

Relative Stabilites of the Crossed vs. Linear σ-Conjugated Group 14 Triplet Diradicals E_4H_8 and E_5H_{10} (E = C, Si, Ge, Sn): Orbital Phase Predictions

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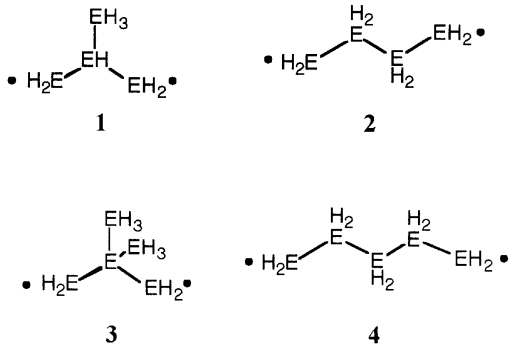
Orbital phase theory was applied to predict that the cross σ-conjugated isomers of acyclic Group 14 triplet diradicals E_4H_8 **1** and E_5H_{10} **3** (E = C, Si, Ge, Sn) are more stable than the linear ones, **2** and **4**, respectively. This prediction was confirmed by ab initio molecular orbital (MO) and density functional theory (DFT) calculations. It was also found that the radicals are preferentially in conjugation with the C–H bond for E = C (**1a** and **2a**), but with the E–E bond for E = Si, Ge, Sn.

With the rapid development of computer techniques, sophisticated ab initio MO and DFT calculations have become popular and useful tools to explain the experimental results. Some simple theories are, however, still important, which give insight into molecular properties and reaction mechanisms. The orbital phase theory, one of such promising simple theories, has been proven to be useful for understanding and predicting interesting properties and reactions of various chemical systems.

The continuity-discontinuity of the orbital phase[1] was shown to underlie the stabilities of the cyclic conjugated systems, i. e., the Hückel rule for the aromaticity and the Woodward–Hoffmann rule for the pericyclic reactions. In 1982, *the cyclic orbital interaction was found to be involved even in acyclic conjugation*.[2] This finding has expanded the application of orbital phase theory to acyclic conjugated systems, such as the regioselectivities of orgamic reactions,[3] the abnormally acute L–M–L angles in ML_2[4a] and ML_3[4b] complexes, the relative stabilities of isomers of π-conjugated polyions,[5] and conformational stabilities of the substituted enamines and vinyl ethers.[6] The usefulness of the simple theory was also demonstrated by a successful prediction of the stabilities of the π-conjugated diradicals.[7]

The remarkable progress in π-conjugation encouraged us to extend the application of orbital phase theory to σ-conjugated systems, which is so far less understood. The saturated and acyclic σ-conjugated triplet diradicals, E_4H_8 and E_5H_{10} (E = C, Si, Ge, Sn), **1**–**4**, are interesting as possible reaction intermediates to be experimentally explored in the near future. The singlet tetramethylene[8] (**2**, E = C) has been investigated by using ab initio computations with the aim to understand the mechanism of thermolyses of deuterated cyclobutane and diazene precursors. However, few studies have been conducted on the triplet states of E_4H_8 and E_5H_{10} diradicals.[9] The relative stability between the isomers is one of the fundamental thermochemical properties, being indispensable for understanding the chemical reactivities and making predictions about the intermediates, products, equilibria, and reaction mechanisms. In this study orbital phase theory was applied to predict that the cross-conjugated isomers, **1** and **3** are more stable than the linear ones, **2** and **4**, respectively (Scheme 1). The predictions were substantiated by ab initio molecular orbital (MO) and density functional theory (DFT) calculations. The radicals were found to prefer conjugation with the C–H bond for E = C (**1a** and **2a**) but with the E–E bond for E = Si, Ge, Sn.



1 **2**

3 **4**

E=C, Si, Ge, Sn

Scheme 1.

Orbital Phase Prediction

Both the branched isomer **1** and linear one **2** can be taken as the two radical centers (P and Q) interacting with each other through one σ-bond (Σ) (Chart 1). Delocalization of excessive α-spins and the bond polarization can take place among the terminal radical orbitals, p and q, and the bonding (σ_{EE}) and antibonding (σ_{EE}*) orbitals of the middle E–E bond, as schematically shown in Fig. 1. In Fig. 1a the radical orbitals, p and q, are singly occupied by α-spin electrons in the ground configura-

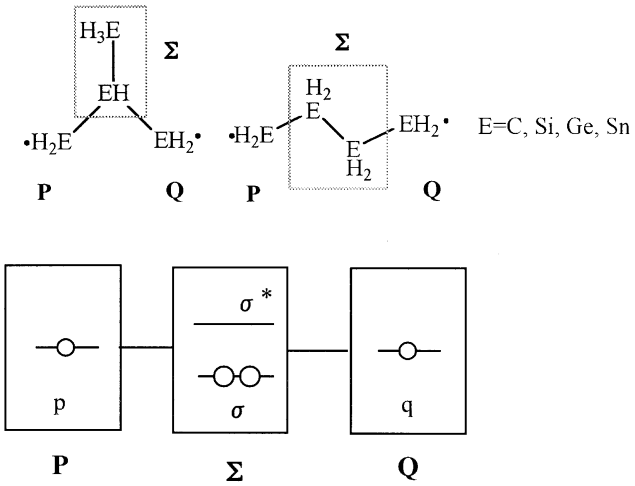


Chart 1.

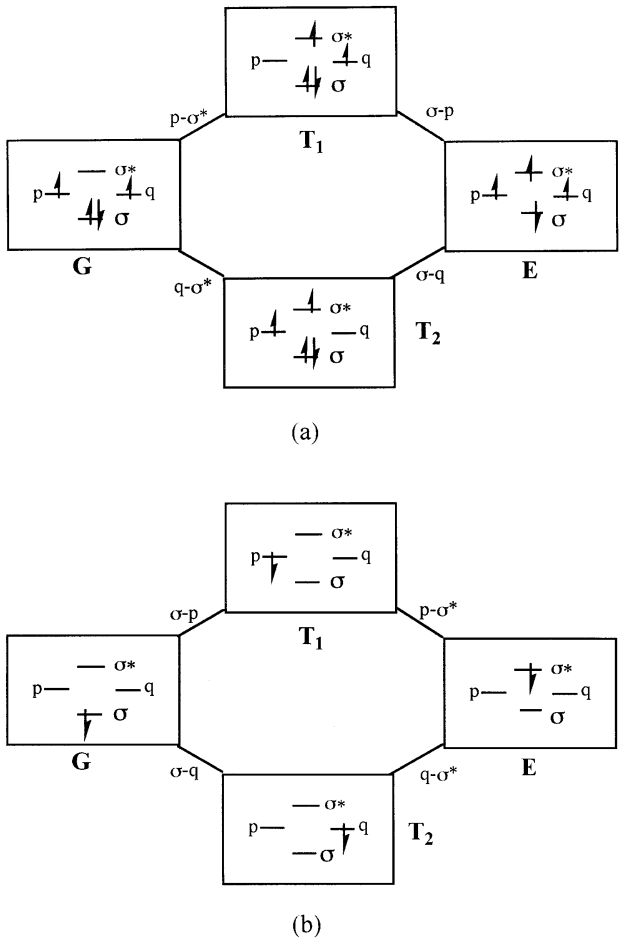


Fig. 1. Delocalization–polarization mechanisms of (a) α-and (b) β-spin electrons in the triplet states.

tion (G) and the σ_{EE} orbital are occupied by two electrons, while the σ_{EE}^* is empty. When one electron in p shifts to σ_{EE}^* through an interaction of the ground configuration G with the transferred cofiguration T_1, mixing of the transferred configuration leads to spin delocalization from p to the middle E–E bond, being approximated by the p–σ_{EE}^* interaction. The resulting electron hole in p is then supplied with an electron by the σ_{EE} orbital via an interaction between the transferred configuration, T_1, and the locally excited configuration, E, which is approximately σ–p interaction. The mixing of the excited configuration polarizes the middle σ bond. That means the G–T_1–E or σ_{EE}–p–σ_{EE}^* interaction is involved in the delocalization–polarization process. Similarly, the delocalization–polarization process through another terminal q orbital consists of the G–T_2–E or σ_{EE}-q-σ_{EE}^* interaction. As a result, the *cyclic*-G–T_1–E–T_2- or –σ_{EE}–p–σ_{EE}^*–q- interaction occurs (Fig. 1a).

The cyclic orbital interaction is under the control of the orbital phase continuity–discontinuity properties.[1–4] When the orbital phase continuity requirements: i. e., (a) the electron-donating orbitals are out of phase; (b) the accepting orbitals are in phase; (c) the donating and accepting orbitals in phase are simultaneously satisfied, this system is stabilized by effective delocalization and polarization. Otherwise, the system is less stable and the delocalization-polarization can not effectively occur.

The delocalization-polarization mechanism of the β-spin (Fig. 1b) is similar to that of α-spin. The difference only lies in that the radical orbitals, p and q, are electron-accepting for the β-spin. The same orbital phase-continuity conditions as those described above are applicable to the β-spin.

In Fig. 2 the orbital phase relations in the branched and linear isomers of Group 14 triplet diradicals E_4H_8 (E = C, Si, Ge, Sn) are given. For the α-spin, the electron-donating orbitals, the radical orbitals p and q in the triplet diradical E_4H_8 can be in phase with the accepting orbital, σ_{EE}^*, and out of phase with the donating orbital, σ_{EE}, at the same time in **1** (for β-spin the accepting radical orbitals, p and q, can be in phase with the donating σ_{EE} and the accepting σ_{EE}^*). Thus, the orbital phase is continuous in **1**. On the contrary, the linear isomer **2** suffers from an orbital phase discontinuity. Therefore, the branched isomer should be more stable than the linear one according to the orbital phase continuity requirements.

In another conformer of the cross-conjugated diradical **1**, where the central E–H bond is in the conjugation with the radicals, another cyclic -σ_{EE}–p–σ_{EE}^*–q- orbital interaction occurs.

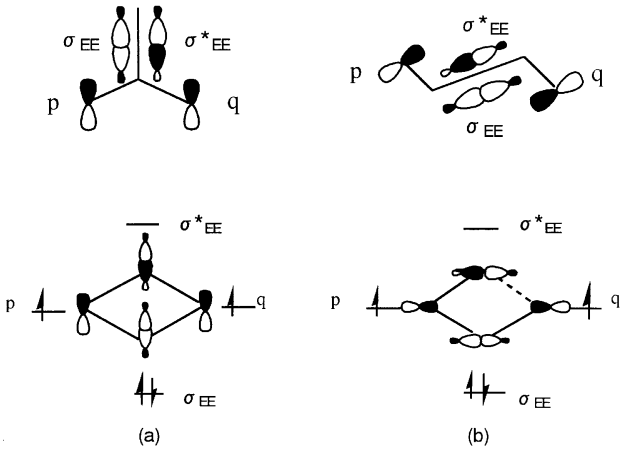


Fig. 2. The orbital phase properties in the triplet states (a) the continuity in **1**; (b) the discontinuity in **2**.

In this case, the orbital phase continuity still holds, so that the diradical **1** is also predicted to be stablilized. On the other hand, the corresponding cyclic orbital interaction does not occur in **2**, since the different E–H bonds interact with p and q. No stabilization due to the cyclic orbital interaction is expected. It follows that **1** is predicted to be more stable than **2**, irrespective of the conformation.

Similarly, we can predict that the cross-conjugated triplet diradicals **3** should be more stable than the linear ones **4**, since it bears orbital phase continuity in **3** (the same phase relation as that of **1** in Fig. 2) while the two diradical centers p and q do not conjugate with the same σ bond in **4** and no cyclic orbital interaction exists.

Computational Confirmation

Ab initio MO and DFT computations[10] have been carried out using GAUSSIAN98[11] to confirm the orbital phase predictions of the relative stabilities.

C_4H_8 Diradicals. The calculated relative energies and the optimized (0, 0), (90, 0), and (90, 90) conformations of the C_4H_8 triplet diradicals, **1a** and **2a**, are given in Fig. 3. All the branched isomers are more stable than the linear ones, but the energy difference is very small. This suggests that there may be some other competing factors than the orbital phase, because of the low σ bonding orbitals and the high antibonding orbitals. The most stable conformers of **1a** and **2a** are of (0, 0) geometry, where the radical p and q orbitals preferentially interact with the C–H bond, rather than with the C–C bond.

E_4H_8 Diradicals (E = Si, Ge, Sn). On going to the heavier homologues, the calculated relative energies of the branched isomers to the linear ones are listed in Table 1, with the most stable geometry given in Fig. 4. As expected from the phase properties, all of the branched isomers are more stable than the linear ones. However, the most stable conformers of **1** and **2** when E = Si, Ge, Sn are different from those of E = C. The radical p and q orbitals preferentially conjugate with the middle E–E bond for E = Si, Ge, Sn (Fig. 4).

Bond Model Confirmation. The effects of the orbital phase continuity in energetically favorable branched isomer **1** were confirmed by employing the bond model method[12] to evaluate the polarization of bonds. Here, we are concerned with the delocalization of σ-electrons in conjugated diradicals, with composite systems of σ E–E bond and radical centers. The delocalization is expressed by mixing the electron trans-

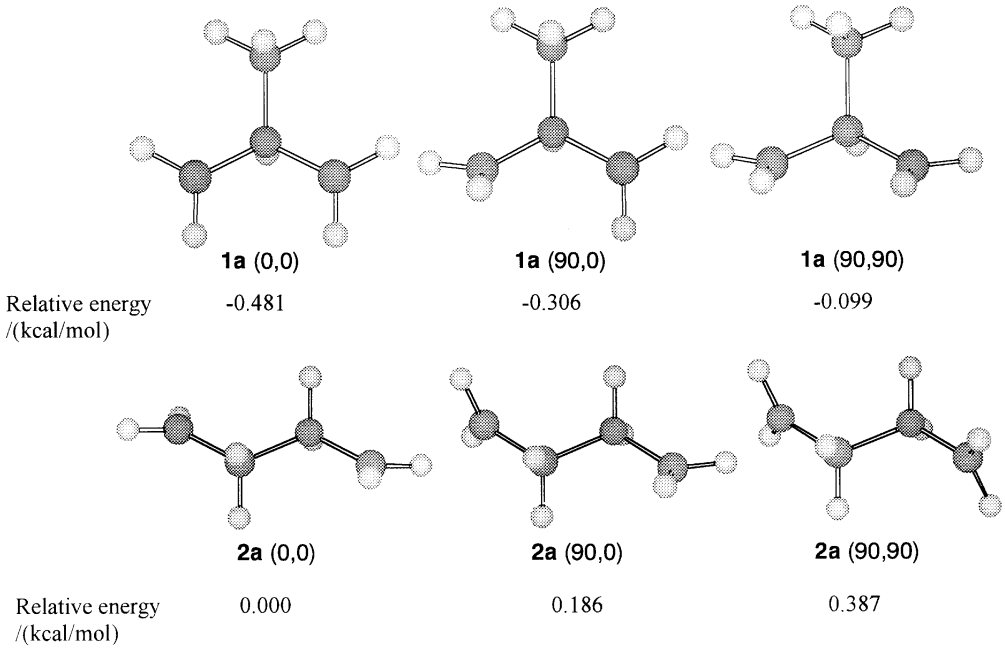
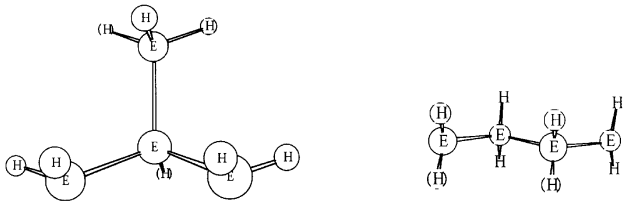


Fig. 3. The relative energies of the optimized conformations of the branched and linear isomers of C_4H_8 triplet diradicals at the UHF/6-311G** +ZPE level.

Table 1. Energies (kcal mol^{-1}) of the Most Stable Conformation of the Branched Isomers (**1**) Relative to That of the Linear Ones (**2**) of the Triplet Diradicals E_4H_8 (E = C, Si, Ge, Sn)

Diradicals	ROHF 6-311G**	UHF+ZPE 6-311G**	MP2[a)]//HF 6-311G**	B3LYP+ZPE 6-311G**	MP2/6-311G** //MP2/ECP[b)]	B3LYP/6-311G** //B3LYP/ECP[b)]
E = C	−0.08	−0.48	−1.38	−0.23		
E = Si	−0.85	−1.01	−1.93	−1.14	−1.93	−1.27
E = Ge	−0.70	−0.99	−1.88	−1.50	−1.88	−1.70
E = Sn[c)]	−1.53	−1.77	−2.93	−1.73	−2.76	−1.78

a) Calculated from the projection technique (PMP2) to annihilate the spin contamination for the triplet states. b) The effective-core potentials (ECP) adopted here are LANL2DZ+p for elements E (E = Si, Ge, Sn). c) The basis of 3-21G* was used for molecule E = Sn.



1b E=Si
c E=Ge
d E=Sn

2b E=Si
c E=Ge
d E=Sn

Fig. 4. The most stable conformations of the heavier triplet diradicals E_4H_8 when E = Si, Ge and Sn.

ferred configurations (T) and locally-excited configurations (E) into G. The ground-state wavefunction is then formulated as

$$\Psi = C_G\Phi_G + \sum C_T\Phi_T + \sum C_E\Phi_E + \ldots. \quad (1)$$

In the ground configuration (Φ_G), a pair of electrons occupies each bonding orbital of the bonds. The interactions between the bond orbitals are accompanied by electron delocalization and polarization. The delocalization is expressed by mixing an electron-transferred configuration (Φ_T), where an electron shifts from the bonding orbital of a bond to the antibonding orbital of another. The polarization is expressed by mixing a locally-excited configuration (Φ_E) where an electron is promoted from the bonding orbital to the antibonding orbital of bond. The extents of delocalization and polarization are, respectively, reflected by C_T/C_G and C_E/C_G, i. e., the ratio of coefficients of the transferred and locally-excited configuration to that of the ground configuration. The cyclic orbital interaction of the present interest is involved in the bond polarization induced by the electron delocalization (cf. Fig. 1). The extent of bond polarization (C_E/C_G) reflects the total effects of the orbital phase properties. For E = C, the C_E/C_G values show that the C–H bond is more polarized in the most stable (0, 0) conformer of the branched isomer **1a** (0.019) than that in **2a** (0.012) of the linear one. The polarization of the Si–Si bond is also appreciable in the branched isomer **1b** (0.017) relative to the linear one **2b** (0.000). The results are in agreement with the orbital phase prediction, supporting the idea that the orbital phase properties control the relative stabilities of the crossed vs. linear conjugated diradicals.

The most stable conformers of the branched and linear C_4H_8 ((0, 0) geometry of **1a** and **2a**) have been found to be different from those of Si (**1b** and **2b**), Ge, and Sn systems (cf. Fig. 3 and 4). The radical orbitals are nearly coplanar with the C–H bonds in the most stable conformation of **1a** and **2a** in E = C,[13] but with the Si–Si bonds in the most stable **1b** and **2b** of E = Si. The different conformational preference results from the relative polarizability of the E–E and E–H bonds. The polarization of the C–H bond is more effective (C_E/C_G = 0.019 and 0.012 in the (0, 0) geometry of **1a** and **2a**) than that of the C–C bond (C_E/C_G = 0.011 and 0.000 in the (90, 90) geometry of **1a** and **2a**) for E = C. In contrast, the polarization of Si–Si bond is more significant in the (90, 90) geometry of **1b** and **2b** (C_E/C_G = 0.017 and 0.000 respectively) compared to the Si–H bond polarization in the (0, 0) geometry of **1b** and **2b** (C_E/C_G = 0.007 and 0.005 respectively). The energy difference between the bonding and antibonding orbitals, $\Delta E_{\sigma\sigma^*}$, may be a determining factor of the bond polarization. The energy gap of the C–C bond orbitals ($\Delta E(\sigma_{CC}\sigma_{CC}^*)$ = 1.473 Hartree) is larger than that of the C–H bond ($\Delta E(\sigma_{CH}\sigma_{CH}^*)$ = 1.456 Hartree), as exemplified by the CH_3CH_3 molecule. The C–H bond σ-conjugation (**1a** and **2a**) is thus preferred. But, in the case of E = Si, the relative order is reversed: $\Delta E(\sigma_{SiSi}\sigma_{SiSi}^*)$ = 1.003 is smaller than $\Delta E(\sigma_{SiH}\sigma_{SiH}^*)$ = 1.029 in SiH_3SiH_3, in agreement with the favorable Si–Si σ-conjugation (**1b** and **2b**).

E_5H_{10} Diradicals. Table 2 gives the calculated relative stabilites between the branched (**3**) and linear conjugated isomers (**4**) of the triplet diradicals of E_5H_{10} (E = C, Si, Ge, Sn). It can be found that for heavier group 14 elements, E = Si, Ge, and Sn, the branched isomers are more stable than the linear ones, consistent with the orbital phase prediction. However, the energy difference in C_5H_{10} is very small. This is easily understood, since the radical centers, p and q, in the carbon compounds prefer to conjugate with the middle C–H bond rather than with the C–C bond, as discussed in the previous parts of C_4H_8 diradicals. In the branched isomer of C_5H_{10}, **3a**, there is no C–H bond conjugate with the radical centers, and consequently no stabilization resulting from a favorable cyclic interaction involving the C–H bond. In Fig. 5, the *asymmetrical* **3a** conformer was found to be more stable than the *symmetrical* **3a** one to avoid a large repulsion between the methylene groups. The most stable conformation of the linear isomer **4a** (Fig. 5) shows that the isomers of C_5H_{10} are in favor of the C–H conjugation, while conjugation with the E–E bond is more favorable for E = Si (Fig. 6). The different conformational preference between the carbon compound and its higher homologues in the triplet state of E_5H_{10} is the same as that of E_4H_8.

Table 2. Energies (kcal mol^{-1}) of the Most Stable Conformation of the Branched Isomers (**3**) Relative to That of the Linear Ones (**4**) of the Triplet Diradicals E_5H_{10} (E = C, Si, Ge, Sn)

Diradicals	ROHF+ZPE 6-311G**	UHF+ZPE 6-311G**	MP2[a)]//HF 6-311G**	B3LYP+ZPE 6-311G**	MP2/6-311G** //MP2/ECP[b)]	B3LYP/6-311G** //B3LYP/ECP[b)]
E = C	−0.23	−0.29	−3.62	−0.09		
E = Si	−1.95	−2.01	−4.68	−1.91	−4.87	−1.80
E = Ge	−1.38	−1.25	−4.04	−0.81	−4.09	−1.20
E = Sn[c)]	−4.26	−4.32	−7.62	−3.99	−7.50	−3.75

a) Calculated from the projection technique (PMP2) to annihilate the spin contamination for the triplet states. b) The effective-core potentials (ECP) adopted here are LANL2DZ+p for elements E (E = Si, Ge, Sn). c) The basis of 3-21G* was used for molecule E = Sn.

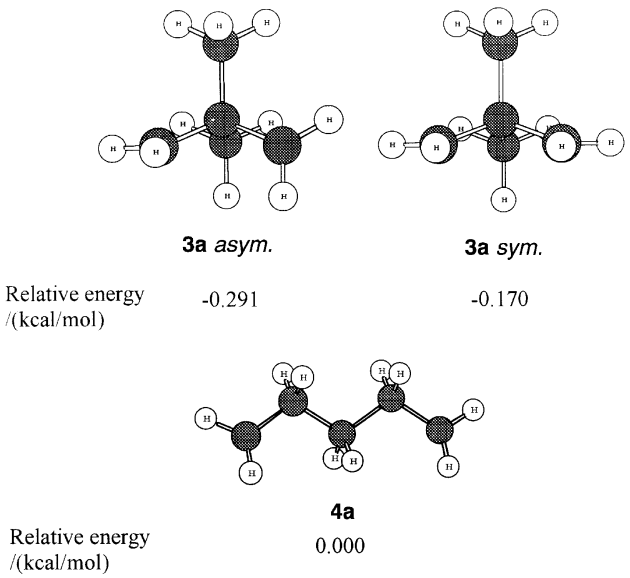


Fig. 5. The relative energies of some conformers of the C_5H_{10} triplet diradicals optimized at the UHF/6-311G**+ZPE level.

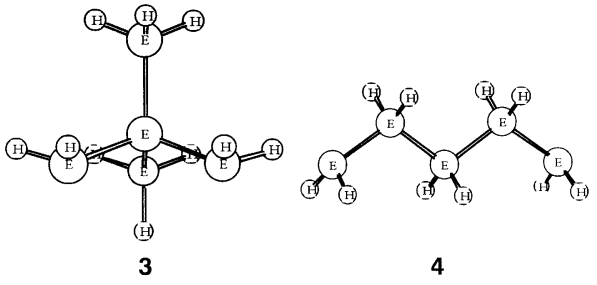


Fig. 6. The most stable conformations of the branched (**3**) and linear (**4**) heavier E_5H_{10} diradicals when E = Si, Ge, and Sn.

Conclusions

The concept of the cyclic orbital interaction was applied to the acyclic σ-conjugated diradicals to predict that the cross-conjugated Group 14 triplet diradicals E_4H_8 (E = C, Si, Ge, Sn) **1** and E_5H_{10}, **3** are more stable than the linear conjugation systems, **2** and **4**, respectively. The orbital phase predictions have been confirmed by ab initio molecular orbital (MO) and density functional theory (DFT) calculations. For the carbon compound, the radical centers prefer to conjugate with the middle C–H bond, and the radical centers and the middle C–H bonds are nearly coplanar in the most stable conformation. However, in the heavier analogies, E = Si, Ge, and Sn, the conjugation with the middle E–E bond is more favorable. The different conformational preference between the carbon system and its higher homologues can be explained by the relative polarizability of the E–E and E–H bonds.

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10 Minimum-energy structures were computed at the unrestricted Hartree–Fock (UHF) and restricted open-shell Hartree–Fock (ROHF) level using a standard 6-311G** basis set for E = C, Si, Ge and 3-21G* basis for Sn by complete optimization. The frequency analysis has been done with the UHF/6-311G**. To take the effect of electron correlation into consideration the second order Møller–Plesset perturbation MP2(fc) method was used for the single-point computations at the UHF optimized structures to determine relative energies. We also employed an alternative method based on density functional theory (DFT). The three-parameter exchange of Becke in conjunction with the Lee–Yang–Parr correlation functional (B3LYP) was applied in our calculations. In addition to the full-electron 6-311G** basis, another type of basis sets, the effective core potentials (ECPs) LANL2DZ+p were used for the heavy atoms E = Si, Ge, and Sn. The d-polarization function for ECP basis set of Sn is taken from: A. Hollwarth, M. Bohme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp, and G. Frenking, *Chem. Phys. Lett.*, **208**, 237 (1993).

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13 The conformers (90, 90) in which radical orbitals conjugate with the central C–C bond are less stable than those (0, 0) of **1a** and **2a** with the energy difference of 0.39 and 0.38 kcal mol^{-1} at the UHF/6-311G**+ZPE level, respectively. The calculations at the UB3LYP/6-311G** level also showed the same conformational preference. The opposite conformational preference of **2a** was reported as the results of the calculations at the MCSCF/STO-3G level.[9]