p^{4.19}d^{0.02}$ | $s^1p^{4.19}d^{0.02}$ | $\mathbf{2}_{\text{s-H}}$ | $s^1p^{1.14}d^{0.01}$ | $s^1p^{1.15}d^{0.01}$ | $\mathbf{3}_{\text{s-H}}$ | – | – |
| $\mathbf{1}_{\text{t-H}}$ | $s^1p^{1.01}d^{0.00}$ | $s^1p^{1.01}d^{0.00}$ | $\mathbf{2}_{\text{t-H}}$ | $s^1p^{7.58}d^{0.04}$ | $s^1p^{1.83}d^{0.01}$ | $\mathbf{3}_{\text{t-H}}$ | $s^1p^{1.20}d^{0.00}$ | $s^1p^{0.90}d^{0.01}$ |
| $\mathbf{1}_{\text{s-CN}}$ | $s^1p^{4.58}d^{0.02}$ | $s^1p^{4.58}d^{0.02}$ | $\mathbf{2}_{\text{s-CN}}$ | $s^1p^{0.94}d^{0.00}$ | $s^1p^{1.07}d^{0.00}$ | $\mathbf{3}_{\text{s-CN}}$ | $s^1p^{1.82}d^{0.01}$ | $s^1p^{1.00}d^{0.00}$ |
| $\mathbf{1}_{\text{t-CN}}$ | $s^1p^{2.54}d^{0.01}$ | – | $\mathbf{2}_{\text{t-CN}}$ | $s^1p^{6.69}d^{0.04}$ | $s^1p^{1.91}d^{0.01}$ | $\mathbf{3}_{\text{t-CN}}$ | $s^1p^{1.25}d^{0.00}$ | $s^1p^{1.00}d^{0.00}$ |
| $\mathbf{1}_{\text{s-NH}_2}$ | $s^1p^{3.92}d^{0.02}$ | $s^1p^{3.92}d^{0.02}$ | $\mathbf{2}_{\text{s-NH}_2}$ | $s^1p^{11.08}d^{0.05}$ | $s^1p^{1.00}d^{0.01}$ | $\mathbf{3}_{\text{s-NH}_2}$ | $s^1p^{0.91}d^{0.00}$ | $s^1p^{1.00}d^{3.15}$ |
| $\mathbf{1}_{\text{t-NH}_2}$ | $s^1p^{3.92}d^{0.02}$ | $s^1p^{1.64}d^{0.25}$ | $\mathbf{2}_{\text{t-NH}_2}$ | $s^1p^{4.29}d^{0.03}$ | $s^1p^{1.52}d^{0.52}$ | $\mathbf{3}_{\text{t-NH}_2}$ | $s^1p^{1.30}d^{0.00}$ | $s^1p^{1.19}d^{0.00}$ |
| $\mathbf{1}_{\text{s-O}Me}$ | $s^1p^{4.01}d^{0.02}$ | $s^1p^{4.01}d^{0.02}$ | $\mathbf{2}_{\text{s-O}Me}$ | $s^1p^{8.58}d^{0.04}$ | $s^1p^{1.00}d^{0.01}$ | $\mathbf{3}_{\text{s-O}Me}$ | $s^1p^{0.89}d^{0.00}$ | $s^1p^{1.00}d^{0.00}$ |
| $\mathbf{1}_{\text{t-O}Me}$ | $s^1p^{2.63}d^{0.01}$ | $s^1p^{3.89}d^{0.02}$ | $\mathbf{2}_{\text{t-O}Me}$ | $s^1p^{1.30}d^{0.00}$ | $s^1p^{1.39}d^{0.17}$ | $\mathbf{3}_{\text{t-O}Me}$ | $s^1p^{0.11}d^{0.00}$ | $s^1p^{2.07}d^{0.01}$ |

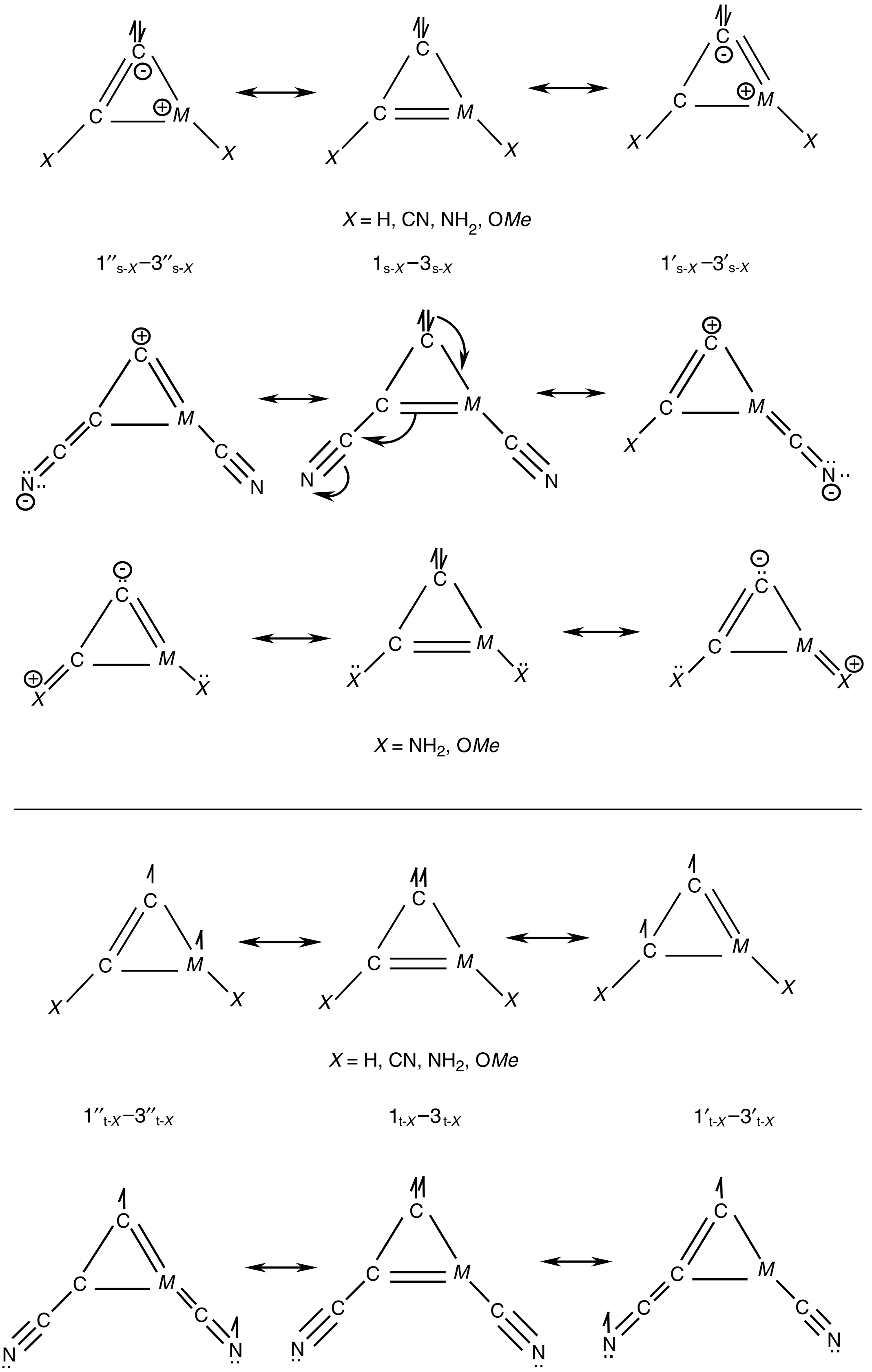


**Fig. 3.** The most significant canonical forms for singlet (s) and triplet (t) states of 2,3-di*X*-cyclopropenylidene and its $\alpha$-*M*-substituted analogues, $\mathbf{1}_{\text{s-}X}$–$\mathbf{3}_{\text{s-}X}$ and $\mathbf{1}_{\text{t-}X}$–$\mathbf{3}_{\text{t-}X}$, where $M = \text{C}$, Si, and Ge; while $X = \text{H}$, CN, $NH_2$, and O*Me*

bond induces an interaction between unpaired electrons of $C^3$ with the divalent center. Interestingly, this interaction appears to be unfeasible for the Si atom due to its larger size compared to C. *Apeloig* and *Karni* have predicted the effects of electron withdrawing groups on C=Si double bond to be more significant than the effects of electron donating groups [37]. The $\mathbf{3}_{\text{s-CN}}$ is not a stable cyclic three-membered structure and undergoes $Ge^2$–$C^1$ bond breaking through optimization, forming an interesting acyclic ruptured structure (a minimum) (Fig. 2). The optimized structure is a planar carbenogermylene with a $C_s$ symmetry. Divalent angle $\angle C^1Ge^2C^3$ is 106.9° and the bond lengths of the two cyano groups are nearly equal. The triplet isomer $\mathbf{3}_{\text{t-CN}}$ is not a stable cyclic three-membered structure and undergoes $Ge^2$=$C^3$ bond breaking through optimization creating an acyclic ruptured structure. This optimized structure is a novel planar triplet germylene with a $C_s$ symmetry. The divalent angle $\angle C^1Ge^2C^3$ is 118.1° confirming that the germylenic center is a triplet ground state. The C≡N bond lengths of the two cyano groups are nearly equal. Hence, cyano groups appear not to have much resonance with the $C^3$≡$C^1$ triple bond and the divalent center. Due to the orientation of the molecules the dipole moment of the triplet isomer $\mathbf{3}_{\text{t-CN}}$ is higher than its corresponding singlet state $\mathbf{3}_{\text{s-CN}}$ (Table 1).

### *Structures of* $\mathbf{1}_{\text{s-NH}_2} - \mathbf{3}_{\text{s-NH}_2}$ *vs.* $\mathbf{1}_{\text{t-NH}_2} - \mathbf{3}_{\text{t-NH}_2}$

The $\mathbf{1}_{\text{s-NH}_2}$ (a minimum) can tolerate the cyclic three-membered rings (Fig. 2). The geometry around the C=C double bond is nearly planar. However, in order to minimize the unfavorable steric interactions, the amino groups somewhat rotate away from each other. Hence, the symmetry of the molecule appears to be $C_2$. Electron donation of amino groups to the aromatic ring causes an increase of the negative charge on the divalent $C^1$ with a partial shortening of the $C^1$–$C^2$ as well as $C^1$–$C^3$ bond lengths. Apparently, in contrast to C=Si and C=Ge double bonds, substitution on C=C bond has little effects on the geometry. The *MP*2 calculations show triplet $\mathbf{1}_{\text{t-NH}_2}$ not to be a stable cyclic three-membered structure. In contrast, the cyclic structure is preserved through optimization at *B*3*LYP* (Fig. 2). The geometry of amino groups around the double bond changes from *cis*, in singlet $\mathbf{1}_{\text{s-NH}_2}$, to *trans*-bent with $C_2$ symmetry. The dipole moment of $\mathbf{1}_{\text{s-NH}_2}$ (5.05 D) is considerably higher than that of the corresponding $\mathbf{1}_{\text{t-NH}_2}$ (2.84 D) (Table 1). Hence, the bond length of $C^2$=$C^3$ increases to 1.51 Å and that of $C^1$–$C^3$ decreases to 1.32 Å. This can also be confirmed by considering the hybridization of bonds to the divalent center, where participation of p orbitals in $C^1$–$C^2$ and $C^1$–$C^3$ bonds of the singlet state $\mathbf{1}_{\text{s-NH}_2}$ is equal (Table 4). In contrast, participation of p orbitals in bonds to the divalent center of triplet state $\mathbf{1}_{\text{t-NH}_2}$ is different. Again as a result of higher repulsion between carbenic bonds, the divalent angle $\angle C^2C^1C^3$ widens to 64.9°. The $\mathbf{2}_{\text{s-NH}_2}$ (a minimum) has a stable cyclic three-membered structure. Due to the decrease of steric hindrances, the geometry of amino groups around C=Si double bond is less twisted compared to that of C=C in $\mathbf{1}_{\text{s-NH}_2}$. However, its symmetry is still $C_1$. The in-plane amino group attached to the carbon atom of C=Si bond can interact with the endocyclic double bond. This is due to the proper orientation of their atomic orbitals. The dipole moment of $\mathbf{2}_{\text{s-NH}_2}$ (5.46 D) is higher than that of the corresponding $\mathbf{2}_{\text{t-NH}_2}$ (3.16 D). In the triplet $\mathbf{2}_{\text{t-NH}_2}$ the $C^1$–$C^3$ bond length shortens to 1.34 Å and the Si=C bond length lengthens to 1.90 Å (Fig. 2). Since $\mathbf{2}_{\text{s-NH}_2}$ enjoys aromaticity, this interaction is less important for the singlet isomer. Participation of p orbitals in the $C^1$–$Si^2$ bond of the singlet isomer $\mathbf{2}_{\text{s-NH}_2}$ is higher than that of the triplet $\mathbf{2}_{\text{t-NH}_2}$. In contrast, participation of p orbitals in the $C^1$–$C^3$ bond of the singlet isomer $\mathbf{2}_{\text{s-NH}_2}$ is considerably less than in the triplet $\mathbf{2}_{\text{t-NH}_2}$, suggesting the existence of resonance for the triplet isomer. Moreover, the negative charge on the divalent carbon of $\mathbf{2}_{\text{t-NH}_2}$ is higher than for the $\mathbf{2}_{\text{s-NH}_2}$ (−0.63 and −0.057) (Table 3). Both divalent angles $\angle Si^2C^1C^3$ of $\mathbf{2}_{\text{s-NH}_2}$ and $\mathbf{2}_{\text{t-NH}_2}$ are slightly different. On the other hand, $\mathbf{3}_{\text{s-NH}_2}$ is not a stable cyclic three-membered structure and undergoes a $Ge^2$=$C^3$ bond cleavage through optimization, forming an acyclic ruptured structure. This optimized structure is a non-planar ethynylgermylene molecule with a $C_1$ symmetry. The divalent angle $\angle C^1Ge^2C^3$ is 96.7°, indicating that the germylenic center has a singlet ground state. The amino group has a resonance interaction with the $C^3$≡$C^1$ triple bond. Moreover, existence of amino group and triple bond attached to the germylenic center greatly stabilizes the singlet isomer. Similarly, the corresponding triplet $\mathbf{3}_{\text{t-NH}_2}$ undergoes a $Ge^2$=$C^3$ bond cleavage through optimization to make an acyclic ruptured structure. This optimized structure is a planar unsaturated germylene with $C_s$ symmetry (Fig. 2). The divalent angle $\angle C^1Ge^2C^3$ is 115°, signifying the triplet ground state of the germylenic center. Comparing the $Ge^2$–$N^4$ bond lengths in $\mathbf{3}_{\text{s-NH}_2}$ and $\mathbf{3}_{\text{t-NH}_2}$ (1.84 and 1.90 Å) shows that the amino group in the singlet isomer has more pronounced stabilizing effects than in the triplet state. The calculated dipole moment of $\mathbf{3}_{\text{s-NH}_2}$ (2.69 D) is higher than that of the corresponding $\mathbf{3}_{\text{t-NH}_2}$ (1.73 D). The negative charge on divalent Ge of $\mathbf{3}_{\text{s-NH}_2}$ is nearly equal to that of $\mathbf{3}_{\text{t-NH}_2}$ (Table 3). Participation of p orbitals in the C–Si bond of the singlet isomer $\mathbf{2}_{\text{s-NH}_2}$ is higher than that of triplet $\mathbf{2}_{\text{t-NH}_2}$ (Table 4). In contrast, participation of p orbitals in the $C^1$–$C^3$ $\sigma$ bond of the singlet isomer $\mathbf{3}_{\text{s-NH}_2}$ is considerably higher than in the triplet $\mathbf{3}_{\text{t-NH}_2}$ (100:1) indicating the existence of a triple bond in the former and a double bond in the latter.

### *Structures of* $\mathbf{1}_{s\text{-}OMe}$–$\mathbf{3}_{s\text{-}OMe}$ *vs.* $\mathbf{1}_{t\text{-}OMe}$–$\mathbf{3}_{t\text{-}OMe}$

The $\mathbf{1}_{\text{s-O}Me}$ (a minimum) adopts a stable cyclic three-membered aromatic structure. The orientation of the methoxy groups around the $C^2$=$C^3$ double bond appears to be *cis* in a symmetric $C_{2v}$ structure (Fig. 2). This stereochemistry may be justified based on reducing the repulsion between the lone pairs of the methoxy groups along with the stabilizing interactions between oxygen orbitals and $\pi$ orbitals of the ring. Therefore, the negative charge on the divalent carbon in the ring increases to $-0.16$ compared to that of the corresponding triplet $\mathbf{1}_{\text{t-O}Me}$ ($-0.04$, Table 3). Interestingly, in this stereochemistry methoxy groups are completely eclipsed, which reveals preference of electronic effects over steric effects (Fig. 2). The divalent angle $\angle C^3C^1C^2$ is 57.0°, which is close to that in $\mathbf{1}_{\text{t-O}Me}$. The corresponding triplet isomer $\mathbf{1}_{\text{t-O}Me}$ is a cyclic three-membered structure. The orientation of methoxy groups around the $C^3$=$C^2$ double bond appears to be *trans*-bent provoking an asymmetric $C_1$ structure. This orientation appears to minimize the steric interaction between methyl groups. Hence, merely one oxygen lone pair is located in the plane of the ring. The in-plane methoxy group attached to the ring can interact through resonance with the endocyclic double bond to stabilize the carbenic center. The in-plane C–O bond length is slightly (0.06 Å) shorter than the out of plane one. The $C^1$–$C^2$ and $C^1$–$C^3$ bond lengths of $\mathbf{1}_{\text{s-O}Me}$ are equal (1.40 Å). However, due to such resonance for the triplet isomer $\mathbf{1}_{\text{t-O}Me}$, the $C^1$–$C^2$ bond is about 0.18 Å shorter than that of the corresponding $C^1$–$C^3$ bond. The highest dipole moment among the $\mathbf{1}_{\text{s-}X}$ species appears to be associated with $\mathbf{1}_{\text{s-O}Me}$ (Table 1). Thus $\mathbf{2}_{\text{s-O}Me}$, like the real isomer $\mathbf{1}_{\text{s-O}Me}$, has a cyclic three-membered structure. This structure with one imaginary frequency is a transition state on its PES. The orientation of methoxy groups around the $C^3$=$Si^2$ double bond is eclipsed with *cis* geometry (Fig. 2). This planar structure has a $C_s$ symmetry. The $C^1$=$Si^2$ bond length (1.72 Å) shows little change with substituents [37]. Interestingly, the Si atom of the ring can form a double bond with the oxygen atom of methoxy, the same interaction is observed for $C^3$ of the ring. This is a $p_\pi$-$d_\pi$ interaction arising from the different orientations of p and d orbitals. Hence, the positive charge on the Si atom increases compared to that of the corresponding triplet state (Table 3). Participation of p orbitals in the $C^1$–$Si^2$ bond of singlet $\mathbf{2}_{\text{s-O}Me}$ is several times higher than that of triplet $\mathbf{2}_{\text{t-O}Me}$ (Table 8). Similar to the singlet one, the corresponding triplet state $\mathbf{2}_{\text{t-O}Me}$ appears as a transition state (Fig. 5, Table 9). The orientation of the methoxy groups around the $C^3$=$Si^2$ double bond is *trans*-bent. This non-planar structure has a $C_1$ symmetry like $\mathbf{1}_{\text{t-O}Me}$. The mentioned Si–O interaction is not observed for triplet $\mathbf{1}_{\text{t-O}Me}$. Instead, the in-plane methoxy group of $\mathbf{1}_{\text{t-O}Me}$ attached to the ring, can interact through resonance with the endocyclic double bond to stabilize the carbenic center (Fig. 2). Hence, the $C^3$=$Si^2$ bond is abnormally long (1.88 Å) and the $C^1$–$C^3$ bond is shortened to 1.33 Å. Participation of p orbitals in the $C^1$–$C^3$ bond of the singlet isomer $\mathbf{2}_{\text{s-O}Me}$ is considerably lower than in that of the triplet $\mathbf{2}_{\text{t-O}Me}$ (1:27), indicating the existence of a double bond in the latter (Table 8).

Finally the $\mathbf{3}_{\text{s-O}Me}$ (a minimum) is not a stable cyclic three-membered structure and undergoes a $Ge^2$=$C^3$ bond cleavage upon optimization to make

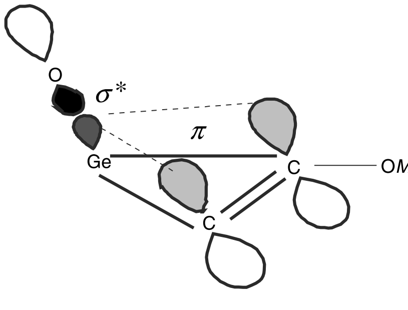
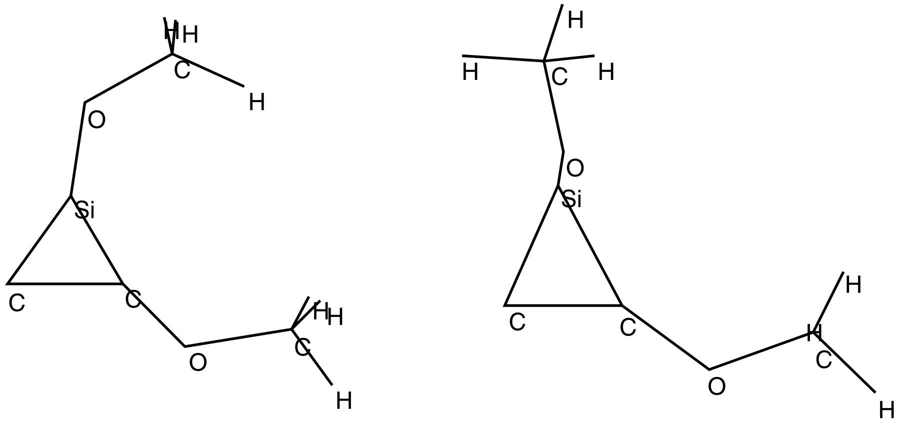


**Fig. 4.** Representation of $\pi$-$\sigma^*$ interaction of the methoxy group in triplet $\mathbf{3}_{\text{t-O}Me}$



$\mathbf{2}_{\text{s-O}Me}$ (Min) $\mathbf{2}_{\text{t-O}Me}$ (Min)

**Fig. 5.** General features of the two minima: $\mathbf{2}_{\text{s-O}Me}$ and $\mathbf{2}_{\text{t-O}Me}$

**Table 9.** Harmonic frequencies/cm$^{-1}$ for the two minima: $\mathbf{2}_{\text{s-O}Me}$ and $\mathbf{2}_{\text{t-O}Me}$ calculated at *B3LYP*/6-311++G$^{**}$

| Symmetry | $\mathbf{2}_{\text{s-O}Me}$ | $\mathbf{2}_{\text{t-O}Me}$ |
|---|---|---|
| $\nu_1$ (a′) | 19.26 | 31.88 |
| $\nu_2$ (a′) | 59.90 | 53.76 |
| $\nu_3$ (a′) | 64.24 | 64.31 |
| $\nu_4$ (a″) | 94.59 | 89.61 |
| $\nu_5$ (a′) | 136.64 | 144.46 |
| $\nu_6$ (a′) | 188.40 | 165.30 |

an acyclic ruptured structure. This optimized structure is a non-planar ethynylgermylene with $C_1$ symmetry. The divalent angle $\angle C^1Ge^2C^3$ is 95.8°, again indicating that the germylenic center has a singlet ground state. Surprisingly, the corresponding triplet $\mathbf{3}_{\text{t-O}Me}$ has a cyclic three-membered structure. The orientation of methoxy groups around the $C^3{=}Ge^2$ double bond is a *trans*-bent. This planar structure has a $C_s$ symmetry. In this triplet isomer, the methoxy group attached to Ge has a $\pi$-$\sigma^*$ interaction to stabilize the three-membered ring (Fig. 4). This arrangement of substituents is not possible in other cases of the $X_2MC_2$ isomers.

## Conclusion

Structures and energies of 24 $X_2MC_2$ cyclopropenylidenes ($M$ = C, Si, and Ge; $X$ = H, CN, NH$_2$, and O*Me*) are investigated at eight *ab initio* and DFT levels: *HF*/6-311++G$^{**}$, *B1LYP*/6-311++G$^{**}$, *B3LYP*/6-311++G$^{**}$, *B3LYP*/cc-pvTZ, *MP*2/6-311++G$^{**}$, *MP*2/cc-pvTZ, *MP*4(SDTQ)/6-311++G$^{**}$, and QCISD(T)/6-311++G$^{**}$. Silicon containing species $\mathbf{2}_{\text{s-O}Me}$ and $\mathbf{2}_{\text{t-O}Me}$ appear as transition states while $\mathbf{1}_{\text{t-H}}$ appears to be a second order saddle point on their PES. Several transformations or rearrangements are observed through optimization of heavier atom containing cyclopropenylidenes. Apparently, the cyano and hydrogen groups promote the existence of carbenogermylene molecules ($\mathbf{3}_{\text{s-CN}}$ and $\mathbf{3}_{\text{s-H}}$) as novel poly-divalent species. The silylenic and germylenic structures are more favorable than their corresponding carbenes *via* transferring "divalency character" from C to Si and Ge atoms. Double bonds including Si and Ge atom are relatively instable and distort the geometry of the three-membered rings. Substituents have substantial effects on the characteristics of C=*M* double bonds. Justifications of transformations or rearrangements are mainly possible based on reversed polarity rule suggested by *Apeloig* and *Karni* [37].

## Computational Methods

All calculations were performed using the Gaussian 98 program package [42]. The geometries and energies of cyclic singlet and triplet $X_2MC_2$ carbenes were calculated using standard quantum chemical *ab initio* and DFT methods ($M$=C, Si, and Ge; $X$ = H, CN, NH$_2$, and O*Me*). All geometries were fully optimized without imposing any symmetry constraints. *Hartree-Fock* calculations were performed with the 6-311++G$^{**}$ basis set [43]. For density functional theory (DFT) calculations the *Becke*'s hybrid one-parameter and three-parameter functional were employed, using the *LYP* correlation with the 6-311++G$^{**}$ [44, 45] and cc-pVTZ basis sets [46]. For the second-order *Møller-Plesset* method the 6-

311++G$^{**}$ and cc-pVTZ basis sets were also used [47]. *MP*2/6-311++G$^{**}$ optimized geometries were used as input for single-point calculations at the *MP*4(SDTQ) and QCISD(T) levels with 6-311++G$^{**}$ basis sets [48–50]. Singlet states were calculated with spin-restricted wave functions. To predict the singlet-triplet energy differences more reliably, spin projected wave functions were employed for triplet states. The harmonic vibrational frequencies and zero point energies (*ZPE*) of *HF* and DFT optimized structures were calculated at the same level of theory used for their optimization (except for *B*3*LYP*/cc-pVTZ). The vibrational frequencies and *ZPE* data at the *HF* and DFT levels were scaled by 0.89 and 0.98 [51, 52]. For minimum state structures only real frequency values (with a positive sign), for transition states only a single imaginary frequency value (with a negative sign), and for second order saddle points two imaginary frequency values were considered. The NBO population analyses were accomplished at the *B*3*LYP*/6-311++G$^{**}$ [53].

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