Orbital Phase Control of the Preferential Branching of Chain Molecules

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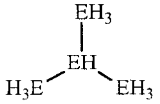
Abstract: The orbital phase theory was applied to the stabilities of the branched isomers (**1**) of E_4H_{10} (E = C, Si, Ge, Sn) relative to the normal ones (**2**). The orbital phase prediction was confirmed by ab initio molecular orbital (MO) and density functional theory (DFT) calculations as well as by some experimental results. Further applications to the relative stabilities of other alkane and alkene isomers lead to the preference of the branched to the normal isomers, the neopentane-type to isobutane-type branching, the terminal to inner methyl branching, and the methyl to ethyl inner substitution in the longer alkanes, as well as the preference of isobutene to 2-butene moieties. The preferential stabilization of the branched isomers was shown to be general and controlled by the orbital phase.

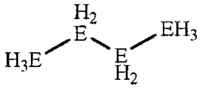
1. Introduction

Isobutane (**1a**) has long been known to be thermodynamically more stable than its normal isomer (**2a**).[1−5] The observed enthalpies of formation of the branched isomer differs by 1.6 kcal/mol from the normal ones.[1,4] Ito found the correlation between the heat of formation and the number of nonbonding atomic interactions to explain the relative stability of isobutane.[3] Wiberg et al.[4b] proposed that branching should be controlled by the electron-withdrawing abilities of the hydrocarbon groups, which decreases in the order of $CH_3 > CH_2 > CH > C$. Laidig[5] found that the branching resulted in the dominance of the nuclear−electron attraction over the electron−electron and nuclear−nuclear repulsion. However, all these explanations cannot be directly applied to relative stabilities of some isomers of longer alkanes. For example, an isomer of C_6H_{14}, 2-methylpentane, was observed to be thermodynamically more stable than 3-methylpentane, although they have the identical numbers of branching and hydrocarbon groups.

On the other hand, it is interesting to know whether the effects of the branching on the stabilities of isomers are general. For example, the relative stability of the silicon counterparts, normal tetrasilane (**1b**) and isotetrasilane (**2b**), has not been discussed yet to the best of our knowledge, although their structural, electronic, and spectroscopic properties have attracted intensive interests.[6−10] Even less has been known about the properties of heavier Ge (**1c** and **2c**) and Sn homologues (**1d** and **2d**).



1a, E=C
b, E=Si
c, E=Ge
d, E=Sn



2a, E=C
b, E=Si
c, E=Ge
d, E=Sn

The continuity−discontinuity of the orbital phase[11] 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 the past twenty years, the finding of *cyclic orbital interaction involved even in acyclic conjugation*[12] has expanded the application of the orbital phase theory to the acyclic conjugated systems such as the regioselectivities of organic reactions,[13] the abnormally acute L−M−L angles in ML_2[14a] and ML_3[14b] complexes, the relative stabilities of isomers of π-conjugated polyions,[15] and the conformational stabilities of the substituted enamines and vinyl ethers.[16] The usefulness of the simple theory was also demonstrated by the successful prediction of the stabilities of the π-conjugated diradicals[17] and the σ-conjugated triplet diradicals E_4H_8 and E_5H_{10} (E = C, Si, Ge, Sn).[18] The orbital phase has been shown to be a general factor controlling the favorable

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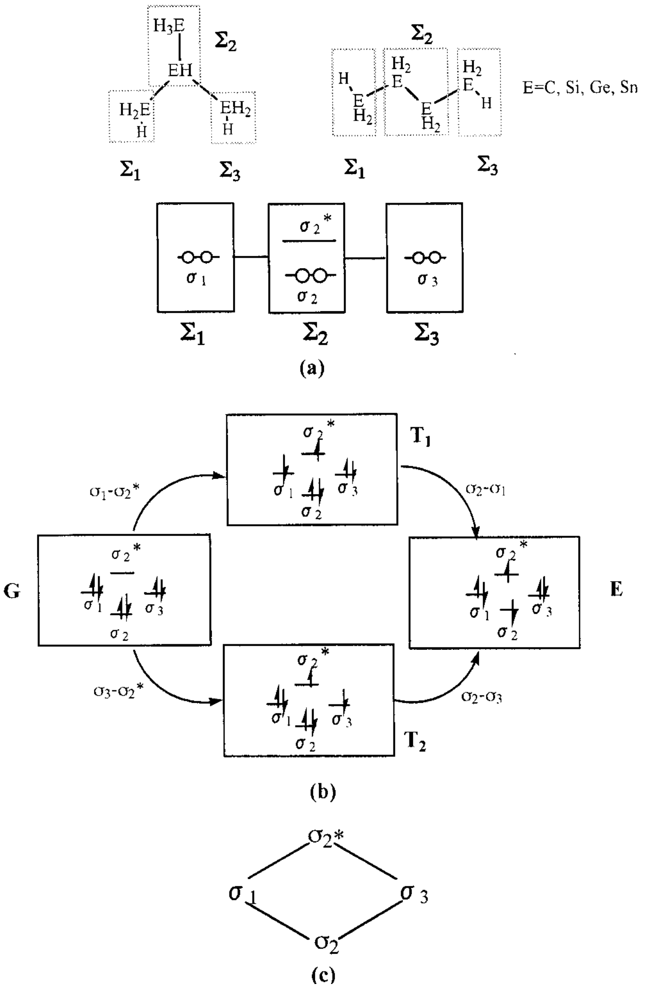


Figure 1. Orbital phase theory: (a) $\Sigma_1-\Sigma_2-\Sigma_3$ systems; (b) delocalization−polarization mechanism; and (c) cyclic orbital interaction in the $\Sigma_1-\Sigma_2-\Sigma_3$ system.

energetic stabilization of the branched isomers in the π-conjugated polyions and diradicals as well as σ-conjugated triplet diradicals. In this paper, we demonstrate that orbital phase controls the effects of branching in the most fundamental systems such as alkanes and alkenes as well as the molecules containing Si, Ge, and Sn atoms.

In the following sections we will first describe the derivation of the orbital phase continuity requirement and its application to the relative stabilities of isomers of Group 14 E_4H_{10} (E = C, Si, Ge, Sn), **1** and **2**. Then the results of ab initio MO and DFT computations will be presented to confirm the predictions of orbital phase theory. Finally, we will extend the applications of the orbital phase theory to various systems.

2. Orbital Phase Continuity Requirement

Both isomers **1** and **2** contain an E−E bond (Σ_2) interacting with the terminal E−H bonds (Σ_1 and Σ_3) as shown in Figure 1. The delocalization of σ-electrons from E−H bonds to the E−E bond and the polarization of the E−E bond take place among the σ-bonding and antibonding orbitals of the middle E−E bond (σ_2 and σ_2*, respectively) and the σ-bonding orbitals, σ_1 and σ_3, of the antiperiplanar E−H bonds in Σ_1 and Σ_3. In the ground configuration (G) the terminal orbitals σ_1 and σ_3 and the bonding σ_2 orbital are occupied by two electrons, while the antibonding σ_2* is empty. One electron in σ_1 shifts to the antibonding σ-orbital (σ_2*) through an interaction of the ground configuration G with the transferred configuration T_1. The mixing of the transferred configuration leads to electron delocalization from the terminal E−H bond to the middle E−E bond. The configuration interaction is approximated by the $\sigma_1-\sigma_2$* interaction. The resulting electron hole in σ_1 is then supplied with an electron by the middle bonding σ_2 orbital via an interaction between the transferred configuration, T_1, and the locally excited configuration, E, which is approximately $\sigma_2-\sigma_1$ interaction. The mixing of the excited configuration polarizes the σ_2 bond. That means the $G-T_1-E$ or $\sigma_2-\sigma_1-\sigma_2$* interaction is involved in the electron delocalization−polarization process between the terminal σ_1 and the central σ_2 bond. Similarly, the delocalization−polarization process through another terminal σ_3 orbital consists of the $G-T_2-E$ or $\sigma_2-\sigma_3-\sigma_2$* interaction. As a result, the cyclic $-G-T_1-E-T_2-$ or $-\sigma_2-\sigma_1-\sigma_2{}^*-\sigma_3-$ interaction occurs (Figure 1c).

For an effective occurrence of the cyclic configuration interaction, $-G-T_1-E-T_2-$, the phase is an important factor. If the coefficients of configuration on mixing E through the T_1 and T_2 paths have the same signs, the cyclic configuration interaction is enhanced to stabilize the delocalization system. The different signs lead to cancellation of the E configuration mixing and consequently diminish the stabilization. The sign relations between the G and T configurations and between the T and E configurations depend on their overlap integrals, S(G,T) and S(T,E), respectively. So the sign relation between the G and E configurations mixing through T_1 ($G-T_1-E$) depend on the sign of $S(G,T_1)S(T_1,E)$. Similarly, the sign relation for another path depends on the sign of $S(G,T_2)S(T_2,E)$. Then the stabilization requirement of the same signs in two paths gives rise to the positive product of those overlaps, i.e.,

$$S(G,T_1)\ S(T_1,E)\ S(G,T_2)\ S(T_2,E) > 0 \tag{1}$$

Now we can present each configuration by the Slater determinants.

$$\mathbf{G} = \frac{1}{\sqrt{6!}}|\sigma_1\overline{\sigma_1}\sigma_2\overline{\sigma_2}\sigma_3\overline{\sigma_3}|$$

$$\mathbf{T}_1 = \frac{1}{\sqrt{2\cdot 6!}}(|\sigma_1\overline{\sigma_2^*}\sigma_2\overline{\sigma_2}\sigma_3\overline{\sigma_3}| + |\sigma_2^*\overline{\sigma_1}\sigma_2\overline{\sigma_2}\sigma_3\overline{\sigma_3}|)$$

$$\mathbf{T}_2 = \frac{1}{\sqrt{2\cdot 6!}}(|\sigma_1\overline{\sigma_1}\sigma_2\overline{\sigma_2}\sigma_3\overline{\sigma_2^*}| + |\sigma_1\overline{\sigma_1}\sigma_2\overline{\sigma_2}\sigma_2^*\overline{\sigma_3}|)$$

$$\mathbf{E} = \frac{1}{\sqrt{2\cdot 6!}}(|\sigma_1\overline{\sigma_1}\sigma_2\overline{\sigma_2^*}\sigma_3\overline{\sigma_3}| + |\sigma_1\overline{\sigma_1}\sigma_2^*\overline{\sigma_2}\sigma_3\overline{\sigma_3}|) \tag{2}$$

Then the overlap integral can be approximated by the overlap between the orbitals, i.e.,

$$S(G,T_1) \approx 2^{1/2}\,s(\sigma_1,\sigma_2{}^*) \tag{3}$$

Similarly, we have

$$S(T_1,E) \approx -s(\sigma_1,\sigma_2),$$
$$S(G,T_2) \approx 2^{1/2}s(\sigma_3,\sigma_2{}^*),$$
$$S(T_2,E) \approx -s(\sigma_3,\sigma_2)$$

Inequality 1 can thus be rewritten as

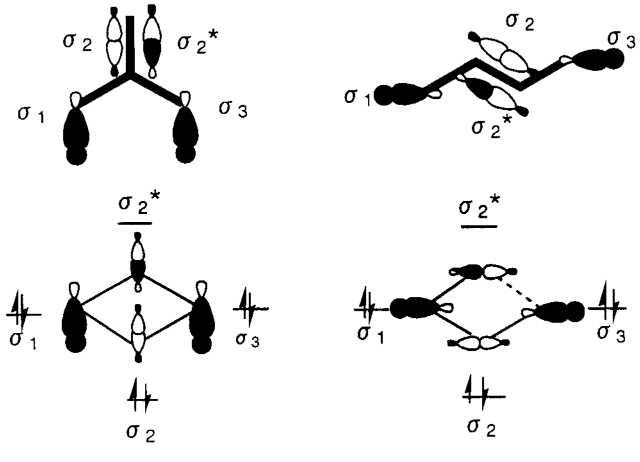
$$(-1)^2\,s(\sigma_1,\sigma_2{}^*)\ s(\sigma_3,\sigma_2{}^*)\ s(\sigma_1,\sigma_2)\ s(\sigma_3,\sigma_2) > 0 \tag{4}$$

where s denotes the orbital overlap integral. In inequality 4 above, the power of (−1), 2 is equivalent to the number of interactions between the electron-donating orbitals, correspond-

Table 1. Energies (kcal/mol) of the Branched Isomers (**1**) Relative to the Normal Ones (**2**) of E_4H_{10} (E = C, Si, Ge, Sn)

molecules	HF/ 6-311G**	MP2//HF 6-311G**	B3LYP/ 6-311G**	MP2/6-311G** //MP2/ECP^a	B3LYP/6-311G** //B3LYP/ECP^a
E = C	−0.40	−1.87	−0.58		
E = Si	−0.62	−1.48	−0.57	−1.51	−0.63
E = Ge	−0.39	−1.26	−0.27	−1.25	−0.64
E = Sn^b	−1.23	−2.26	−0.98	−2.18	−0.34

^{a} The effective-core potentials (ECP) adopted here are LANL2DZ+p for elements E (E = Si, Ge, Sn). ^{b} The basis of 3-21G* is used for molecule E = Sn.



(a) (b)

Figure 2. The orbital phase properties in E_4H_{10}: (a) the continuity in **1** and (b) the discontinuity in **2**.

ing to the $\sigma_1-\sigma_2$ and $\sigma_3-\sigma_2$ interactions here. Generally, if there are interactions between n pairs of donating orbitals, the factor is $(-1)^n$.

The orbital phase continuity requirements (inequality 4) can be rewritten in terms of orbital as the simultaneous satisfaction of the following conditions: (1) the electron-donating orbitals are out of phase; (2) the accepting orbitals are in phase; and (3) the donating and accepting orbitals are in phase.

The donating and accepting orbitals are occupied and unoccupied, respectively, by electrons in the ground configurations. In **1** and **2**, σ_1 and σ_3 orbitals of the terminal group EH_3 are electron donating, and the bonding σ_2 and the antibonding σ_2* are electron-donating and -accepting orbitals, respectively. When all the orbital phase continuity requirements are satisfied [$s(\sigma_1,\sigma_2^*) > 0$, $s(\sigma_3,\sigma_2^*) > 0$, $s(\sigma_1,\sigma_2) < 0$, $s(\sigma_3,\sigma_2) < 0$] inequality 4 is satisfied. So the orbital phase continuity requirement is essentially equivalent to inequality 4. It should be noted that the phase conditions of continuity are the same for both cyclic[11] and acyclic,[12−18] closed-shell[12−17] and open-shell,[17,18] and π-conjugated[17] and σ-conjugated systems.[18]

3. Relative Stability of Isomers of E_4H_{10}

Orbital Phase Prediction. The orbital phase relations in the branched (**1**) and normal (**2**) isomers of E_4H_{10} are given in Figure 2. The branched isomer meets the phase requirements. The electron-donating orbitals σ_1 and σ_3 in E_4H_{10} can be in phase with the accepting orbital σ_2* and out of phase with the donating orbital σ_2 at the same time, so that the orbital phase is continuous. On the contrary, the normal isomer suffers from the orbital phase discontinuity. Therefore, the branched isomers (**1**) should be more stable than the normal ones (**2**). The orbital phase prediction on the stability of isobautane (**1a**) relative to butane (**2a**) is in agreement with experimental fact[1,2] and calculation results.[3,4,19,20]

Computational Confirmation. The prediction of the preferential branching in the heavier homologues E = Si, Ge, and Sn was confirmed by ab initio MO and DFT calculations[21] using GAUSSIAN98.[22] The relative energies of the branched isomers (**1**) to the normal ones (**2**) were listed in Table 1. The branched isomers are more stable than the normal ones at various theory levels. The energies of the branched Si_4H_{10} (C_{3v}, **1b**) and normal isomer (*trans*-, C_{2h}, **2b**) calculated by others for the different aims[9,23] (−1161.48320 and −1161.48209 hartrees, respectively at the RHF/6-311G**, −1161.86891 and −1161.86625 hartrees at the MP2/6-311G**) are in agreement with our orbital phase predictions of the branching preference. The orbital phase theory similarly predicts that the branched $(CH_3)_2SiHSiH_3$ (**3**) should be more stable than the straight-chain $CH_3SiH_2SiH_2CH_3$ (**4**). This is also substantiated by their experimental standard heat of formation $\Delta_fH°(298)$, i.e., −11.0 kcal/mol for species **3** and −9.0 kcal/mol for **4**.[24]

Analysis of Electronic Structures. The effects of the orbital phase continuity were confirmed by the analysis of the electronic structure based on the bond model method[12−18,25−29] to evaluate the electron delocalization from bond to bond and the polarization of bonds. The delocalization and the polarization are expressed by mixing the electron transferred configurations (T)

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(21) Minimum-energy structures were computed at the Hartree−Fock (HF) level with use of a standard 6-311G** basis set for E = C, Si, Ge and a 3-21G* basis for Sn by complete optimization. To take the effect of electron correlation into consideration the second-order Møller−Plesset perturbation MP2(fc) method was used for the single-point computions at the optimized structures to determine relative energies. We also employed the method based on density functional theory (DFT), an alternative approach that has gained increasing popularity in the theoretical study of various chemical systems. 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-electrons 6-311G** basis, another type of basis set, the effective core potential (ECPs) LANL2DZ+p, was used for the heavy atoms E = Si, Ge, and Sn.

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Table 2. Electron Delocalization (C_T/C_G) from Bond to Bond and Polarization (C_E/C_G) of Bonds

molecules	delocalization $\sigma_1 \rightarrow \sigma_2^*$	polarization $\sigma_2 \rightarrow \sigma_2^*$
1a	0.031	0.010
2a	0.030	0.000

and locally excited configurations (E) into G, respectively. The ground-state wavefunction is expanded as[25,26]

$$\Psi = C_G\Phi_G + \sum C_T\Phi_T + \sum C_E\Phi_E + ... \qquad (5)$$

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 the bond. The extents of delocalization and polarization are shown 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, respectively.[17]

A set of bond orbitals, i.e., hybrid orbitals and bond polarities, give the coefficients of the configurations, C_G, C_T, and C_E. The bonding and antibonding orbitals ϕ_i and ϕ_i^* of the ith bond are expressed by a linear combination of hybrid atomic orbitals χ_{ia} and χ_{ib} on the bonded atoms a and b:

$$\phi_i = c_{ia}\chi_{ia} + c_{ib}\chi_{ib}$$

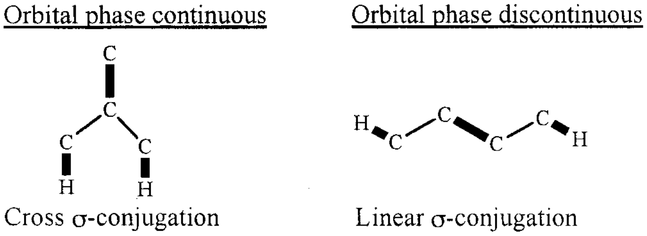
$$\phi_i^* = c_{ia}^*\chi_{ia} + c_{ib}^*\chi_{ib} \qquad (6)$$

The bond (bonding and antibonding) orbitals of each bond are obtained by the diagonalization of the 2 × 2 Fock matrix on the basis of the hybrid orbitals.[25] A set of bond orbitals are optimized to give the maximum value of the coefficient of the ground configuration, C_G.

The cyclic orbital interaction of the present interest is involved in the bond polarization induced by the electron delocalization (cf. Figure 1). Thus, the effectiveness of the cyclic orbital interaction is evaluated by the C_T/C_G values of the $\sigma_1 \rightarrow \sigma_2^*$ delocalization and the $\sigma_2 \rightarrow \sigma_2^*$ local excitation. The RHF/6-31G* wavefunctions were employed for the bond model analysis of the electronic structures. The results of **1a** and **2a** (Table 2) showed that the $\sigma_1 \rightarrow \sigma_2^*$ interaction increases from 0.030 in n-butane (**2a**) to 0.031 in isobutane (**1a**). The central C−C bond is more significantly polarized in the branched isomer **1a** (0.010) than that in the normal one **2a** (0.000). The results are in agreement with the orbital phase prediction, supporting that the orbital phase properties control the relative stabilities of the branched vs. normal isomers.

Bond Length Changes in Branching. Another interesting difference between the isobutane and n-butane lies in that each C−C bond distance in the branched isomer is greater than the C−C distances in the corresponding normal isomer.[5] The bond elongation usually weakens the bond and destabilizes the whole molecule. This is not the case with the energetic preference of branching. This was noticed by Laidig,[5] but unfortunately the origin of the lengthening in bond distance has not been discussed yet. The bond lengthening of the C−C bonds in isobutane relative to n-butane is caused by the effective cyclic orbital interaction in the branched structure. The C−C bond in isobutane is significantly polarized. This implies that electron population is lower in the bonding orbital of the C−C bond and higher in the antibonding orbital in the branched isomer. In fact, this was confirmed by the calculated population of bonding and antibonding orbitals ($P_{\sigma\sigma}$ and $P_{\sigma^*\sigma^*}$: the diagonal element of the density matrix). The σ_{CC} orbital is less populated in isobutane ($P_{\sigma\sigma} = 2.3423$) than in n-butane ($P_{\sigma\sigma} = 2.3435$). The $P_{\sigma^*\sigma^*}$ values, 0.0187 in isobutane and 0.0183 in n-butane, showed that the antibonding σ_{CC}^* orbital is more densely populated on branching. The significant loss of the population by the bonding (σ_{CC}) and the acceptance by the antibonding (σ_{CC}^*) orbital in the branched isomer lengthen the C−C bond distance.

Chart 1



4. Branching Rules

We derived some interesting rules of the branching effects on the stabilities of higher alkane isomers and alkene derivatives to demonstrate the extensive applicability of the orbital phase theory.

Alkanes. The orbital phase theory has shown the preference of the cross σ-conjugation of two C−H bonds with one C−C bond antiperiplanar to each other to the linear conjugation (Chart 1). The relative stabilities should depend primarily on the numbers (n_c) of the cross σ-conjugations contained in isomers. The more cross conjugation an isomer has, the more stable it is. We used the n_c values of the conformers where the longest C−C chains have trans zigzag structures.

Rule 1: *The branching stabilizes the isomers. The* n-C_nH_{2n+2} *are the most unstable isomers.* There is no cross σ-conjugation in the normal isomers. However, any branching gives rise to at least one cross conjugation, leading to the relative stabilities of the branched isomers. This rule was substantiated by the experimental observation[2] (Figure 3). In fact, both the terminal (2-methyl-substituted) and the inner (3-methyl-substituted, etc.) branched, both the methyl- and ethyl-substituted, and both the singly and multiply branched isomers are all more stable than the n-alkanes. Nevertheless, different kinds of branching causes stabilization to different degrees, as indicated in the following rules.

Rule 2: *The neopentane-type branching is more stabilizing than the isobutane-type branching.* Neopentane (**15**) contains 12-fold cross σ-conjugations ($n_c = 12$), while isopentane (**5**) only contains two cross conjugations ($n_c = 2$). Thus, neopentane is predicted to be more stable than the isopentane. This was confirmed by experimental observations[2] as shown in Figure 4, together with the more favorable neopentane-type branching in higher alkanes **16**−**23**. In fact, all the most stable isomers of C_nH_{2n+2} contain the neopentane unit when $n \geq 5$. In addition, the C−C bond length in neopentane (1.5351 Å) is longer than that in isobutane (1.5307 Å),[5] as expected from the more significant C−C bond polarization.

Rule 3: *The terminal branching is more stabilizing than the inner branching.* The change of the branching position from the terminal ends to the inner carbons results in the loss of one

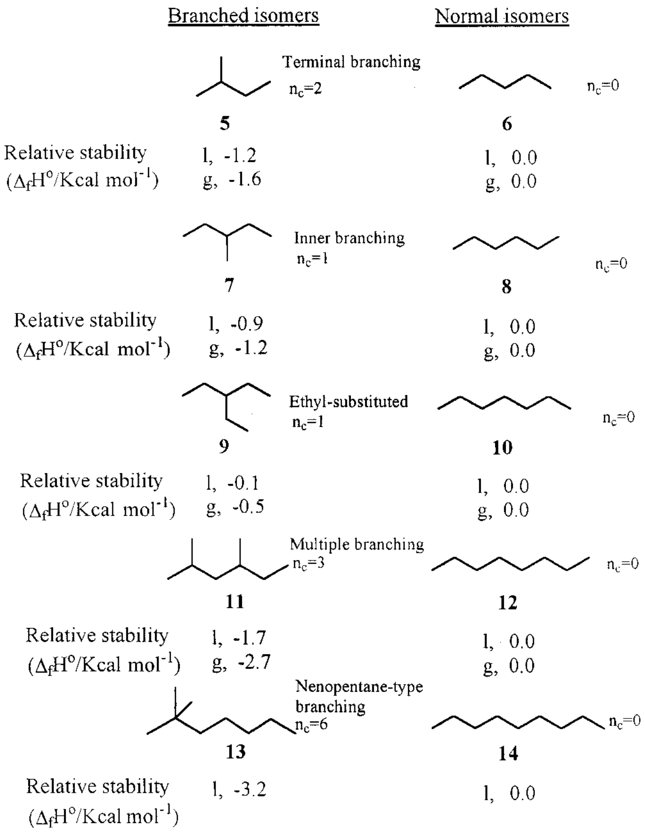


Figure 3. The observed relative stabilities, $\Delta_f H°(298.15)$, of the branched vs normal isomers. The letters l and g denote the liquid and gas phases, respectively.

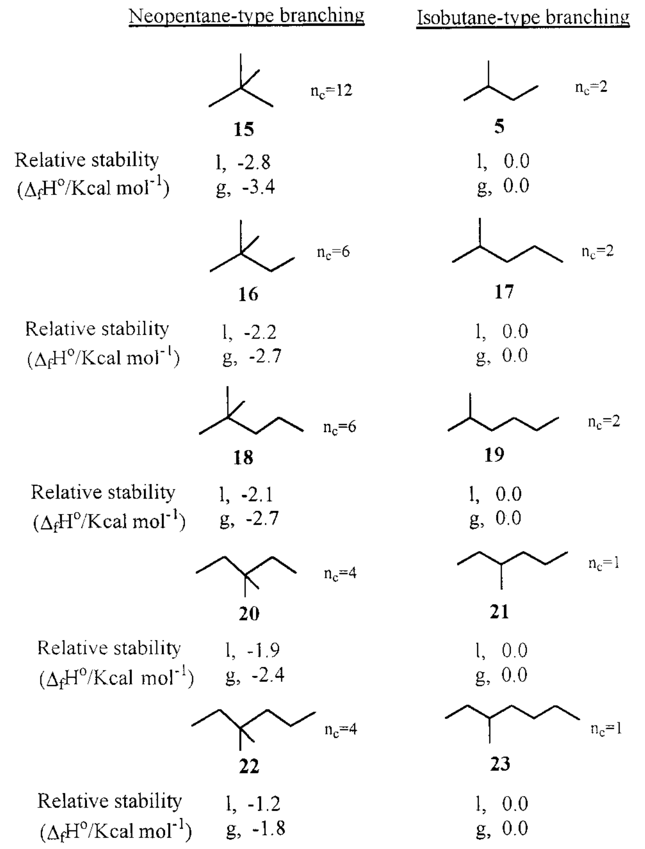


Figure 4. The observed relative stabilities, $\Delta_f H°(298.15)$, of neopentane-type branching vs isobutane-type branching. The letters l and g denote the liquid and gas phases, respectively.

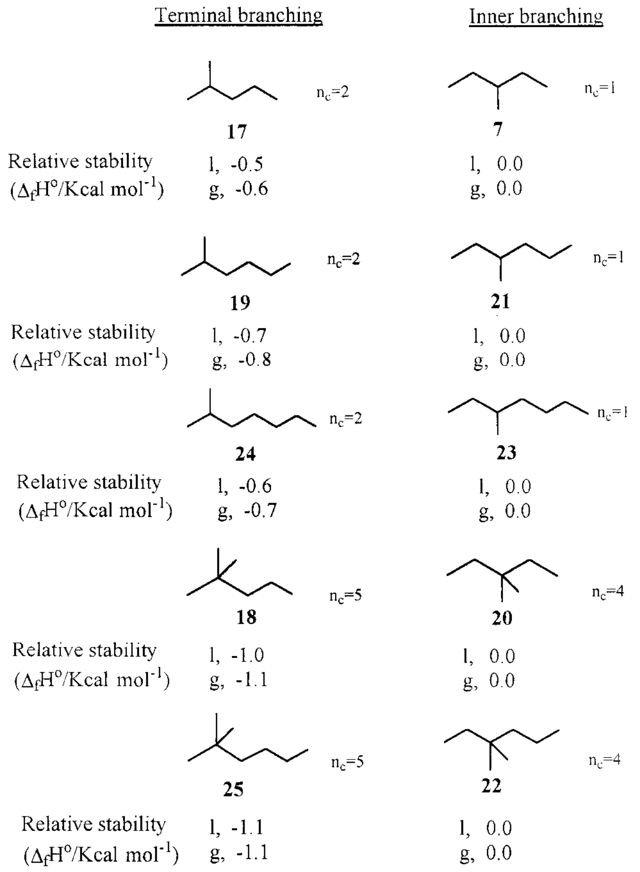


Figure 5. The observed relative stabilities, $\Delta_f H°(298.15)$, of the terminal branching vs inner branching. The letters l and g denote the liquid and gas phases, respectively.

cross conjugation. For example, 2-methylpentane (**17**) has two cross conjugations ($n_c = 2$), while 3-methylpentane (**7**) has only one ($n_c = 1$). The 2-methyl isomer is more stable than the 3-methyl isomer (Figure 5).[2] By analogy, the preferential terminal branchings to the inner ones were also predicted in other alkanes and confirmed by the experimental data. The numbers of the cross conjugations are identical as far as the branching occurs at the inner carbons. The difference in the stabilities is very small between two inner branched isomers. For example, the observed stability[2] of 4-methylheptane relative to 3-methylheptane (**23**) only differs by 0.17 kcal/mol in the liquid phase and by 0.12 kcal/mol in the gas phase, while that relative to 2-methylheptane (**24**) differs by 0.81 kcal/mol in both the liquid and gas phases.

Rule 4: *The methyl substitution is more stabilizing than the ethyl substitution.* There is an identical number ($n_c = 1$) for cross σ conjugation in the isomers substituted by methyl and ethyl groups. The number of linear σ-conjugations (n_l) of two C−H bonds with one antiperiplanar C−C bond (Chart 1) is expected to determine the relative stabilities of the methyl- and ethyl-substituted isomers. The orbital phase is discontinuous in the linear σ conjugation. The stability decreases when the isomers contain the linear σ conjugation. The ethyl-substituted isomers contain a linear conjugation ($n_l = 1$), while the methyl-substituted isomers contain none ($n_l = 0$). Thus the ethyl substitution stabilizes the isomers less. The experimental $\Delta_f H°$ values of **21** vs **9** and **23** vs **26** confirmed the preferred methyl substitution (Figure 6).[2] This rule is applicable to the stability of 3,3-dimethylhexane (**22**) relative to 3-methyl-3-ethylpentane (**27**). However, the numbers of cross σ conjugations are different

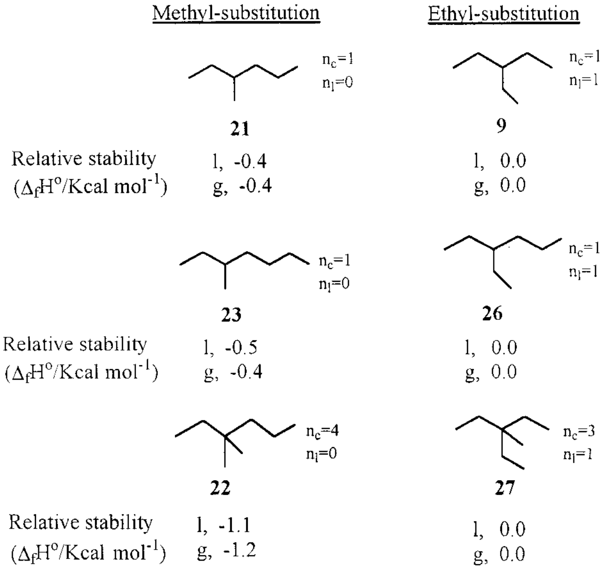


Figure 6. The observed relative stabilities, $\Delta_f H°$(298.15) of methyl substitution vs ethyl substitution. The letters l and g denote the liquid and gas phases, respectively.

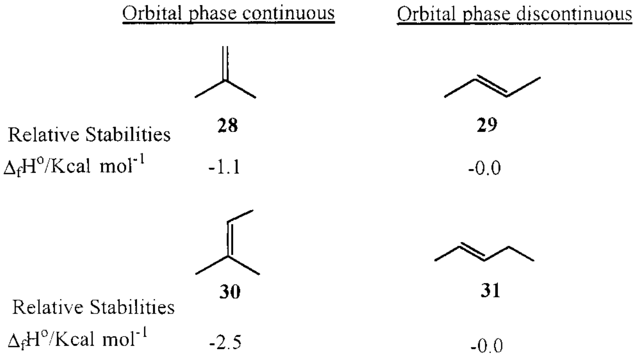


Figure 7. The observed relative stabilities, $\Delta_f H°$(298.15, liquid state), of the branched vs normal isomers of alkenes.

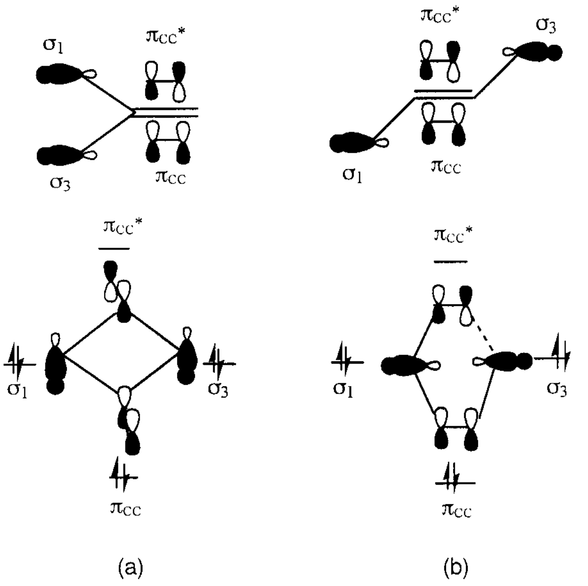


Figure 8. The orbital phase properties in C_4H_8: (a) the continuity in **28** and (b) the discontinuity in **29**.

from each other ($n_c = 4$ in **22**; $n_c = 3$ in **27**). The energy difference is greater than that between **21** and **9** and that between **23** and **26**.

Alkenes. When the central C−C σ bond is replaced by a C=C π bond, the σ-conjugated molecules **1a** and **2a** are transferred into 2-methylpropene (**28**) and *trans*-2-butene (**29**) (Figure 7). In place of the cyclic orbital interaction of $-\sigma_2-\sigma_1-\sigma_2{}^*-\sigma_3-$ in **1a** and **2a** (Figure 1), the similar cyclic interaction among the σ_1, σ_3, π_{CC}, and $\pi_{CC}{}^*$ orbitals occurs in **28** and **29**. The olefins **28** and **29** have the same orbital phase properties as their σ-conjugated counterparts of **1a** and **2a**, respectively (Figure 8). The branched isomer **28** should be more stable than the linear conjugated one due to the phase continuity of the cross-conjugation in **28**. The experimental data[2] also showed this branching preference as presented in Figure 7. The similar orbital phase analysis can be applied to the stability of 2-methyl-2-butene (**30**) relative to 2-pentene (**31**) (Figure 7). In alkenes there also exists the preferential stabilization of the branched isomers relative to the corresponding normal ones.

5. Conclusions

The orbital phase theory has been employed to predict that the branched isomers of E_4H_{10} (E = C, Si, Ge, Sn), **1**, are more stable than the normal ones, **2**. The preferred branching was confirmed by ab initio molecular orbital and density functional theory calculations as well as by some experimental data.[1,2] The orbital phase theory leads to the following rules: the preference of the branched isomers to normal ones, neopentane-type to isobutane-type branching, the terminal to the inner branching, the methyl to ethyl substitution in the longer alkanes, and the isobutene to 2-butene moieties. The preferential stabilization of the branched isomer has been shown to be a general phenomenon in the σ- and π-conjugated closed-shell molecules[11] as well as the open-shell species,[17,18] except for polyenes.[12]

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