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Correlation Effects on the Relative Stabilities of Alkanes

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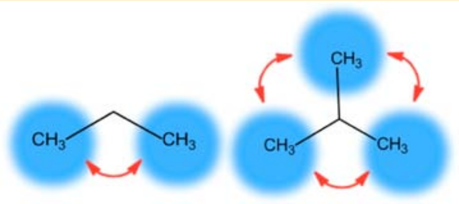
Supporting Information



ABSTRACT: The "alkane branching effect" denotes the fact that simple alkanes with more highly branched carbon skeletons, for example, isobutane and neopentane, are more stable than their normal isomers, for example, *n*-butane and *n*-pentane. Although *n*-alkanes have no branches, the "kinks" (or "protobranches") in their chains (defined as the composite of 1,3-alkyl−alkyl interactions—including methine, methylene, and methyl groups as alkyl entities—present in most linear, cyclic, and branched alkanes, but not methane or ethane) also are associated with lower energies. Branching and protobranching stabilization energies are evaluated by isodesmic comparisons of protobranched alkanes with ethane. Accurate ab initio characterization of branching and protobranching stability requires post-self-consistent field (SCF) treatments, which account for medium range (∼1.5−3.0 Å) electron correlation. Localized molecular orbital second-order Møller−Plesset (LMO-MP2) partitioning of the correlation energies of simple alkanes into localized contributions indicates that correlation effects between electrons in 1,3-alkyl groups are largely responsible for the enhanced correlation energies and general stabilities of branched and protobranched alkanes.

■ INTRODUCTION

Nearly 80 years have passed since it was established that branched alkanes like isobutane and neopentane are more stable energetically than their "normal" isomers, *n*-butane and *n*-pentane.[1,2] Since then myriad proposed explanations of this "branching effect" have appeared,[3−23] but general consensus regarding the origins of branching stability is still lacking. One of the first and best known explanations is that of Pitzer and Catalano,[8] who suggested that the electron correlation energies of more highly branched alkane isomers exceed those of their less branched counterparts. Though they never speculated which intramolecular interactions were responsible for the greater correlation energies of branched alkanes, modern ab initio studies have now definitively established that reliable branching energies are reproduced only by electron correlated methods and that Hartree−Fock and density functional theory (DFT) treatments which do not adequately account for such correlation effects fail to recover the alkane branching effect satisfactorily.[17a,21,25−38]

Another explanation for branching stability supposes that imbalances in geminal electron delocalization (i.e., resonance or hyperconjugation between adjacent bonds) effects favor branching in isomeric alkanes. Interest in hyperconjugative models of alkane branching first appeared in the early work of Brown,[6] Dewar et al.,[7] and Pople and Santry[10] and has been recently renewed. Inagaki[14] argued that electron delocalization from C−H to vicinal C−C bonds favors branching in alkanes, and Kemnitz et al.[22] suggested that increased C−C−C geminal hyperconjugation is responsible for the branching effect. Such studies provide insight into the origins of branching stability at the self-consistent field (SCF) level, but the question of why electron correlation effects strongly stabilize branched alkanes remains unsettled.

Based on the early ideas of Bartell et al.,[11,24] Gronert[18] advanced a geminal repulsion model of alkane branching, positing that more highly branched alkanes are subject to decreased intramolecular repulsion compared to their less branched isomers. However, Bartell[39] has recently criticized Gronert's model, and several theoretical studies indicate that alkane branching increases intramolecular repulsions. Laidig[13a] showed that the repulsive (energy raising) components of the Hartree−Fock Hamiltonian, that is, electron−electron repulsion, nuclear−nuclear repulsion, and the electron kinetic energy, all increase with increasing branching in alkanes but are overcome by an even larger increase in electron nuclear attraction.[13b] De Proft et al.'s[21] DFT energetic component analysis also suggests that branched alkanes are destabilized by increased Pauli exchange and classical electrostatic repulsions but that greater electrostatic attraction and electron correlation stabilization overcome these effects, giving rise to branching stability. Finally, Kemnitz et al.'s[22] natural bond orbital steric analysis[40] of geminal Pauli-exchange repulsions in alkanes also found that branching in alkanes increases their intramolecular repulsion. Each of these works indicates that branching stability is an attractive dominant process (i.e., governed by attractive interactions).

Our "protobranching" model, based on the effect of electron correlation,[17a] attributes the enhanced stability of branched alkanes to their greater number of 1,3-alkyl−alkyl interactions, or "protobranches" (taking methine, methylene, and methyl groups of alkanes as alkyl units, cf. Figure 1). The simplest example of a protobranching interaction is the 1,3-methyl−methyl interaction in propane. However, 1,3-methyl−methyl-

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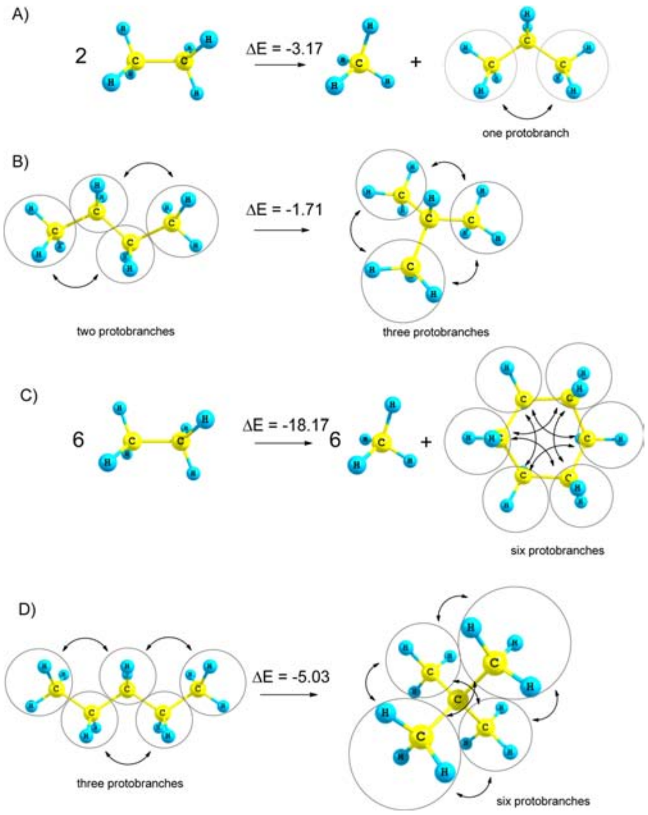


Figure 1. Equations for evaluating protobranching (A, C) and branching (B, D) stabilization. Energy changes (kcal/mol) are taken from experimental heats of formation data at 0 K.[42]

ene and methylene–methylene interactions also constitute protobranches, and their near-energetic equivalence to 1,3-methyl–methyl interactions is suggested by the nearly constant (ca. 5 kcal/mol) increase in *n*-alkane heats of formation along the series propane, *n*-butane, *n*-pentane, and so forth. As originally conceived, "protobranching" is a descriptive term designating "the onset of branching." The designation "protobranch" was introduced to call attention to the structural relationship between the "kinked" geometry of propane (and other *n*-alkanes) and the similar "kinks" in branched alkanes, like isobutane and neopentane. Propane is the smallest alkane with a protobranch, since by definition, by usage, and by analogy with isobutane and neopentane, there must be an open edge lacking a conventional bond.[17a] The energy-lowering effects of "protobranching" refer to the "net stabilizing composite of 1,3-alkyl–alkyl interactions not present in methane or ethane."[17b,41] Such protobranching stabilization involves all of the various nonbonded interactions among all the 1,3-alkyl–alkyl group atoms, for example, 1,4- and 1,5-interatomic interactions.

Our previous discussion of the protobranching concept[17] focused on the interpretive implications of regarding 1,3-alkyl–alkyl interactions as stabilizing, postponing detailed exploration the underlying origins of this "attraction" (i.e., stabilization). We examine here the origins of the strong electron correlation stabilization of branched and protobranched alkanes and the extent to which 1,3-alkyl–alkyl interactions are responsible. We note that electron correlation effects are not the only source of branching and protobranching stability. In some cases, SCF treatments recover a portion of this stabilization, and the ZPVEs of alkane isomers also favor branching. However, these contributions to the branching effect have been examined in detail elsewhere.[6,7,10,12,13,21,22,34]

■ RESULTS AND DISCUSSION

Redfern et al.[25] noted more than 10 years ago that theoretical treatments which do not properly account for electron correlation effects fail to describe alkane isomerization energies adequately; since then these shortcomings have been well-documented.[26−37] Similarly, such treatments also fail to recover protobranching stabilization satisfactorily, for example, the enhanced stability of linear alkanes with 1,3-alkyl–alkyl interactions relative to ethane. This problem has been evaluated extensively by assessing the errors associated with theoretical evaluations of the energy change of eq 1, where the product alkane is taken to be the linear isomer.[28,33,36,38]

$$(m-1)C_2H_6 \rightarrow C_mH_{2m+2} + (m-2)CH_4 \qquad (1)$$

Moreover, even greater errors are encountered when the product of eq 1 is taken to be the most branched isomer (which contains more protobranching interactions). For illustrative purposes Table 1 presents these errors at the HF, B3LYP, B3LYP-D3, and MP2 levels (far more extensive tabulations may be found elsewhere).[28,33,36,38]

The comparisons between theory and experiment presented in Table 1 are subject to the usual caveats regarding the limitations of the harmonic frequency approximation,[43] but clearly protobranching stabilization is not adequately described

Table 1. Energy Changes (kcal/mol) of Selected Isodesmic Equations Involving Alkanes Given by Experimental Heats of Formation Data at 0 K[42a] and the HF, B3LYP, B3LYP-D3, and MP2 Levels (cc-pVTZ Basis Set)[a]

equation	HF	B3LYP	B3LYP-D3	MP2	expt
2 ethane → propane + methane	−1.66 (+1.51)	−1.92 (+1.25)	−2.44 (+0.73)	−3.14 (+0.03)	−3.17
3 ethane → butane + 2 methane	−3.37 (+3.38)	−3.89 (+2.86)	−5.03 (+1.72)	−6.47 (+0.28)	−6.75
3 ethane → isobutane + 2 methane	−3.97 (+4.49)	−4.67 (+3.79)	−6.29 (+2.17)	−8.59 (−0.13)	−8.46
4 ethane → pentane + 3 methane	−5.06 (+5.10)	−5.81 (+4.35)	−7.61 (+2.55)	−9.81 (+0.35)	−10.16
4 ethane → neopentane + 3 methane	−6.04 (+9.15)	−7.21 (+7.98)	−10.51 (+4.68)	−15.50 (−0.31)	−15.19
5 ethane → hexane + 4 methane	−6.78 (+6.81)	−7.78 (+5.81)	−10.24 (+3.35)	−13.18 (+0.41)	−13.59
5 ethane → 2,2-dimethylbutane + 4 methane	−5.04 (+11.74)	−7.04 (+9.74)	−11.64 (+5.14)	−17.80 (−1.02)	−16.78
6 ethane → heptane + 5 methane	−8.50 (+8.52)	−9.73 (+7.29)	−12.85 (+4.17)	−16.56 (+0.46)	−17.02
6 ethane → 2,2,3-trimethylbutane + 5 methane	−3.14 (+16.47)	−6.31 (+13.30)	−12.84 (+6.77)	−21.20 (−1.59)	−19.61
7 ethane → octane + 6 methane	−10.22 (+10.23)	−11.71 (+8.74)	−15.49 (+4.96)	−19.95 (+0.50)	−20.45
7 ethane → 2,2,3,3-tetramethylbutane + 6 methane	+0.02 (+23.15)	−4.50 (+18.63)	−13.56 (+9.57)	−25.57 (−2.43)	−23.13

[a] Errors relative to experiment are given in parentheses. Computational data include ZPE corrections.

at the HF or B3LYP levels. Appending the empirical "D3" dispersion correction[44] to the B3LYP functional improves agreement between theory and experiment, but significant discrepancies remain,[45] and similar errors have also been reported for the popular M06 family of functionals.[36,38] Only the MP2 values in Table 1 match experimental data, underscoring the need for post-SCF treatments when computing of the energy change of isodesmic or isomerization equations which are protobranching imbalanced. Of course, more accurate protobranching energies may be obtained by employing higher levels of theory (see refs 33, 43, and 46 for high-accuracy computations of alkane energies), but we are concerned here with understanding *why* electron correlation effects preferentially stabilize branched and protobranched alkanes.

Clearly, branched alkanes are stabilized by electron correlation effects relative to their less branched isomers because their structures and hence electron distributions are more compact. This is demonstrated by the decrease in the molecular surface areas of simple alkane isomers with increasing branching (see the Supporting Information). Similarly, the products of eq 1, which evaluates protobranching stabilization, also have a lower combined surface area than the reactants (Figure 2). Moreover, a linear relationship exists between the decrease in the total molecular surface area of the products of eq 1 relative to the reactants and their enhanced stability due to electron correlation effects (Figure 2 plots this data for all possible alkane products of eq 1 where $3 \leq m \leq 7$). This trend illustrates a general relationship among alkanes with 3−7 carbon atoms between the number protobranching interactions they contain, their molecular compactness, and their correlation energy.

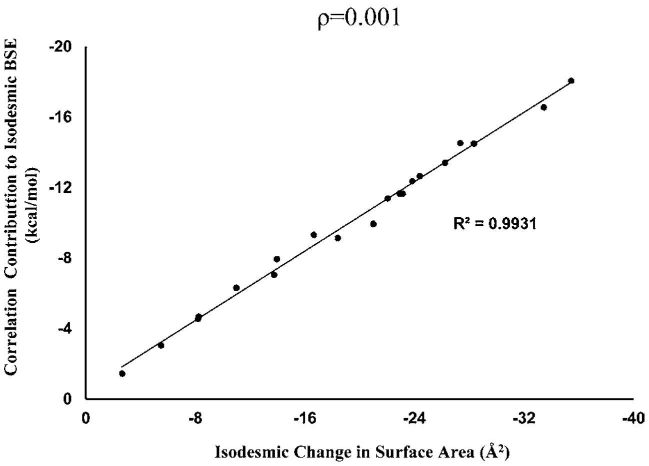
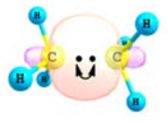


Figure 2. Correlation contribution ($\Delta E_{[\mathrm{MP2}]} - \Delta E_{[\mathrm{HF}]}$, kcal/mol) to the change in electronic isodesmic bond separation energy (BSE) of eq 1 for all alkane products with 3−7 carbon atoms vs the change in molecular surface area (in Å^2). Results are based on MP2/cc-pVTZ geometries. Molecular surface areas were computed in Chimera[47] with $\rho = 0.001$.

But can the correlation stabilization of branched and protobranched alkanes be explained in terms of specific intramolecular interactions? To examine this we partition the MP2 correlation energy into localized contributions as in Grimme's[26] 2006 survey of branching stabilization.[48] The frozen-core MP2 correction ($E^{(2)}$) to the HF energy may be interpreted physically as the sum of individual two-electron correlation energies between all possible pairs of valence electrons in a molecule. These electron-pair correlation energies, or "pair energies" more simply, are usually evaluated between two electrons in canonical MOs and hence are not easily interpretable in terms of specific intramolecular interactions. However, since the MP2 correction is invariant to unitary transformations of the occupied MOs, the same correlation energy is obtained whether canonical or localized MOs (LMO) are used as a basis for an MP2 treatment.[49a] The advantage of LMO-MP2 is that the total correlation energy of a molecule can be partitioned into additive contributions from electron pairs occupying localized bonding or lone pair orbitals. Each localized pair energy is typically classified as being either an "intrapair" energy, which results from correlation effects between two electrons occupying the same LMO, or an "interpair" energy, which corresponds to correlation effects between two electrons each in different LMOs. We emphasize that the designation "LMO-MP2" refers to an MP2 treatment with localized occupied orbitals and canonical virtual orbitals, which differs from local correlation methods (e.g., LMP2) which localize both occupied and virtual orbitals as a means of improving the computational efficiency of post-SCF levels of theory.[49b]

Grimme's[26] LMO-MP2 decomposition of the branching effect revealed that the intrapair correlation energies of isomeric alkanes are essentially equal, and hence that branching stabilization results solely from interpair correlation effects (i.e., correlation between pairs of electrons in different orbitals). The result is sensible as isomers necessarily contain the same number and types of bonds but differ in intramolecular interactions. Grimme also partitioned electron interpairs into groups based on the distance between the centroids of the two LMOs occupied by each electron of a given pair and showed that the bulk of branching stability results from electron correlation effects over medium range distances (i.e., ∼1.5−3.0 Å). An alternative partitioning of interpair energies is advantageous for our purposes. We divide interpairs into groups based on the spatial relationship of the LMOs each electron of a given pair occupies. Two electrons occupying LMOs in a geminal relationship are denoted a 1,2-pair; those occupying vicinal LMOs are a 1,3-pair, and so forth. Examples of this partitioning scheme, which essentially divides the electron correlation energies of alkanes into geminal (1,2), vicinal (1,3), and longer range correlation contributions (1,N where $N \geq 4$) are depicted in Figure 3. Note that in an LMO basis, 1,3-alkyl−alkyl interactions correspond precisely to 1,4-electron pairs, since 1,3-pairs are present in ethane, which experiences vicinal correlation effects but contains no protobranches, while 1,5 and more distant pairs are not present in propane, the smallest protobranched alkane.

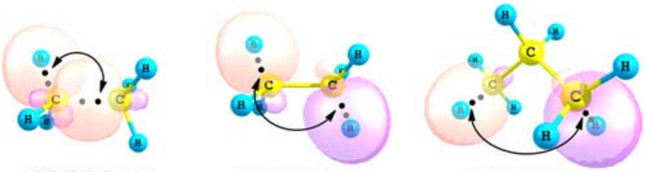
Table 2 presents the changes in intrapair and 1,N interpair correlation energies for several isodesmic and isomerization equations involving simple alkanes. We employed Pipek−Mezey orbital localization,[50a] but alternative localization methods (e.g., the Boys,[50b] minimum population,[50c] and Ruedenberg[50d] methods) give similar results. If 1,3-alkyl−alkyl interactions are responsible for branching and protobranching stability, then 1,4-pair energies are expected to contribute dominantly to the electron correlation stabilization of protobranched and branched alkanes, respectively. This is clearly the case for the protobranching stabilization of propane (eq a in Table 2). The changes in intrapair and vicinal (i.e., 1,3) interpair correlation energies are small and stabilize the



Intrapair

1,1 C-C pair

Interpairs



1,2 C-H/C-C pair (geminal correlation)

1,3 C-H/C-H pair (vicinal correlation)

1,4 C-H/C-H pair (1,3 alkyl-alkyl correlation)

Figure 3. Representative examples of the pair energy partitioning used in this work. An "electron pair" consists of two electrons in either the same LMO (intrapair) or two electrons in separate LMOs (interpair).

reactants, while the change in the 1,2-interpair correlation is nearly zero. Thus 98% of the interpair correlation stabilization of the products is due to 1,4-pair correlation effects between the C—H bonds in the methyl groups of propane (see Figure 3 for a representative example), which have no counterpart in ethane or methane. The changes in pair energies of eqs b and c in Table 2, which evaluate the branching stabilization of isobutane and neopentane, are largely similar. Aside from a relatively small stabilization from geminal correlation effects, the bulk of the enhanced electron correlation stabilization of isobutane and neopentane relative to *n*-butane and *n*-pentane is due to increased 1,4-interpair stabilization. This corresponds again to correlation effects between pairs of C—H bonds in 1,3-methyl groups.

The trends in Table 2 result largely from imbalances in the number of 1,*N* interpairs between the reactants and products and the fact that the magnitude of interpair energies decreases sharply (approximately as $1/r^6$)[49] as the distance between the two LMOs occupied by an given electron pair is increased. For example, although 1,2- and 1,3-pair interactions are largest in magnitude, their numbers are balanced in eqs a—d. Thus there are only small discrepancies in their sums between the reactants and products, which are due mainly to differences in the types of geminal and vicinal bonds being correlated (e.g., eqs a and b trade two 1,3-C—H/C—C interpairs for one 1,3-C—C/C—C and one 1,3-C—H/C—H interpair). In contrast, the number of 1,4-pair energies in eqs a—c is not balanced. Indeed any isodesmic or isomerization equation involving only alkanes which is not protobranching balanced cannot balance the number of 1,4-interpairs, as 1,3-alkyl—alkyl correlation effects and 1,4-pair energies are equivalent in such cases. Hence, the 1,4-interpair stabilization of propane, isobutane, and neopentane arises simply because they contain more 1,4-interpairs than the reactants in eqs a, b, and c. Ethane has no protobranches and hence no 1,4-interpairs, while the isomerization of *n*-butane to isobutane and *n*-pentane to neopentane trades 1,5 (and in the case of *n*-pentane also 1,6) interpairs for 1,4-interpairs. Since 1,4-pair energies are larger than those of the 1,5- and 1,6-types, this trade is favorable. Indeed 1,5- and longer range correlation effects generally contribute little to the relative stabilities of simple alkanes. This is illustrated by eq d in Table 2, which is protobranching balanced, and as a result conserves the numbers of 1,2-, 1,3-, and 1,4-interpairs between reactants and products. The MP2 correction to the HF energy change is small in this case, as the 1,5-pairs energies of butane, which correspond to long-range dispersion interactions, only weakly favor the products. Since no substantial correlation contribution to the reaction energy exists, it is not surprising that the HF and DFT treatments which do not accurately describe protobranching stabilization predict the energy change of eq d to within less than half a kilocalorie of the −0.41 kcal/mol experimental value at 0 K.[42,51] This further highlights that the failure of such methods to adequately reproduce protobranching energies results principally from deficiencies in their description of medium range electron correlation effects.

The stabilization of propane, isobutane, and neopentane by 1,3-alkyl—alkyl correlation effects also is present in other linear, branched, and cyclic alkanes. This is apparent from Table 3, which evaluates the correlation contribution to a variety of protobranching imbalanced isodesmic and isomerization equations. While the intrapair contribution to each reaction energy is small, the interpair correlation energy stabilizes the more highly protobranched products, predominately due to their greater number of 1,4-interpairs. The large protobranching energy of cyclohexane (given by the eq: 6 ethane → cyclohexane + 6 methane) is particularly noteworthy. Though generally considered to be "strain free", cyclohexane, like neopentane, contains six protobranching interactions and exhibits comparable protobranching stabilization (−12.62 vs −11.93 kcal/mol, respectively, see Table 3). Hence, rather than being regarded as a strain free paradigm, cyclohexane has a considerable "negative strain". The isomerization of pentane to isopentane also is interesting. In this case increased 1,4-interpair stabilization accounts for only 58% of the total electron correlation stabilization of isopentane, while the rest results from remarkably large 1,5-pair correlations in isopentane. These large 1,5-pair contributions are due to the gauche interaction between isopentane's 1,4-methyl groups, which causes crowding between the neighboring 1,6-hydrogen atoms (whose distances resemble those typical of hydrogens in 1,3-

Table 2. Change in the Sum of Intrapair and 1,*N*-Interpair Correlation Energies ($\Delta e^{(2)}_{\text{intra}}$ and $\Delta e^{(2)}_{1,N\text{-inter}}$) along with the Total Change in Correlation Energy ($\Delta E^{(2)}$) for Selected Equations[a]

	$\Delta e^{(2)}_{\text{intra}}$	$\Delta e^{(2)}_{1,N\text{-inter}}$					
	1,1	1,2	1,3	1,4	1,5	1,6	$\Delta E^{(2)}$
(a) 2 ethane → propane + methane	+0.20	0.04	+0.17	−1.80			−1.47
(b) *n*-butane → isobutane	+0.11	−0.22	+0.43	−2.06	+0.24		−1.50
(c) *n*-pentane → neopentane	+0.24	−0.57	+1.43	−6.23	+0.46	+0.05	−4.62
(d) 2 propane → *n*-butane + ethane	+0.02	+0.08	−0.03	+0.05	−0.24		−0.12

[a] Electronic energies (in kcal/mol) were computed at the MP2/cc-pVTZ level.

Table 3. LMO-MP2 Decomposition of the Correlation Contribution ($\Delta E^{(2)} = \Delta E_{MP2} - \Delta E_{HF}$) to the Electronic Energy Change of Selected Isodesmic and Isomerization Equations of Simple Alkanes[a]

	ΔE_{HF}	ΔE_{MP2}	$\Delta E^{(2)}$	$\Delta e^{(2)}_{intra}$	$\Delta e^{(2)}_{inter}$	% $\Delta e^{(2)}_{inter}$ stabilization due to 1,4-pair energy imbalances
			Protobranching Equations			
2 ethane → propane + methane	−0.87	−2.34	−1.47	0.20	−1.67	98
3 ethane → butane + 2 methane	−1.69	−4.75	−3.06	0.41	−3.47	94
3 ethane → isobutane + 2 methane	−1.96	−6.52	−4.56	0.53	−5.09	96
4 ethane → pentane + 3 methane	−2.47	−7.14	−4.67	0.63	−5.30	91
4 ethane → isopentane + 3 methane	−1.44	−8.49	−7.05	0.72	−7.78	81
4 ethane → neopentane + 3 methane	−2.64	−11.93	−9.29	0.86	−10.16	96
5 ethane → cyclopentane + 5 methane	2.13	−3.69	−5.82	0.92	−6.73	73
6 ethane → cyclohexane + 6 methane	−4.43	−12.62	−8.19	1.13	−9.33	87
			Branching Equations			
butane→ isobutane	−0.27	−1.77	−1.50	0.11	−1.61	90
pentane→ isopentane	1.02	−1.36	−2.38	0.10	−2.48	58
pentane → neopentane	−0.17	−4.79	−4.62	0.24	−4.86	92
isopentane→ neopentane	−1.20	−3.44	−2.24	0.14	−2.37	96

[a] $\Delta E^{(2)}$ is the total change in correlation energy, and $\Delta e^{(2)}_{intra}$ and $\Delta e^{(2)}_{inter}$ are the changes in the sum of intrapair and interpair energies, respectively. The percent of the total interpair stabilization of the products due to 1,4-interpair energies is given in the rightmost column. Both the HF and the MP2 energy changes (kcal/mol, cc-pvTZ basis set) are based on the MP2/cc-pVTZ geometries.

methyl groups, see Figure 4) and increased 1,5-C−H/C−H pair energies.

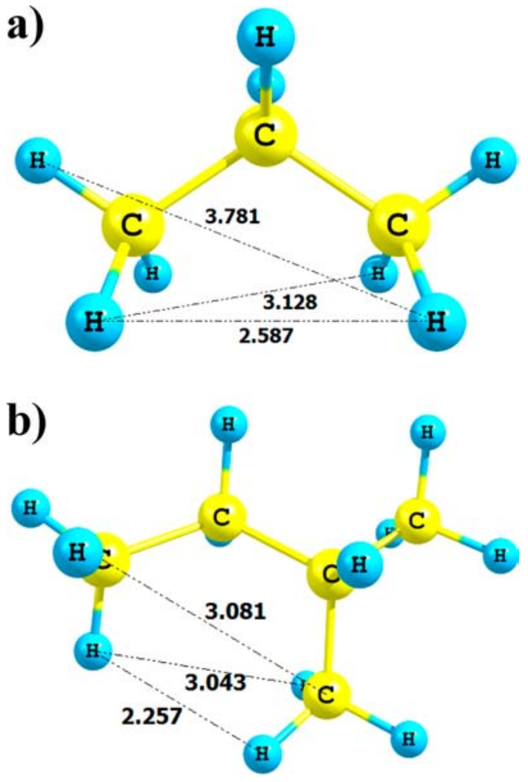


Figure 4. Selected distances (Å) between 1,5-hydrogens in propane and 1,6-hydrogens and 1,4-carbons in isopentane at the MP2/cc-pVTZ level.

On the basis of our LMO-MP2 analysis, it is clear that 1,3-alkyl−alkyl electron correlation effects stabilize protobranched alkanes considerably. But are such interactions "attractive"? Simple vdW considerations are suggestive. In our alkane set, most 1,4-pairs correspond to correlation effects between the C−H bonds in 1,3-alkyl groups. The shortest distances between the 1,5-hydrogen atoms involved in these 1,3-alkyl−alkyl interactions are about 2.59 Å (see Figure 4a). This value exceeds twice the sum of the various estimates for the vdW radius of hydrogen given by Bondi,[52] Rowland and Taylor,[53] and Truhlar et al. (1.2 Å),[54] as well as that of Badenhoop and Weinhold (1.26−1.31 Å),[40] and Pauling (1.29 Å).[55] Hence these contacts are expected to be stabilizing. Aside from 1,5-C−H/C−H pairs, a smaller number of 1,5-C−H/C−C and C−C/C−C pair energies also contribute to the enhanced stability of protobranched alkanes whose carbon chain lengths are long enough to accommodate such interactions. However the 1,5 H/C and C/C distances of typical alkanes are generally also greater than the sum of their respective vdW radii (2.9 and 3.4 Å), so an attractive potential is expected.

Several recent investigations which attribute "attractive" character to the ~2.6−3.1 Å 1,5 H/H interactions in hydrocarbons are also noteworthy. Tsuzuki et al.'s[56] analysis of dispersion interactions in *n*-alkane dimers revealed surprisingly strong association energies, −2.80, −3.57, and −4.58 kcal/mol for *n*-butane, *n*-pentane, and *n*-hexane dimers, respectively, as well as intermolecular H···H contact distances ranging from 2.407 to 3.625 Å, which are like the 1,5-H/H distances in propane. Shaik et al.'s[57] QTAIM study of the binding of methane and polyhedrane dimers attributed the stabilization of these species to their short H/H contacts in the 2.15−3.20 Å range. Yang and co-workers'[58] noncovalent interaction (NCI) analysis, which identifies stabilizing or destabilizing through space interactions based on the electron density topology of a molecule, found the 1,5-H/H interactions in hexamethylethane to be attractive. Finally Schreiner et al.[23] attributed the remarkable thermal stability of coupled diamondoid molecules subject to extreme steric crowding to attractive intramolecular H/H interactions in the 1.9−2.6 Å range and speculated that a similar H/H attractions might explain the origin of protobranching stabilization. Our own findings provide a basis for this hypothesis.

If the interactions between hydrogen atoms in 1,3-alkyl groups are indeed attractive, a caveat regarding 1,4-alkyl−alkyl interactions is warranted. Gauche 1,4-alkyl−alkyl interactions force short H/H and C/C contacts which are smaller than the sum of their combined vdW radii. This leads to intramolecular repulsion,[18c] as is evidenced by, for example, the lowered branching energy of isopentane relative to isobutane. Both isoalkanes contain one more protobranch than their linear isomers, but the energy difference between *n*-pentane and isopentane is smaller than that between *n*-butane and isobutane (1.77 vs 1.36 kcal/mol, MP2/cc-pVTZ electronic energies, see Table 3). This can be explained by repulsive interactions in isopentane between a pair of 1,6-hydrogen atoms and 1,4-carbon atoms, whose interatomic distances are less than the sum of their combined vdW radii (2.26 and 3.08 Å vs 2.40 and 3.40 Å, respectively). Hence only a portion of the electron correlation stabilization of isopentane relative to pentane is attributable to branching stabilization (about 58%, see Table 3), while the remaining correlation energy counteracts the overly repulsive vdW potential of the isopentane gauche interaction given by HF theory.

The HF vs MP2 energy difference between anti and gauche *n*-butane conformations, both of which have two protobranches, also is illustrative. HF theory overestimates the (electronic) energy difference of the two conformers, giving 1.14 kcal/mol, but the MP2/cc-pVTZ value of 0.56 kcal/mol agrees well with the high level ab initio estimate of Allinger et al., 0.62 kcal/mol.[59] In this case about 80% of the MP2 electron correlation stabilization of gauche *n*-butane is due to pair correlation effects contained in its 1,4-methyl−methyl interaction (see the Supporting Information). However, as in isopentane, the 1,4-methyl−methyl interaction in gauche *n*-butane forces a pair of 1,6-hydrogen and 1,4-carbon atoms to distances (2.29 Å and 3.11 Å, respectively) shorter than the sum of their combined vdW radii; hence the correlation stabilization of gauche relative to anti *n*-butane does not represent an attractive interaction. We note that large, highly branched alkane isomers have many gauche interactions, and these are likely to play a significant role in determining their relative stabilities.[60]

■ CONCLUSION

Electron correlation effects contribute strongly to both branching and protobranching stability. Isomerization and isodesmic evaluations of branching and protobranching stabilization tend to balance short-range correlation, while unbalanced long-range contributions usually are negligible. Unbalanced medium range effects are primarily responsible for the correlation stabilization of both branched and protobranched alkanes. This medium range correlation is due to 1,3-alkyl−alkyl interactions, or more precisely the 1,4-electron pair correlations contained in these interactions. Most 1,4-pair energies correspond to correlations between the C−H bonds in 1,3-alkyl moieties, and simple vdW considerations of the 1,5-H/H distances involved suggest these interactions might be viewed as "attractive".

■ METHODS

All geometry optimizations and harmonic frequency computations at the HF and MP2 levels were performed using the Gaussian 2009 program. Molecular surface area calculations were performed in Chimera[47] with $\rho = 0.001$. LMO-MP2 pair energies and B3LYP and B3LYP-D3 energies and harmonic frequencies were computed in GAMESS (version 2009).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimized geometries and electronic energies of all alkanes considered, the LMO-MP2 pair energy partitioning of the correlation energy change for all isodesmic and isomerization equations in Table 3, and the energetic component analysis and change in molecular surface area of selected alkane isodesmic and isomerization equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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