

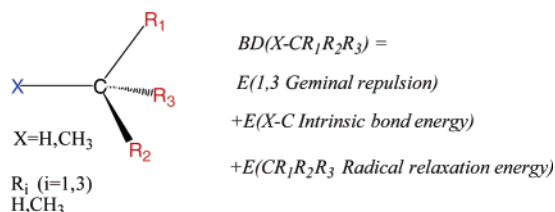
# 1,3 Geminal Interactions as the Possible Trend Setting Factors for C–H and C–C Bond Energies in Alkanes. Support from a Density Functional Theory Based Bond Energy Decomposition Study

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A bond energy decomposition analysis has been carried out to rationalize the well-established experimental fact that C–C and C–H bond energies decrease with increasing substitution on the carbon. It is shown that this trend is set by steric 1,3 repulsive interactions (geminal repulsion) that increase in the order 1,3 hydrogen–hydrogen < 1,3 hydrogen–carbon < 1,3 carbon–carbon. On the other hand, the radical stabilization energy has little influence on the observed trend for the C–H bond energy in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> or the C–C bond energy in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>. Thus, it varies in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> from –7.2 kcal/mol (H–CH<sub>3</sub>) to –6.5 kcal/mol (H–C(CH<sub>3</sub>)<sub>3</sub>) and in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> from –19.0 kcal/mol (H<sub>3</sub>C–CH<sub>3</sub>) to –16.9 kcal/mol (H<sub>3</sub>C–C(CH<sub>3</sub>)<sub>3</sub>). It was further found that the average intrinsic C–H bond energy in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> of 129.2 kcal/mol is smaller than the average intrinsic C–C bond energy in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> of 143.4 kcal/mol. However, after the inclusion of steric effects, the overall C–H bond becomes stronger than the C–C bond. The role of steric 1,3 repulsive interactions as the trend setting factor has most recently been suggested by Gronert (*J. Org. Chem.* **2006**, *71*, 1209) based on an empirical fit of alkane atomization energies.

## 1. Introduction

The strength of C–H and C–C bonds in alkanes is a key parameter in the chemistry of hydrocarbons. The well-established experimental fact that C–H and C–C bond strengths decrease with increasing substitution on the carbon has far reaching consequences in the areas of polymer chemistry, radiation damage of proteins, and functionalization of alkanes by metalloenzymes or homogeneous catalysts, as well as the processing of petrochemicals. The decrease in C–C and C–H bond strength with increasing substitution on the carbon is most often explained in terms of increasing stabilization of the radical formed after bond fission. The radical stabilization is explained in terms of hyperconjugation involving the donation of charge from the fully occupied bonding  $\sigma$ -alkane orbitals into the singly

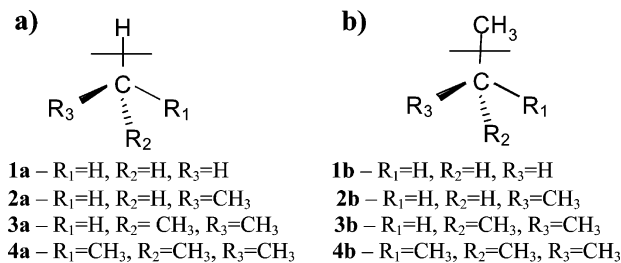
unoccupied radical alkyl orbital, as well as involving the donation of charge from the singly occupied radical alkyl orbital into the empty antibonding  $\sigma^*$ -alkane orbitals. Hyperconjugation is assumed to be more important for systems with substituted carbons as they hold more bonding  $\sigma$ -alkane orbitals and antibonding  $\sigma^*$ -alkane orbitals.

Quite recently, Gronert<sup>1</sup> has put forward an alternative interpretation of the dependence of C–H and C–C bond energies on the carbon substitution. In his work, Gronert fit the experimental atomization energies of numerous alkanes within five parameters involving the “intrinsic” C–H and C–C bond energies as well as the repulsive 1,3 geminal interactions involving hydrogen–hydrogen, hydrogen–carbon, and carbon–carbon. From his model, Gronert managed to reproduce trends in C–C and C–H bond energies and attribute them to an

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(1) Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209.



**FIGURE 1.** Hydrocarbons studied in the present work:  $\text{H}-\text{CR}_1\text{R}_2\text{R}_3$  (panel a) and  $\text{CH}_3-\text{CR}_1\text{R}_2\text{R}_3$  (panel b).

increase in steric repulsion. It is important to note that Gronert was able to fit the atomization energies to within an accuracy of 0.5 kcal/mol without implicitly taking into account the radical stabilization energy. As pointed out by Gronert, the idea of correlating trends in C–C and C–H bond energies with steric interactions is not new and seems first to have been suggested by Eyring<sup>2a</sup> in 1932 and later substantiated by Rüchardt.<sup>2b,c</sup> The role of radical stabilization has also been assessed critically by Zavitsas,<sup>2e</sup> Matsunaga<sup>2f</sup> et al., and Coote<sup>2g</sup> et al.

The work by Gronert is based on the fitting of experimental data, and one might question the validity or chemical significance of the parameters obtained in such a fit. In fact, alternative fits with different parameters including 1,3 geminal attraction terms have recently been put forward by Wodrich and Schleyer.<sup>2h</sup> It is, however, possible to use density functional theory (DFT) to decompose the C–C and C–H bond energies in terms similar to those of steric interactions, intrinsic bond energies, and radical stabilization energies.<sup>3–5</sup> We present here results from such a decomposition analysis of the C–H and C–C bonds with different substitutions on the carbon. Our analysis not only demonstrates that the variations in C–C and C–H bond energies with increasing substitution are due to steric factors but also confirms that the values obtained for the steric interaction energy and “intrinsic” bond energies are realistic estimates. It should be mentioned that Grimme recently has used DFT to study alkane branching.<sup>2d</sup>

## 2. Computational Details and Models

The systems under investigation in the current study are shown in Figure 1. The alkane geometries were optimized on the basis of DFT at the level of the nonlocal Becke–Perdew exchange–correlation functional<sup>6–8</sup> BP86, as implemented in the Amsterdam density functional (ADF) program version<sup>9–15</sup> 2005.04. Use was made of the Ziegler–Rauk bond energy decomposition analysis (EDA)<sup>3–5</sup> scheme for the description of the bonding between the radical fragments H and  $\text{CR}_1\text{R}_2\text{R}_3$  (Figure 1a) or  $\text{CH}_3$  and  $\text{CR}_1\text{R}_2\text{R}_3$  (Figure 1b). The Slater-type orbital (STO) basis set employed was of double  $\zeta$  quality with a single polarization function. The 1s

electrons of carbon were treated as a frozen core. Finally, a bond-order analysis was conducted based on the Nalewajski–Mrozek (N–M),<sup>16–20</sup> the Mayer,<sup>21,22</sup> and the Gopinathan–Jug (G–J)<sup>23,24</sup> schemes. Finite temperature enthalpic corrections as well as zero energy frequency effects were neglected. Their absence is not likely to change the conclusions drawn in this investigation.

## 3. Results and Discussion

We shall start by outlining the basic concepts of the EDA method.<sup>3–5</sup> In this scheme, the total bonding energy between the interacting fragments ( $\Delta E_{\text{bond}}^{\text{tot}}$ ) is divided into four components (eq 1):

$$\Delta E_{\text{bond}}^{\text{tot}} = \Delta E_{\text{dist}} + [\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}}] + \Delta E_{\text{orbital}} = \Delta E_{\text{dist}} + \Delta E_{\text{steric}} + \Delta E_{\text{orbital}} \quad (1)$$

The first component, referred to as the distortion term  $\Delta E_{\text{dist}}$ , represents the amount of energy required to promote the separated fragments from their equilibrium geometry to the structure they will take up in the combined molecule. This term is often referred to as  $\Delta E_{\text{prep}}$  in applications of the EDA scheme. The second term,  $\Delta E_{\text{elstat}}$ , corresponds to the classical electrostatic interaction between the promoted fragments. The third term,  $\Delta E_{\text{Pauli}}$ , accounts for the repulsive Pauli interaction between occupied orbitals on the two fragments. The sum  $\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}}$  is referred to as the steric repulsion term  $\Delta E_{\text{steric}}$  between the two promoted fragments. Finally, the last term,  $\Delta E_{\text{orbital}}$ , represents the interactions between the occupied molecular orbitals on one fragment with the unoccupied molecular orbitals of the other fragment as well as mixing of occupied and virtual orbitals within the same fragment (inner-fragment polarization). Further analysis of the orbital interaction term  $\Delta E_{\text{orbital}}$  revealed two important contributions. The major contribution is due to the bonding interaction between the singly occupied 1s<sub>H</sub> hydrogen orbital and the singly occupied alkyl orbital  $\sigma_{\text{alkyl}}$ . The minor contribution involves donation of charge into the  $\sigma^*$  orbitals of the alkyl fragment. By eliminating the virtual  $\sigma^*$  orbitals from our calculation we get a new orbital

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TABLE 1. Bond Energy<sup>a</sup> Decomposition<sup>b</sup> of the C–H Bond in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>

| H–CR <sub>1</sub> R <sub>2</sub> R <sub>3</sub> | $\Delta E_{\text{Pauli}}$ | $\Delta E_{\text{elstat}}$ | $\Delta E_{\text{steric}}$ | $\Delta E_{\text{orbital}}$ | $\Delta E_{\text{orbital}-\sigma^*}$ | $\Delta E_{\text{dist}}$ | $\Delta E_{\text{bond}}^{\text{tot}}$ |
|---|---------------------------|----------------------------|----------------------------|-----------------------------|--------------------------------------|--------------------------|---------------------------------------|
| <b>1a</b> <sup>c</sup>                          | 75.50                     | –58.36                     | 17.14                      | –134.95                     | –127.43                              | 7.22                     | –110.59                               |
| <b>2a</b>                                       | 90.82                     | –65.59                     | 25.23                      | –138.19                     | –129.43                              | 6.43                     | –106.53                               |
| <b>3a</b>                                       | 101.24                    | –70.17                     | 31.07                      | –140.28                     | –130.10                              | 6.25                     | –102.96                               |
| <b>4a</b>                                       | 108.76                    | –72.86                     | 35.90                      | –142.04                     | –129.93                              | 6.24                     | –99.90                                |

<sup>a</sup> Energies are in kcal/mol. <sup>b</sup> For a definition of the different energy terms, see eq 1. <sup>c</sup> The species **1a**, **2a**, **3a**, and **4a** are defined in Figure 1a.

TABLE 2. C–H Distances Together with the Corresponding Bond-Order Values Calculated by the Mayer, the Gopinathan–Jug, and the Nalewajski–Mrozek Bond-Order Methods<sup>a</sup>

| C–H       | distance(Å) | Mayer <sup>b</sup> | G–J <sup>c</sup> | N–M <sup>d</sup> |
|-----------|-------------|--------------------|------------------|------------------|
| <b>1a</b> | 1.098       | 0.9912             | 0.9585           | 1.0345           |
| <b>2a</b> | 1.103       | 0.9801             | 0.9393           | 0.9981           |
| <b>3a</b> | 1.107       | 0.9608             | 0.9164           | 0.9625           |
| <b>4a</b> | 1.109       | 0.9378             | 0.8910           | 0.9280           |

<sup>a</sup> The species **1a**, **2a**, **3a**, and **4a** are defined in Figure 1a. <sup>b</sup> See ref 21. <sup>c</sup> See ref 23. <sup>d</sup> See ref 20.

interaction energy  $\Delta E_{\text{orbital}-\sigma^*}$  which allows us to estimate the minor contribution from the  $\sigma^*$  orbitals as  $\Delta E_{\text{orbital}} - \Delta E_{\text{orbital}-\sigma^*}$  whereas the major contribution is presented as  $\Delta E_{\text{orbital}-\sigma^*}$ . The EDA scheme has recently been used in an elegant study of hyperconjugation in alkanes by Fernandez and Frenking.<sup>21</sup> The results from our decomposition analysis of the C–H bond strengths in **1a–4a** are given in Table 1.

We find, in agreement with the experiment, that the total C–H bond energy  $\Delta E_{\text{bond}}^{\text{tot}}$  (in absolute terms) decreases with increasing substitution on carbon, Table 1. The term responsible for this trend is  $\Delta E_{\text{steric}}$  which becomes more and more destabilizing (positive) with increasing substitution on carbon. This finding is in line with the analysis by Gronert<sup>1</sup> according to which C–H bonds are destabilized with increasing substitution because the steric 1,3 geminal interactions between hydrogen and carbon are more destabilizing than steric 1,3 geminal hydrogen–hydrogen interactions. The orbital interaction term  $\Delta E_{\text{orbital}}$  is responsible for the stability of the C–H bond. It is slightly favored by an increase in substitution, Table 1. We can understand this trend by observing that the contribution to  $\Delta E_{\text{orbital}}$  from the  $\sigma^*$  orbitals which is given by  $\Delta E_{\text{orbital}} - \Delta E_{\text{orbital}-\sigma^*}$  becomes more stabilizing as the number of  $\sigma^*$  orbitals grows. On the other hand, the intrinsic C–H bond interaction  $\Delta E_{\text{orbital}-\sigma^*}$  between  $\sigma_{\text{alkyl}}$  and  $1s_{\text{H}}$  is nearly independent of carbon substitution, in line with the analysis by Gronert.<sup>1</sup> We finally note that the positive distortion term  $\Delta E_{\text{dist}}$  representing the energy required to change the geometry of the radical from its ground state conformation to the geometry it has in the combined alkane is small and constant throughout the series **1a–4a**. That implies that the “radical stabilization”  $-\Delta E_{\text{dist}}$  of the alkyl fragment after C–H bond fission is independent of carbon substitution. This is an interesting result as the radical stabilization  $-\Delta E_{\text{dist}}$  is assumed to increase with carbon substitution because of the growing role of hyperconjugation.

Table 2 compares optimized C–H distances with the corresponding bond-order values evaluated by the Mayer,<sup>21,22</sup> the G–J,<sup>23,24</sup> and the N–M<sup>16–20</sup> methods. It follows from Table 2 that the calculated C–H bond orders decrease in the same order, **1a** > **2a** > **3a** > **4a**, for all three methods. Further, the decrease in the C–H bond-order values with increasing substitution correlates well with a lengthening of the C–H bond distance as well as the decrease in the total C–H bonding energy.

We shall now turn to an analysis of the C–C bond strength  $\Delta E_{\text{bond}}^{\text{tot}}$  between the radicals CH<sub>3</sub>–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (see Figure 1b). It follows from Table 3 that  $\Delta E_{\text{bond}}^{\text{tot}}$ , in agreement with the experiment, decreases in absolute terms with increasing substitution on CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>. This trend is again set by the steric term  $\Delta E_{\text{steric}}$  that becomes increasingly destabilizing as the number of steric 1,3 geminal carbon–hydrogen interactions are replaced by the more repulsive steric 1,3 geminal carbon–carbon interactions. Our  $\Delta E_{\text{steric}}$  values in Tables 1 and 3 are consistent with those of the 1,3 geminal steric repulsions and follow the order hydrogen–hydrogen < hydrogen–carbon < carbon–carbon as found by Gronert.<sup>1</sup>

The stabilizing orbital interaction term  $\Delta E_{\text{orbital}}$  is seen to increase in absolute terms with substitution. This is in part due to the increase in the number of  $\sigma^*$  orbitals as reflected by  $\Delta E_{\text{orbital}} - \Delta E_{\text{orbital}-\sigma^*}$ , Table 3. However, even the term  $\Delta E_{\text{orbital}-\sigma^*}$  representing the interaction between the partially occupied  $\sigma_{\text{alkyl}}$  and  $\sigma_{\text{CH}_3}$  orbitals becomes more stabilizing with substitution. It is interesting that the “intrinsic” C–H and C–C bond energies of 124.2 kcal/mol and 146.0 kcal/mol adopted by Gronert<sup>1</sup> are very close to the average value for  $-\Delta E_{\text{orbital}-\sigma^*}$  of 129.2 kcal/mol for the C–H bond in Table 1 and the average value for  $-\Delta E_{\text{orbital}-\sigma^*}$  of 143.4 kcal/mol for the C–C bond in Table 3.

We finally note that the positive distortion term  $\Delta E_{\text{dist}}$ , representing the energy required to change the geometry of the radical CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> from its ground state conformation to the geometry it has in the combined alkane, is nearly constant throughout the series **1b–4b** with 19 kcal/mol for **1b** and 17 kcal/mol for **4b**. That implies that the “radical stabilization”  $-\Delta E_{\text{dist}}$  of the alkyl fragment after C–C bond fission is modest and independent of carbon substitution. This is an important result as the radical stabilization  $-\Delta E_{\text{dist}}$  is assumed to increase with carbon substitution because of the growing role of hyperconjugation.

We present, finally, in Table 4 the optimized C–C bond distances and the corresponding bond-order values evaluated according to the Mayer, the G–J, and the N–M methods. It is clear from Table 4 that all of the methods lead to the conclusion that an increase in the substitution on the carbon atom causes a decrease in the C–C bond order. The C–C bond order decrease correlates well with an increase in the C–C bond distance and a decrease (in absolute terms) in the total bond energy  $-\Delta E_{\text{bond}}^{\text{tot}}$  through the series **1b–4b**.

#### 4. Concluding Remarks

We have carried out an EDA<sup>3–5</sup> of the H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> and H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> bonds in alkanes; see eq 1 and Tables 1 and 3. We find in agreement with the experiment that the bond energy (in absolute terms) decreases with increasing substitution on carbon as the R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> groups are transformed from hydrogen to methyl. It follows further, from our analysis based on eq 1, that the trend setting term is the steric interaction energy

**TABLE 3.** Bond Energy<sup>a</sup> Decomposition<sup>b</sup> of the C–C Bond in CH<sub>3</sub>–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub><sup>c</sup>

| CH <sub>3</sub> –CR <sub>1</sub> R <sub>2</sub> R <sub>3</sub> | $\Delta E_{\text{Pauli}}$ | $\Delta E_{\text{elstat}}$ | $\Delta E_{\text{steric}}$ | $\Delta E_{\text{orbital}}$ | $\Delta E_{\text{orbital}-\sigma^*}$ | $\Delta E_{\text{dist}}$ | $\Delta E_{\text{bond}}^{\text{tot}}$ |
|--|---------------------------|----------------------------|----------------------------|-----------------------------|--------------------------------------|--------------------------|---------------------------------------|
| <b>1b</b>  | 229.91                    | –156.20                    | 73.71                      | –186.99                     | –138.50                              | 19.00                    | –94.28                                |
| <b>2b</b>  | 253.47                    | –169.44                    | 84.03                      | –193.20                     | –143.53                              | 17.56                    | –91.61                                |
| <b>3b</b>  | 267.57                    | –176.96                    | 90.62                      | –196.51                     | –145.75                              | 17.09                    | –88.80                                |
| <b>4b</b>  | 275.59                    | –180.38                    | 95.21                      | –197.86                     | –146.01                              | 16.91                    | –85.74                                |

<sup>a</sup> Energies are in kcal/mol. <sup>b</sup> For a definition of the different energy terms, see eq 1. <sup>c</sup> The species **1b**, **2b**, **3b**, and **4b** are defined in Figure 1b.

**TABLE 4.** C–C Distances Together with the Corresponding Bond-Order Values Calculated by the Mayer, the Gopinathan–Jug, and the Nalewajski–Mrozek Bond-Order Methods<sup>a</sup>

| C–C       | distance (Å) | Mayer <sup>b</sup> | G–J <sup>c</sup> | N–M <sup>d</sup> |
|-----------|--------------|--------------------|------------------|------------------|
| <b>1b</b> | 1.5073       | 1.0635             | 1.1298           | 1.2789           |
| <b>2b</b> | 1.5062       | 1.0420             | 1.0974           | 1.2130           |
| <b>3b</b> | 1.5071       | 1.0180             | 1.0655           | 1.1513           |
| <b>4b</b> | 1.5105       | 0.9923             | 1.0338           | 1.0933           |

<sup>a</sup> The species **1b**, **2b**, **3b**, and **4b** are defined in Figure 1b. <sup>b</sup> See ref 21. <sup>c</sup> See ref 23. <sup>d</sup> See ref 20.

$\Delta E_{\text{steric}}$ . Thus, the steric term  $\Delta E_{\text{steric}}$  becomes increasingly destabilizing as the number of steric 1,3 geminal hydrogen–hydrogen interactions are replaced by the more repulsive steric 1,3 geminal hydrogen–carbon interactions in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> or as the number of steric 1,3 geminal carbon–hydrogen interactions are replaced by the more repulsive steric 1,3 geminal carbon–carbon interactions in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>. Our  $\Delta E_{\text{steric}}$  values in Tables 1 and 3 are consistent with those of the 1,3 geminal steric repulsions and follow the order hydrogen–hydrogen < hydrogen–carbon < carbon–carbon as suggested by Gronert.<sup>1</sup>

The term stabilizing the H–C and C–C bonds is  $\Delta E_{\text{orbital}}$ . It has a part ( $\Delta E_{\text{orbital}} - \Delta E_{\text{orbital}-\sigma^*}$ ) which is due to donation of charge into the  $\sigma^*$  alkyl orbitals. This part becomes more stabilizing with substitution as the number of  $\sigma^*$  bonds increases. The second part is  $-\Delta E_{\text{orbital}-\sigma^*}$ ; it represents in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> the intrinsic C–H bond energy and has an average value of 129.2 kcal/mol which is close to the intrinsic C–H bond energy of 124.2 kcal/mol adopted by Gronert.<sup>1</sup> The corresponding  $-\Delta E_{\text{orbital}-\sigma^*}$  term in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> represents the intrinsic C–C

bond energy with an average value of 143.4 kcal/mol compared to the value of 146.0 kcal/mol adopted by Gronert.<sup>1</sup> It is interesting to note that our decomposition scheme as well as the work by Gronert<sup>1</sup> finds the intrinsic C–H bond, on the average, to be weaker than the corresponding C–C bond, whereas the overall bond energies  $\Delta E_{\text{bond}}^{\text{tot}}$  have the opposite trend because of the  $\Delta E_{\text{steric}}$  as the 1,3 geminal steric repulsions follow the order hydrogen–hydrogen < hydrogen–carbon < carbon–carbon.<sup>1</sup> We finally note that the radical stabilization term  $-\Delta E_{\text{dist}}$  has little influence on the observed trend for the C–H bond energy in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> or the C–C bond energy in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>. Thus,  $\Delta E_{\text{dist}}$  varies in H–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> from 7.2 kcal/mol (H–CH<sub>3</sub>) to 6.5 kcal/mol (H–C(CH<sub>3</sub>)<sub>3</sub>) and varies in H<sub>3</sub>C–CR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> from 19.0 kcal/mol (H<sub>3</sub>C–CH<sub>3</sub>) to 16.9 kcal/mol (H<sub>3</sub>C–C(CH<sub>3</sub>)<sub>3</sub>). This has also been substantiated in a recent theoretical study by Gronert.<sup>21</sup> The bond energy analysis presented here lends further support for the notion most recently put forward by Gronert,<sup>1</sup> according to which the observed trends in C–H and C–C bond energies of alkanes are determined by repulsive 1,3 geminal repulsions.

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**Supporting Information Available:** Geometries and total energies of all hydrocarbons and hydrocarbyl radicals mentioned in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>

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