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Origin of Stability in Branched Alkanes

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Abstract: The potential origins of stability in branched alkanes are investigated, paying close attention to two recent hypotheses: geminal steric repulsion and protobranching. All alkane isomers through C_6H_{14} along with heptane and octane were investigated at the MPW1B95/6-311++G(d,p) level. Their geminal steric repulsion, total steric repulsion, and orbital interactions were evaluated by using natural bond orbital analysis. All measures of steric repulsion fail to explain the stability of branched alkanes. The extra stability of branched alkanes and protobranching, in general, is tied to stabilizing geminal $\sigma \rightarrow \sigma^*$ delocalization, particularly of the type that involves adjacent C–C bonds and, thus, preferentially stabilizes branched alkanes. This picture is corroborated by valence bond calculations that attribute the effect to additional ionic structures (e.g., CH_3^+ $:CH_2$ $:CH_3^-$ and $CH_3:^-$ $CH_2:$ CH_3^+ for propane) that are not possible without protobranching.

Keywords: alkanes · bond theory · electronic structure · protobranching · steric hindrance

Introduction

It has long been known that branched alkanes are more stable than their linear isomers (Figure 1), but the origins of this stability are unclear. For each branch in an alkane, the measured heat of formation is lower than expected by about 2 kcal mol^{-1} in comparison to the linear isomer.[1,2] Although a variety of additivity schemes, such as those utilized by Cohen and Benson,[3] can reproduce these stability trends well, they offer few convincing arguments for the physical origins of the stability difference. Recently, two new and controversial additivity schemes purport to explain the additional stability of branched hydrocarbons. However, their explanations are diametrically opposed; one invokes repulsive steric factors, whereas the other relies on stabilizing terms.

Gronert's additivity scheme challenged the prevailing argument for the substitution effects on bond dissociation enthalpies (BDEs) of alkanes.[4] He suggested that hyperconjugative stabilization of alkyl radicals is negligible and that geminal steric interactions govern the stability of both alkanes and their radicals. The lower BDE of a more substi-

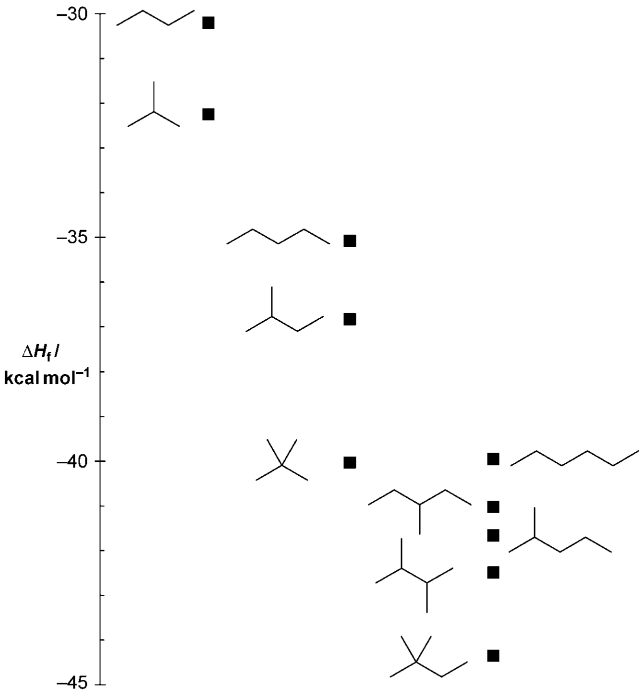

Figure 1. NIST standard enthalpies of formation, ΔH_f, demonstrating the greater stability of branched alkanes relative to their linear isomers.

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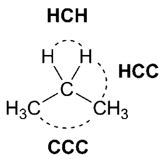


Scheme 1. Gronert's geminal steric repulsion terms are illustrated for the bonds surrounding the central carbon in propane.

tuted alkane is explained by the greater relief of geminal steric interactions present in the original alkane. For saturated hydrocarbons, one finds three classes of geminal steric interactions: HCH, HCC, and CCC as shown for propane in Scheme 1. Gronert was able to show that experimental heats of formation for alkanes, their radicals, $^3CH_2$, and ^4CH could be described well by a single equation containing different values for these three terms. Since alkanes, both linear and branched, also follow this equation, the seemingly counterintuitive explanation for the stability of branched alkanes is that they are sterically less hindered.

A number of responses quickly followed.[5] Wodrich and Schleyer countered that the data could be described equally well by terms for hyperconjugative stabilization of radicals and a 1,3-alkyl–alkyl stabilizing interaction that accounts for the enhanced stability of branched alkanes.[5a] This stabilizing interaction, later called "protobranching," is manifest even in straight chain alkanes, as shown with dashed arrows for the butane isomers in Figure 2.[6] The isodesmic reaction expressed by Equation (1) reveals a stabilizing factor of more than 2 kcal mol^{-1} for each protobranch (PB) when linear or branched alkanes are compared with ethane and methane, alkanes lacking any protobranching stabilization. With propane as the simplest protobranching example [Eq. (2)], the reaction is balanced in terms of the number of C–C bonds and C–H bonds, but has one more protobranching interaction in the products, resulting in a stabilization of 2.8 kcal mol^{-1} by using the National Institute of Standards and Technology (NIST) thermochemical data.[1]

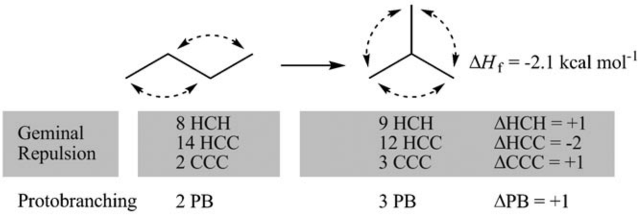


Figure 2. The functional equivalence of the geminal repulsion and protobranching additivity schemes is demonstrated for the isomerization reaction of butane.

$$(n-1)CH_3CH_3 \rightarrow C_nH_{(2n+2)} + (n-2)CH_4 \quad \Delta H_{PB} \tag{1}$$

$$\begin{gathered} 2CH_3CH_3 \rightarrow CH_3CH_2CH_3 + CH_4 \\ \Delta H_{PB}(\text{propane}) = -2.8\,\text{kcal mol}^{-1} \end{gathered} \tag{2}$$

One key difference between the explanation given by Gronert and that given by Wodrich and co-workers is the designation of 1,3-interactions as stabilizing or destabilizing. Although these rationalizations cite opposing physical forces, Fishtik[5b] pointed out that even excellent correlation within a group additivity scheme does not necessarily shed any light on the underlying cause of the phenomenon when variables are linearly dependent. In the case of protobranching reactions or isomerization reactions, such as the one shown in Figure 2, it is notable that each additional protobranch is always accompanied by an exchange of two HCC geminal steric repulsions for one HCH and one CCC geminal repulsion [Eq. (3)]. Thus, even though Wodrich and co-workers call their protobranching interaction stabilizing, that does not preclude the possibility that it could be caused by a difference in destabilizing interactions. For steric repulsion to be able to explain the stabilizing effect of protobranching or branching, the sum of HCH and CCC interactions must be less than twice the HCC interaction [Eq. (4)].

$$E_{PB} = E_{HCH} + E_{CCC} - 2E_{HCC} \tag{3}$$

$$E_{HCH} + E_{CCC} < 2E_{HCC} \tag{4}$$

Gronert is careful to note that though his model fits the data admirably this does not prove that geminal steric factors are the root cause of the observed effects. The true beauty of the geminal steric explanation is the straightforwardness of the model and clarity of the physical effect behind it. Gronert has recently criticized the protobranching theory as having no clear physical basis.[7] In this study, we seek to determine the origin of protobranching stability, whether it proves to be due to steric repulsion or some heretofore ill-characterized stabilizing factor. The simplicity of acyclic alkanes makes them an ideal starting point for the controversy regarding alkyl radical stability. However, since radicals are not required to test either new theory of hydrocarbon stability they were not included in this investigation.

The geminal steric repulsive interactions in alkanes are evaluated herein, by using a natural bond orbital (NBO) analysis with the ultimate purpose of determining if alkane stability trends are caused by steric repulsion. Similarly an NBO analysis provides clues as to the physical origin of the stabilizing effect of protobranching that is elucidated further with valence bond (VB) calculations.

Computational Methods

All alkane isomers through C_6H_{14} along with heptane and octane were optimized at the MPW1B95/6-311++G(d,p) level and verified as minima by frequency analysis using Gaussian 03.[8] Calculated heats of formation were evaluated at 298 K with thermal and zero-point vibrational energy (ZPVE) corrections. This density functional was chosen based on its established suitability for evaluation of nonbonding interactions.[9] "Lewis energies" were evaluated by using the NBO facility within Gaussian. Steric analysis was performed by using the NBO 5.0 program.[10] NBOs are localized orbitals obtained from a Hartree–Fock (HF) or DFT wave function by maximizing occupancy in 1-center and 2-center regions. Thus, valence electrons occupy orbitals that can be clearly identified as lone pair electrons or bonds and can thus be represented in a way familiar to chemists as a Lewis structure. For all of the alkanes studied here, well over 99 % of the electron density is described by this Lewis structure. The remaining non-Lewis electron density is due to excitation from localized Lewis orbitals into non-Lewis orbitals (e.g., antibonding orbitals). The delocalization energy can be assessed directly by deleting all non-Lewis orbitals and evaluating the energy of the localized wave function without any excitations. Natural steric analysis[11] is based on the electronic permutation antisymmetry of natural localized molecular orbitals (Pauli exchange repulsion). The use of localized orbitals allows the assessment of the energetic consequences of pairwise steric interactions or total steric interaction energies. The sum of the pairwise interaction energies differs from the total steric energy due to higher order effects caused by simultaneous interactions of many electron pairs.[12] VB calculations were performed with the VB2000 program[13] using the TZVP basis set.[14] All C−C bonds were treated in a single VB group with a localization enhancement factor of 1.0 to achieve a localization of well over 99 % on the target carbon atom so that ionic structures can be investigated. The remaining CH bonds were treated in separate VB groups for each carbon atom; for example, the CASVB calculation of propane was treated as a CASVB(4,4).VB(6).VB(4).VB(6), in which only the atom-localized orbitals making up C−C bonds were utilized in the active space.

Results and Discussion

The heats of formation for all alkane isomers through C_6H_{14}, along with heptane and octane, are represented in Table 1 after being normalized for the number of protobranches.[1] Those alkanes without any interfering *gauche* destabilizations average 2.8 kcal mol^{-1} of stabilization per protobranch. The average is virtually unchanged if one uses the entire set and compensates for steric repulsion due to *gauche* interactions.[2] The consistency of the protobranching stabilization for linear and branched alkanes lends credence to the suggestion that both are stabilized by the same root cause and thus, the protobranching reactions are used throughout this study as representative of the branching stabilization.[15] Since the steric analysis is not applicable to post self-consistent field (SCF) methods, we chose the MPW1B95/6-311++G(d,p) DFT method based on its established suitability for the evaluation of nonbonding interactions.[9] This method reproduces the same trends as the experimental values, but with notably smaller absolute values. In this study, the calculated ΔH_{PB} values are consistently too high by 0.8–1.0 kcal mol^{-1}PB^{-1}. Though Hartree–Fock (HF) and DFT methods are unable to reproduce the full extent of the protobranching stabilization[16,17] and the need for electron correlation (see below) has been noted,[6,16] our DFT method shows branched alkanes as more stable than their linear isomers. Since the error is linear with respect to the number of protobranches (Figure 3) and the protobranching stabilization is reproduced at two-thirds of its full effect by this DFT method, it is suitable for investigating protobranching trends.

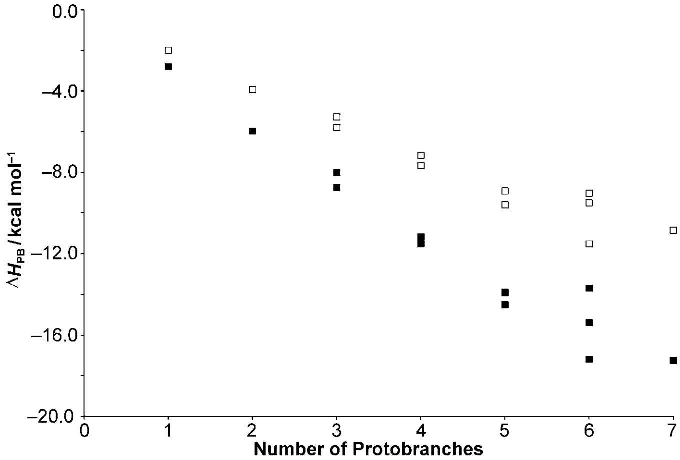


Figure 3. Experimental and calculated trends in ΔH_{PB} as a function of the number of protobranches. ■ = experimental values with *gauche* corrections (ref. [2]), □ = calculated value with *gauche* corrections (ref. [2]).

Measures of steric repulsion: The preference for the *anti* conformation of butane over the *gauche* conformation is widely accepted as due to steric interactions. Thus, it serves as a test case for the computational methodology used herein. The latest spectroscopic experimental measurements place the *gauche* conformation 0.67 kcal mol^{-1} higher than the *anti*.[18] Table 2 shows that the computed enthalpy change and electronic energy change match the experiment well. This and other test calculations show that the "Lewis energy" most closely matches the energetic interaction in these systems and is consistent (across different computational methods). Thus, the Lewis energy can be used as a quantitative measure of interaction energies due to steric hindrance in these simple systems. The Lewis energy is due to the localized bonding orbitals without any excitations into virtual orbitals and, thus, includes all

Table 1. NIST experimental and MPW1B95/6-311++G(d,p) calculated protobranching enthalpies.

Protobranching reaction	PB[a]	*gauche*[b]	Experimental ΔH_{PB}/PB	Calculated ΔH_{PB}/PB
$2CH_3CH_3 \rightarrow$ propane + CH_4	1	0	−2.8	−2.0
$3CH_3CH_3 \rightarrow$ butane + $2CH_4$	2	0	−3.0	−2.0
$3CH_3CH_3 \rightarrow$ isobutane + $2CH_4$	3	0	−2.7	−1.8
$4CH_3CH_3 \rightarrow$ pentane + $3CH_4$	3	0	−2.9	−1.9
$4CH_3CH_3 \rightarrow$ 2-methylbutane + $3CH_4$	4	1	−2.6	−1.6
$4CH_3CH_3 \rightarrow$ 2,2-dimethylpropane + $3CH_4$	6	0	−2.3	−1.5
$5CH_3CH_3 \rightarrow$ hexane + $4CH_4$	4	0	−2.9	−1.9
$5CH_3CH_3 \rightarrow$ 2-methylpentane + $4CH_4$	5	1	−2.6	−1.7
$5CH_3CH_3 \rightarrow$ 3-methylpentane + $4CH_4$	5	2	−2.5	−1.7
$5CH_3CH_3 \rightarrow$ 2,2-dimethylbutane + $4CH_4$	7	2	−2.3	−1.4
$5CH_3CH_3 \rightarrow$ 2,3-dimethylbutane + $4CH_4$	6	2	−2.3	−1.4
$6CH_3CH_3 \rightarrow$ heptane + $5CH_4$	5	0	−2.9	−1.9
$7CH_3CH_3 \rightarrow$ octane + $6CH_4$	6	0	−2.9	−1.9

[a] Number of protobranches. [b] Number of *gauche* interactions.

Table 2. Relative energy of butane conformations, *gauche–anti*, calculated at the MPW1B95/6-311++G(d,p) level.

	ΔE [kcal mol^{-1}]
experimental enthalpy	0.67
calculated enthalpy	0.64
calculated electronic energy	0.62
Lewis energy	0.73
steric energy	3.4
steric pairwise sum	3.2

steric, electrostatic, and bonding effects one would expect from a simple Lewis representation of the molecule without any contributions from hyperconjugation or similar factors. Unfortunately, it does not allow one to separate these effects and assess steric repulsion directly. Thus, it only serves as a good surrogate for the steric energy in cases, such as acyclic alkanes, in which the other effects are expected to be very similar across the series of comparison molecules. Steric repulsion can be assessed by using natural steric analysis, which gives two types of steric energy associated with Pauli repulsion between bonding orbitals: total steric energy and pairwise repulsion energies between any two localized orbitals. The pairwise interactions may not add up to the total steric energy due to many electron interactions. In this case, for each individual conformer the sum of pairwise steric interactions leads to a total that is over three times the total steric energy, but this error cancels when computing the difference between the two conformations. Nevertheless, both methods give consistently larger energies than the experimental difference between the two conformations of butane. Other effects must counterbalance the steric repulsion by stabilizing the *gauche* conformation preferentially. It is worth noting that the energies provided by the NBO steric analysis measure the purely repulsive interaction and do not included attractive nonbonded interactions, such as coulombic and van der Waals attractions. Thus, a caveat must be offered if Gronert's model is found to be predicated upon inclusion of attractive nonbonded interactions, since we consider only the steric repulsive interaction herein.[19] Although the pairwise steric interactions are exaggerated, they are valuable to further break down the steric energy into its component parts and evaluate trends. The analysis of conformational preference for *anti*-butane establishes all three methods as having the appropriate sign to measure the steric effect; furthermore, the Lewis energy matches the total experimental energy differences quantitatively.

In all of the alkanes studied, the geminal steric interactions are dominant in the overall steric energy of the molecule. As expected, the pairwise steric repulsion drops off rapidly with distance. For example, individual geminal values in butane range from 13–34 kcal mol^{-1}, vicinal steric repulsion energies range from 1–6 kcal mol^{-1}, and those from more remote interactions are all less than 1.5 kcal mol^{-1}. The geminal steric interactions can be further broken down into HCH, HCC, and CCC interactions as shown in Figure 4. In agreement with Gronert's proposal, we find that CCC steric repulsions are the largest (32.1 ± 1.9 kcal mol^{-1}), followed by the HCC (22.1 ± 1.2 kcal mol^{-1}), and HCH (14.8 ± 0.9 kcal mol^{-1}) repulsions.[20] The values in each class of interaction do not overlap other classes and even the smallest geminal interactions are at least twice as large as the largest nongeminal interaction. However, the support for Gronert's hypothesis ends here. The size of these steric repulsions cannot explain the stabilizing effect of branching or protobranching. The prerequisite inequality of Equation (4), necessary to establish the feasibility of the geminal steric argument, is not satisfied. In other words, using the average geminal steric repulsions as values for Equation (3), one discovers that ΔE_{PB} is positive and steric factors destabilize branched isomers. Although average values are most in keeping with Gronert's original proposal, they can be misleading and, thus, further investigation is warranted using total steric energy for specific protobranching and isomerization reactions. However, this gives even larger computed steric destabilizations. For example, the change in steric energy in the exothermic isomerization of butane to isobutane is +17 kcal mol^{-1} as measured by total steric repulsion and +5 kcal mol^{-1} as a sum of pairwise interactions. The difference in Lewis energy for this isomerization is the smallest of all isomerizations studied, but is still positive, measuring +0.2 kcal mol^{-1}.

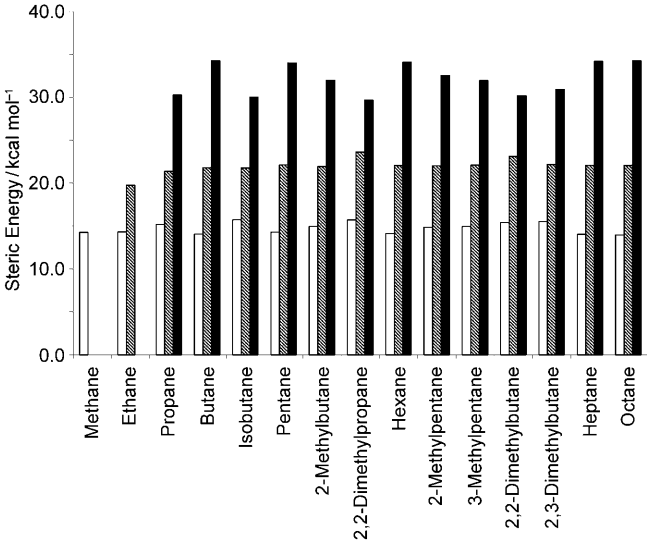


Figure 4. Average pairwise geminal steric interactions: HCH (white), HCC (striped), and CCC (black).

A plot of the above measurements (Figure 5) shows, graphically, the inadequacy of steric repulsion to explain the experimental and calculated stabilization trend on increased protobranching. The steric energy appears to be roughly linear with respect to the number of protobranches and increases with the number of protobranches, as measured by the total steric energy (filled circles) or the sum of the geminal steric interactions (empty circles). Since the Lewis energy, ΔE_{Lewis}, was the closest quantitative match to the experimental strain found in *gauche* butane it is worth noting that, though the ΔE values are attenuated in comparison to

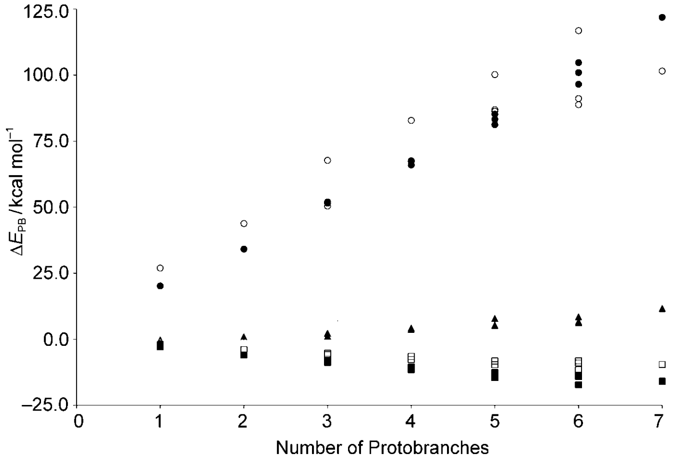


Figure 5. Measures of steric repulsion for Equation (1) compared with ΔH_{PB}. ■ = experimental ΔH_{PB}, □ = calculated ΔH_{PB}, ▲ = Lewis energy, ● = total steric repulsion, ○ = geminal steric repulsion.

the other steric measures, it too displays a destabilizing trend (filled triangles). Whereas, the experimental heats of formation show a commensurate stabilization as the number of protobranches increases, all three measures of steric repulsion show the opposite trend. In fact, this is perfectly in line with chemical intuition. One should expect that as more electrons are confined into a smaller space—this crowding will result in a greater steric repulsion and, thus, a destabilization of branched alkanes relative to their straight chain isomers. Although geminal steric interactions are sizable in comparison to other steric interactions and the terms follow the general trend predicted by Gronert, every measure of steric repulsion indicates that sterics are not responsible for protobranching stabilization or the stability of branched isomers.

Physical origin of protobranching: Having found no support for a purely repulsive force as the origin of protobranching stability, an investigation is in order to determine if it is plausible that an attractive force is the root cause. Wodrich and co-workers posit an attractive force, but state that they are not concerned at this point with the detailed analysis of the effects responsible for protobranching stability and do not attribute it to any specific origin.[6] Nevertheless, they do characterize Pitzer and Catalano's dispersion hypothesis[21] as being insufficient. They note that electron correlation is important to describe the protobranching stabilization. Grimme reports that deficiencies in middle-range correlation are responsible for the failure of density functional methods to calculate the relative stability of hydrocarbon isomers.[16a] Wodrich and co-workers use electron correlation as the key test for the applicability of the protobranching effect and this has opened them up to criticism.[7] In particular, it seems questionable that propene is deemed to have no protobranching stabilization simply because the effect of additional electron correlation on the ΔE_{PB} is minimal. Using electron correlation as the sole criterion for evaluation is problematic because many reaction energies are improved by electron correlation. Furthermore, the line dividing minimal and substantial improvement is a blurry one. Thus, an in-depth description of the physical origin is necessary, if for no other reason than as a starting point for making qualitative arguments about which molecules benefit from protobranching and which do not.

Our investigations into the effect of electron correlation on the calculated protobranching reaction energies are represented in Table 3 and confirm its importance in reproducing the full energetic effect. All of the computational methods shown there underestimate the experimental stabilization of protobranching. The errors in the calculated values were about half of the total stabilization for HF and diminished as additional excitations were added through the coupled-cluster method to an error of about one-tenth of the total with the inclusion of triple excitations. Our DFT method exhibited errors closer to the coupled cluster single and double excitation (CCSD) method than to HF, with an error of about one-third of the total. Though the DFT results were not as good as the coupled-cluster methods, they allow calculations on the full range of molecules and by using NBO analyses, like the steric analysis, that are not possible with the post-SCF methods.

Table 3. Signed error per protobranch at the DFT geometry with 6-311++G(d,p) basis set.

		Exptl. [kcal mol^{-1}]	Calculated error per protobranch [kcal mol^{-1}][a]			
	PB	ΔH_f/PB	HF	DFT[b]	CCSD	CCSD(T)
propane	1	−2.8	1.4	0.8	0.5	0.3
butane	2	−3.0	1.6	1.0	0.7	0.5
isobutane	3	−2.7	1.5	0.9	0.5	0.3
pentane	3	−2.9	1.6	1.0	0.6	0.4
neopentane	6	−2.3	1.7	0.8	0.3	0.1

[a] Error = ΔE_{PB}(calcd.) + DFT thermal/ZPVE correction −ΔH_{PB}(exptl.). [b] MPW1B95/6-311++G(d,p).

The NBO-calculated Lewis energy reveals the importance of electron delocalization to this phenomenon. In alkanes, the natural bond orbitals (NBOs) describe the portion of the wave function that can be localized in bonding regions (two-center regions) with occupancies very close to 2.0. In our DFT calculations, well over 99 % of the electron density of each wave function and about 99.9 % of each electronic energy is described by this simplified set of orbitals. Therefore, it is remarkable that the protobranching stabilization is eradicated when Lewis energies are used in place of the complete electronic energy (Figure 5). Figure 6 shows that the delocalization energy for the protobranching reaction (open diamonds) corresponds well with the actual energetic stabilization of the reaction (filled squares). Thus, a plausible cause for the enhanced stability of branched alkanes is delocalization, which is present to some extent even in a standard HF or DFT calculation and is not fully described without electron correlation. For simple saturated hydrocarbons, $\sigma \rightarrow \sigma^*$ excitations are the primary delocalizations. Ac-

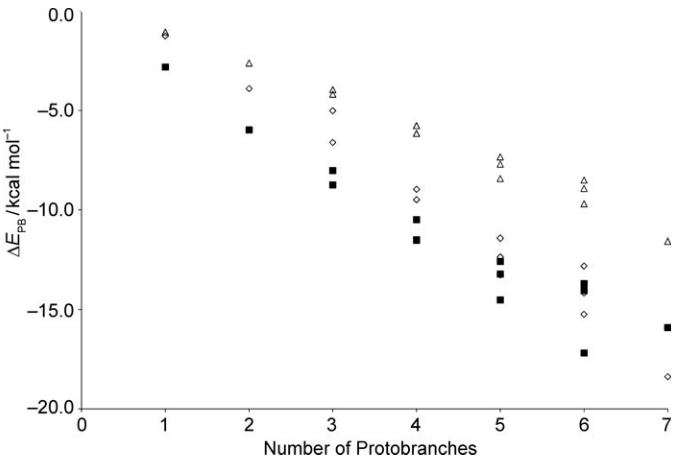
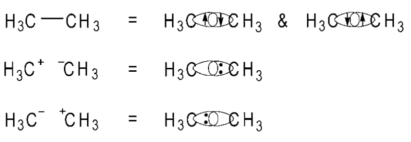


Figure 6. Delocalization energies for Equation (1) compared with ΔH_{PB}. ■ = experimental ΔH_{PB}, ◇ = total delocalization energy, △ = delocalization energy due only to geminal excitations.

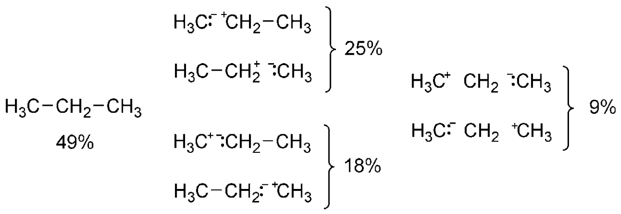
cording to NBO second-order perturbation analysis of individual alkanes, vicinal σ→σ* excitations contribute most to the delocalization energy, but what is more important is the role each type of delocalization plays in ΔE_{PB}. Though in this case delocalization stabilizes all alkanes, those with more branching and protobranching are preferentially stabilized by delocalization. Despite the fact that geminal σ→σ* excitations contribute less than vicinal excitations for any single alkane (on average, geminal excitations contribute only 15 % of the total delocalization energy, or about 0.02 % of E_0), the net effect of geminal delocalizations is the dominant factor in the protobranching delocalization energy (open triangles, Figure 6). Of the geminal interactions, $\sigma_{CC}\rightarrow\sigma_{CC}{}^*$ excitations are by far the most important and this explains why the geminal delocalizations preferentially stabilize branched alkanes, since they have more adjacent C–C bonds.

Valence bond (VB) calculations can be used to shed light on the specific interactions involved and provide independent corroboration of the importance of delocalization as the physical origin of the protobranching stabilization. Bonding between any two atoms can be described by three valence bond structures: X–Y, X^+ :Y^-, and X:$^-$ Y^+. Shaik, Hiberty, and co-workers have shown that even in purely covalent, homonuclear bonds like H_2 and ethane (Scheme 2), there is a significant contribution from ionic VB structures.[22] They have coined a term, "charge-shift" bonding, to describe bonds, such as F_2, for which the energetic contribution of the ionic structures is dominant despite the lack of any permanent dipole. Very recently, they identified the inverted C–C bond in [1.1.1]propellane as being a charge-shift bond.[23] They found that the energetic contribution from ionic structures is substantially higher for the C–C bond of ethane than the C–H bond in methane or the H_2 bond. The significance of these ionic structures in homonuclear bonds are revealed only when the orbitals are localized, as shown in Scheme 2. Delocalized orbitals, such as those utilized in molecular orbital theory, incorporate all three VB structures implicitly, but mask the contributions of the ionic structures. Since the bond-localized NBO analysis was revealing, an exploration using atom-localized valence bond calculations was undertaken.



Scheme 2. The three VB structures necessary to describe the C–C σ bond in ethane.

The NBO analysis implicated the role of adjacent C–C bonds in protobranching stabilization. In VB formalism, the presence of adjacent C–C bonds allows additional structures that are not otherwise possible. We included both C–C bonds of propane in the complete active space of a CASVB-(4,4) calculation, utilizing all 20 permutations of four electrons in four atom-localized orbitals. The CASVB(4,4) Coulson–Chirgwin weights (similar to Mulliken populations) that make up the wave function are shown in Scheme 3. Whereas, the five most important VB structures involve covalent and 1,2-ionic structures analogous to those found in ethane, two additional 1,3-ionic structures that are not possible without adjacent C–C bonds were found to have a significant weight (9 % of the total).[24] The energetic consequence of these 1,3-ionic structures can be assessed by a comparison of the VB-calculated energy of propane by using only the five most important structures compared with the energy obtained after adding the 1,3-ionic structures. The result is a lowering of the energy by 1.6 kcal mol^{-1}, which could account for a large portion of the protobranching stabilization of propane.[25]



Scheme 3. The VB structure weights for propane include 1,3-ionic structures that are only possible with protobranching and lower the energy by 1.6 kcal mol^{-1}.

To further probe the concept that ionic structures could elucidate the nature of protobranching stabilization, the energetics of Equation (2) were investigated by using VB methods with the inclusion of varying VB structures (Table 4). In this reaction, all C–C bonds on both sides of the reaction were treated as the active space. Thus, the two C–C bonds in the two molecules of ethane on the left were matched by the two C–C bonds in propane on the right. The CASVB calculation comes very close to matching the experimental ΔH_{PB}, but the VB calculation utilizing only covalent structures shows no protobranching stabilization

Table 4. VB-calculated ΔE_{PB} (propane) [Eq. (2)].

VB structures utilized	ΔE_{PB} [kcal mol^{-1}]
only covalent	$+0.2$
covalent + 1,2-ionic	-0.7
covalent + 1,2-ionic + 1,3-ionic	-2.3
CASVB	-2.5
experimental ΔH_{PB}	-2.8

whatsoever. This finding is reminiscent of the effect of using only the localized Lewis energy in the NBO calculations. When 1,2-ionic structures are added into the calculation, a modest protobranching stabilization is obtained. The bulk of the protobranching stabilization is achieved merely by adding the 1,3-ionic structures that are only possible when there are adjacent C–C bonds.

Both the VB calculations and the NBO calculations are telling complementary stories. The protobranching stabilization vanishes when only localized orbitals are used. The physical cause of protobranching stabilization can be generally described as delocalization, but specifically the most important delocalizations, according to both methods, are those that involve adjacent C–C bonds. In molecular orbital parlance these are geminal $\sigma_{CC}\rightarrow\sigma_{CC}{}^{*}$ excitations. In VB parlance, structures like H_3C^+ $:CH_2$ $:CH_3{}^-$ and $H_3C:^-$ $CH_2:$ $CH_3{}^+$ are key. In both cases, there is no net polarization because each terminal carbon serves as both donor and acceptor in equal parts. Thus, the protobranching stabilization is found to be a direct consequence of geminal bonding and not originating from steric or nonbonded interactions whatsoever.

Conclusion

Gronert's hypothesis was intriguing because it introduced a bold new way of looking at sterics and had a remarkably predictive value for hydrocarbon heats of formation, but the data presented here show that this correlation was likely to be due to linearly dependent variables and is not indicative of the underlying physical cause. On the contrary, our analysis suggests that steric repulsions destabilize branched alkanes more than straight chain alkanes. The new concept of protobranching is shown to be valuable for measuring the branching effect. The data suggest that branching and protobranching are stabilizing because they allow greater electron delocalization, chiefly by geminal $\sigma\rightarrow\sigma^*$ excitations of the type that involve adjacent C–C bonds and, thus, preferentially stabilize branched alkanes. Valance bond calculations further clarify the interaction as being due, in large part, to additional ionic structures (e.g., $CH_3{}^+$ $:CH_2$ $:CH_3{}^-$ and $CH_3:^-$ $CH_2:$ $CH_3{}^+$ for propane) that are not possible without protobranching. Further studies are necessary to determine the role of sterics and protobranching in homolytic bond dissociation enthalpies and the role of protobranching stabilization in cycloalkanes, alkenes, alkynes, and radicals.

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[25] The importance of these 1,3-ionic structures indicated by CASVB calculations is not inconsistent with Grimme's proposed rationale for the failure of DFT methods to reproduce the stability of branched alkanes.[16a]

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