

# Enthalpies of Formation of Hydrocarbons by Hydrogen Atom Counting. Theoretical Implications.

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Standard enthalpies of formation at 298 K of unstrained alkanes, alkenes, alkynes, and alkylbenzenes can be expressed as a simple sum in which each term consists of the number of hydrogen atoms  $n$  of one of eight different types ( $n_1$ – $n_8$ ) multiplied by an associated coefficient ( $c_1$ – $c_8$ ) derived from the known enthalpy of formation of a typical molecule. Alkylbenzenes require one additive constant for each benzene ring, accounting for a possible ninth term in the sum. Terms are not needed to account for repulsive or attractive 1,3 interactions, hyperconjugation, or for protobranching, rendering them irrelevant. Conjugated enynes and diynes show thermodynamic stabilizations much smaller than that observed for 1,3-butadiene, bringing into question the usual explanation for the thermodynamic stabilization of conjugated multiple bonds ( $p$  orbital overlap,  $\pi$  electron delocalization, etc.).

## Introduction

Certainly, there is no paucity of additive methods that reproduce or predict the enthalpies of formation at 298 K,  $\Delta_f H^\circ$ , of unstrained hydrocarbons to acceptable accuracy, generally within experimental error. Some are quite recent,<sup>1,2</sup> whereas others properly belong to the history of chemistry. We hope that the understandably jaded reader will consider yet another method for achieving the same goal for three reasons:

1. The method is the simplest possible.
2. The sum

$$\Delta_f H^\circ = \sum_{i=1}^9 c_i n_i$$

requires counting hydrogen atoms only and segregating them into eight categories.

3. No global fitting is used.

Aside from simplicity and utility, the method offers new insights into the whole process of group or bond enthalpy summation. Explicit terms involving three- and four-center interactions are eliminated, along with hypothetical constructs that come with them, such as 1–3 attractions and repulsions, hyperconjugation, and protobranching.

We present data for over 120 unstrained hydrocarbons in four classes: alkanes, alkenes, alkynes, and, by adding a term for each benzene ring, alkylbenzenes. Calculated values exhibit a grand unsigned mean deviation from experiment of 0.37 kcal mol<sup>−1</sup>. Where others find strain or conjugation energies by other methods, we find similar energies in amounts that agree with prior literature values. The energetic importance of conjugation in ene–ynes is small, and for dialkynes, it is nearly zero.

## Method

**Alkanes.** Enthalpies of formation of unstrained alkanes are given by eq 1, where  $n_1$  is the number of primary hydrogens,  $n_2$  is the number of secondary hydrogens, and  $n_3$  is the number of tertiary hydrogens. The units are kcal mol<sup>−1</sup> at 298 K.

$$\Delta_f H^\circ(\text{alkane}) = (-3.345)n_1 + (-2.490)n_2 + (-1.590)n_3$$

$$= \sum_{i=1}^3 c_i n_i \quad (1)$$

The coefficient  $c_1 = -3.345$  was obtained from the enthalpy of formation of 2,2-dimethylpropane,<sup>3</sup>  $-40.14$  kcal mol<sup>−1</sup>, divided by its 12 primary hydrogens;  $c_2$  was obtained from the enthalpy of formation of butane<sup>3</sup> and the contribution of its six primary hydrogens divided by its 4 secondary hydrogens [ $-30.03 - (-3.345 \times 6)$ ]/4 =  $-2.490$ . The coefficient  $c_3$  was obtained from the enthalpy of formation of 2,4-dimethylpentane<sup>3</sup> and the contribution of six primary and two secondary hydrogens divided by its two tertiary hydrogens [ $-48.30 - (-3.345 \times 12) - (-2.490 \times 2)$ ]/2 =  $-1.590$  kcal mol<sup>−1</sup>. There are many reference compounds that can be used in selecting parameters  $c_1$ – $c_9$  (see Supporting Information for further discussion and our reasons for selecting the compounds that we did).

**Alkenes.** The process of counting hydrogens was extended to unstrained and unconjugated alkenes by retaining the coefficients of eq 1 for hydrogens connected to sp<sup>3</sup> carbons and assigning values according to eq 2 for vinyl hydrogens, where  $n_4$  is the number of vinyl hydrogens and  $n_5$  is the number of hydrogens absent from sp<sup>2</sup> carbons.

$$\Delta_f H^\circ(\text{alkene}) = \sum_{i=1}^3 c_i n_i + c_4 n_4 + c_5 n_5 = \sum_{i=1}^5 c_i n_i \quad (2)$$

The coefficient  $c_4$  was obtained from the enthalpy of formation of ethene,<sup>3</sup> 12.54 kcal mol<sup>−1</sup>, divided by the number of vinyl hydrogens, 12.54/4 = 3.135, and  $c_5$  is from the enthalpy of formation of *trans*-2-butene<sup>3</sup> and the contributions of  $n_1$  and  $n_4$ , divided by the number of hydrogens absent from sp<sup>2</sup> carbons, [ $-2.6 - (-3.345 \times 6) - (3.135 \times 2)$ ]/2 = 5.600.

**Alkynes.** Enthalpies of formation of unstrained and unconjugated alkynes were calculated by retaining the coefficients of eq 1 for hydrogens on sp<sup>3</sup> carbons and assigning coefficients according to eq 3, where  $n_6$  indicates that there is at least one hydrogen on a triple bond (terminal alkyne) and  $n_7$  indicates the absence of any hydrogens on a triple bond (internal alkyne).

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$$\Delta_f H^\circ(\text{alkyne}) = \sum_{i=1}^3 c_i n_i + c_6 n_6 + c_7 n_7 \quad (3)$$

The coefficient  $c_6 = 54.42$  was obtained from the experimental<sup>3</sup>  $\Delta_f H^\circ$  of 1-butyne and the contributions of  $n_1$  and  $n_2$ ,  $[39.4 - (-3.345 \times 3) - (-2.490 \times 2)]$ ; similarly  $c_7 = 55.31$  is the average of the experimental<sup>3</sup>  $\Delta_f H^\circ$  values of two internal alkynes, 2-butyne and 2-pentyne, and the contributions of  $n_1$  and  $n_2$ .

**Alkylbenzenes.** Enthalpies of formation of unstrained and unconjugated alkylbenzenes are given by eq 4, where  $n_8$  denotes the number of aromatic hydrogens missing from the ring. The same coefficients  $c_1$ – $c_3$  were used as in eq 1.

$$\Delta_f H^\circ(\text{alkylbenzene}) = \sum_{i=1}^3 c_i n_i + c_8 n_8 + \Delta_f H^\circ(\text{benzene}) \quad (4)$$

The coefficient  $c_8$  was obtained from  $\Delta_f H^\circ(\text{toluene})^3 = 11.95$ ,  $n_1$ , and  $\Delta_f H^\circ(\text{benzene})^3 = 19.82 \text{ kcal mol}^{-1}$  as follows:  $[11.95 - 19.82 - (-3.345 \times 3)] = 2.17 \text{ kcal mol}^{-1}$ .  $\Delta_f H^\circ(\text{benzene})$  is added for each benzene ring.

A combination of eqs 1–4 permits estimation of conjugation stabilization in dienes, enynes, and diyne (vide infra).

## Results

**Alkanes.** Table 1 lists  $\Delta_f H^\circ$  calculated by eq 1 and experimental values from the NIST Database No. 69,<sup>3</sup> supplemented from other sources as indicated. Notably absent from Table 1

is methane. It is unique in having no carbon–carbon bonds, and it does not fit the pattern of the other alkanes. The average unsigned deviation between calculated and experimental values in Table 1 is  $0.28 \text{ kcal mol}^{-1}$  for 36 typical unstrained alkanes and cycloalkanes.

Eq 1 makes no allowance for steric crowding, ring strain, or other “special effects.” It gives calculated values that are more negative than those of experimental enthalpies of formation in such cases, indicating greater stability than actually exists. The difference between experimental enthalpies of formation and values calculated by eq 1 is a good measure of the extent of strain in the molecule, a positive value indicating strain. Table 2 shows some examples of strain energies along with literature values, which were obtained by methods quite different and frequently much more complicated than eq 1.

**Alkenes.** Table 3 lists  $\Delta_f H^\circ$  for 39 typical unstrained alkenes calculated by eq 2 along with experimental values from the NIST Database No. 69,<sup>3</sup> when available, or other sources, as indicated. The average unsigned deviation between calculated values and 79 literature values in Table 3 is  $0.48 \text{ kcal mol}^{-1}$ .

Strained alkenes do not fit the pattern of eq 2 nor do alkenes that are subject to the “special effect” of stabilization by conjugation. The difference between the experimental value and the value calculated by eq 2 is a measure of the magnitude of the effect, a positive value indicating strain and a negative value indicating stabilization. Some typical strained alkenes are shown below the dashed line in Table 3. *cis*-Alkenes are more strained

TABLE 1: Calculated by Equation 1 and Experimental Enthalpies of Formation of Unstrained Alkanes (kcal mol<sup>−1</sup>)

alkane	$n_1$	$n_2$	$n_3$	$\Delta_f H^\circ$ , eq 1	$\Delta_f H^\circ$ , lit. <sup>a</sup>
ethane	6	0	0	−20.07	−20.04 ± 0.1
propane	6	2	0	−25.05	−25.02 ± 0.1
butane	6	4	0	−30.03	−30.03 ± 0.2
isobutane <sup>b</sup>	9	0	1	−31.7	−32.1 ± 0.2
pentane	6	6	0	−35.0	−35.1 ± 0.1
isopentane <sup>c</sup>	9	2	1	−36.7	−36.7 ± 0.1
neopentane <sup>d</sup>	12	0	0	−40.1	−40.1 ± 0.2
cyclohexane	0	12	0	−29.9	−29.4 ± 0.2
hexane	6	8	0	−40.0	−40.0 ± 0.2
2,3-dimethylbutane	12	0	1	−41.7	−42.4 ± 0.3
2-methylpentane	9	4	1	−41.7	−41.7 ± 0.3
3-methylpentane	9	4	1	−41.7	−41.0 ± 0.2
heptane	6	10	0	−45.0	−44.9 ± 0.2
methylcyclohexane	3	10	1	−36.5	−37.0 ± 0.3
(Z)-1,2-dimethylcyclohexane	6	8	2	−43.2	−43.0 ± 0.4 <sup>e</sup>
ethylcyclohexane	3	12	1	−41.5	−41.1 ± 0.4
2,4-dimethylpentane	12	2	2	−48.3	−48.3 ± 0.2
octane	6	12	0	−50.0	−49.8 ± 0.2
2-methylheptane	9	8	1	−51.6	−51.5 ± 0.3
3-methylheptane	9	8	1	−51.6	−50.8 ± 0.3
4-methylheptane	9	8	1	−51.6	−50.7 ± 0.3
2,5-dimethylhexane	12	4	2	−53.3	−53.2 ± 0.4
propylcyclohexane	3	14	1	−46.5	−46.2 ± 0.3
nonane	6	14	0	−54.9	−54.5 ± 0.1 <sup>e</sup>
butylcyclohexane	3	16	1	−51.5	−50.9 ± 0.3
trans-decalin <sup>f</sup>	0	16	2	−43.0	−43.5 ± 0.6
decane	6	16	0	−59.9	−59.7 ± 0.3
2-methylnonane	9	12	1	−61.6	−62.1
5-methylnonane	9	12	1	−61.6	−61.8
undecane	6	18	0	−64.9	−64.6 ± 0.3
dodecane	6	20	0	−69.9	−69.5 ± 0.3
bicyclohexyl <sup>g</sup>	0	20	2	−52.9	−52.2 ± 0.7
octylcyclohexane	3	24	1	−71.4	−70.7 ± 0.5
tetradecane	6	24	0	−79.8	−79.4 ± 0.4
hexadecane	6	28	0	−89.6	−89.6
octadecane	6	32	0	−99.7	−99.1 ± 0.6

<sup>a</sup> From ref 3, unless indicated otherwise. <sup>b</sup> 2-Methylpropane. <sup>c</sup> 2-Methylbutane. <sup>d</sup> 2,2-Dimethylpropane. <sup>e</sup> Ref 4. <sup>f</sup> (E)-Decahydronaphthalene.

<sup>g</sup> Cyclohexylcyclohexane.

**TABLE 2: Calculated and Experimental Enthalpies of Formation of Strained Alkanes, Calculated Strain Values by Equation 1 and Literature Strain (kcal mol<sup>-1</sup>)**

alkane	$\Delta_f H^\circ$ , eq 1	$\Delta_f H^\circ$ , lit. <sup>a</sup>	diff.	lit. strain
cyclopropane	-14.9	9.4	24.3	24.1, <sup>b</sup> 27.5 <sup>c</sup>
cyclobutane	-19.9	6.8 <sup>d</sup>	26.7	26.4, <sup>b</sup> 26.5, <sup>c</sup> 27.0 <sup>e</sup>
cyclopentane	-24.9	-18.3	6.6	6.2, <sup>b</sup> 7.3, <sup>f</sup> 7.3 <sup>e</sup>
cycloheptane	-34.9	-28.3 <sup>d</sup>	6.7	6.0, <sup>b</sup> 7.4, <sup>e</sup> 7.7, <sup>f</sup> 6.2 <sup>g</sup>
cyclooctane	-39.8	-29.7 <sup>d</sup>	10.1	9.5, <sup>b</sup> 11.3, <sup>e</sup> 11.9, <sup>f</sup> 9.6 <sup>g</sup>
cyclodecane	-49.8	-36.9 <sup>d</sup>	12.9	12.1, <sup>b</sup> 16.4, <sup>f</sup> 12.3 <sup>g</sup>
cyclododecane	-59.8	-55.0 <sup>d</sup>	4.8	3.8, <sup>b</sup> 11.8, <sup>f</sup> 4.0 <sup>g</sup>
cyclotetradecane	-69.7	-65.6 <sup>g</sup>	4.1	3.0, <sup>b</sup> 3.8 <sup>g</sup>
2,2-dimethylbutane	-45.1	-44.4	0.7	1.1 <sup>h</sup>
2,3-dimethylbutane	-43.3	-42.5	0.8	2.1, <sup>h</sup> 0.4 <sup>i</sup>
2,2,3-trimethylbutane	-51.8	-49.0	2.8	3.7, <sup>e</sup> 2.7 <sup>i</sup>
2,2,3,3-tetramethylbutane	-60.2	-54.0	6.2	7.7, <sup>f</sup> 6.4, <sup>i</sup> 6.7 <sup>j</sup>
2,2,4-trimethylpentane	-56.7	-53.5	3.2	4.2 <sup>e</sup>
3,3,4,4-tetramethylhexane	-70.2	-58.8 <sup>j</sup>	11.4	11.5 <sup>j</sup>
4,4,5,5-tetramethyloctane	-80.1	-69.4 <sup>j</sup>	10.7	11.5 <sup>j</sup>
2,2,4,4,5,5,7,7-octamethyloctane	-110.3	-86.6 <sup>j</sup>	23.7	24.4 <sup>j</sup>
1,1,2,2-tetra- <i>tert</i> -butylethane	-123.5	-59.9	63.7	66.3 <sup>k</sup>
spiropentane	-19.9	44.2	64.1	63.2, <sup>c</sup> 65.1, <sup>h</sup> 64.1 <sup>l</sup>
bicyclo[1.1.0]butane	-13.1	51.9	65.0	63.9, <sup>c</sup> 66.7, <sup>h</sup> 64.7 <sup>l</sup>
bicyclo[2.1.0]pentane	-18.1	37.7	55.8	54.7, <sup>c</sup> 57.7, <sup>h</sup> 53.3 <sup>l</sup>
<i>cis</i> -bicyclo[2.2.0]hexane	-23.1	29.8	52.9	51.8, <sup>c</sup> 55.0 <sup>h</sup>
norbornane (bicyclo[2.2.1]heptane)	-28.1	-13.1	15.0	14.4, <sup>c</sup> 17.0 <sup>l</sup>
cubane	-12.7	148.7	161.4	154.7, <sup>c</sup> 166.8 <sup>h</sup>
bicyclo[2.2.2]octane	-33.1	-23.7	9.4	7.4, <sup>c</sup> 12.9 <sup>f</sup>
adamantane	-36.2	-32.1	4.1	6.9, <sup>f</sup> 7.7 <sup>h</sup>
[2.2.1]-propellane	-28.1	87 <sup>m</sup>	115.1	109 <sup>m</sup>
[3.2.1]-propellane	-33.1	36.3	69.4	67 <sup>m</sup>
[2.2.2]-propellane	-33.1	69.3 <sup>n</sup>	102.4	97 <sup>n</sup>
3,3,4,4-tetraethylhexane	-90.1	63.5 <sup>k</sup>	26.6	28.2 <sup>k</sup>
2,2,3,3,4,4,5,5-octamethylhexane	-100.4	-59.3 <sup>k</sup>	41.1	42.4 <sup>k</sup>
tri- <i>tert</i> -butylmethane	-91.9	-56.2 <sup>k</sup>	35.7	37.3 <sup>k</sup>
bicyclopropyl	-23.1	30.9 <sup>l</sup>	54.0	54.4 <sup>l</sup>

<sup>a</sup> From ref 3, unless indicated otherwise. <sup>b</sup> From the difference of experimental<sup>3</sup>  $\Delta_f H^\circ$  of the cycloalkane and one-sixth of that of cyclohexane multiplied by the number of carbons of the cycloalkane. <sup>c</sup> Ref 5. <sup>d</sup> Ref 4. <sup>e</sup> Ref 6. <sup>f</sup> Ref 7. <sup>g</sup> Ref 8. <sup>h</sup> Ref 9a. <sup>i</sup> Ref 10. <sup>j</sup> Ref 11. <sup>k</sup> Ref 12. <sup>l</sup> Ref 9b. <sup>m</sup> Estimated value, ref 13. <sup>n</sup> 6-31G\* calculation, ref 14.

than *trans*-alkenes by about  $1.1 \pm 0.3$ , and so are tetra-substituted simple alkenes such as 2,3-dimethyl-2-butene. In rare cases, strain and conjugation can commingle in such a way that neither can be determined by a single comparison of  $\Delta_f H^\circ$  values.

**Alkynes.** Table 4 lists 28 examples of enthalpies of formation of simple, unconjugated alkynes calculated by eq 3 and literature values with their specified uncertainties. Values from the NIST Database No. 69<sup>3</sup> are given, supplemented by other values, as indicated. The average unsigned deviation of calculated values from 37 literature values in Table 4 is 0.37 kcal mol<sup>-1</sup>. In the case of alkynes, experimental enthalpies of formation generally have greater uncertainties than those of alkanes and alkenes.

Strain has been reported in unconjugated diynes when triply bonded carbons are separated by a CH<sub>2</sub> group. The reported<sup>25a</sup> instability of about 3.6 kcal mol<sup>-1</sup> introduced by the group RC≡C-CH<sub>2</sub>-C≡CR, where R represents H or a linear alkyl group, is confirmed here, as shown by examples below the dashed line in Table 4. Experimental  $\Delta_f H^\circ$  values of 2-, 3-, and 4-octyne as well as that of 5-decyne suggest small diminution of  $\Delta_f H^\circ$  as the triple bond approaches the center of the molecule due to the difference between the statistical average of conformers in the alkyne and the product alkane.<sup>26</sup>

**Alkylbenzenes.** Alkylbenzenes, a class not treated in recent methods,<sup>1,2</sup> are included here. Table 5 lists  $\Delta_f H^\circ$  values calculated by eq 4 for 20 unstrained alkylbenzenes and literature values from the NIST Database No. 69,<sup>3</sup> supplemented by other values, as indicated. The average unsigned deviation of calculated values from 21 literature values is 0.29 kcal mol<sup>-1</sup>. Entries

below the dashed line of the table pertain to compounds that may or may not exhibit thermodynamic effects due to steric crowding or conjugation. The difference between experimental  $\Delta_f H^\circ$  and  $\Delta_f H^\circ$  calculated by eq 4 is the magnitude of the effect.

## Discussion

**Alkanes and Alkenes.** Enthalpies of formation of unstrained alkanes follow very regular patterns, and the many methods that have been proposed reproduce experimentally established stabilities within probable experimental error. Equations 1–4 are, in effect, a very simple group additivity method that is considerably simpler than Benson's widely used method.<sup>31</sup> For unstrained alkanes, alkenes, alkynes, and alkylbenzenes, we use a total of 8 coefficients versus Benson's 30, without loss of accuracy. For unstrained alkanes, Benson uses 4 coefficients; for unstrained alkenes, an additional 10; for unstrained alkynes, an additional 7; and for unstrained alkylbenzenes, an additional 9. Benson corrects calculated values for cyclohexanes by adding 0.7 kcal mol<sup>-1</sup>, while we find no need for such correction for all eight typical cyclohexanes of Table 1, including bicyclohexyl and *trans*-decalin. We also find no need for a coefficient pertaining to quaternary carbons (no hydrogens). Equation 1 performs well for unstrained alkenes, alkanes, and cyclohexanes, except when "special effects" come into play, such as angle strain in cyclopropane, steric crowding in di-*tert*-butyl (2,2,3,3-tetramethylbutane), conjugation in dienes, and so on. Calculated strain energies are generally consistent with reported values, most of which were obtained by more elaborate methods.

TABLE 3: Calculated by Equation 2 and Literature Enthalpies of Formation of Alkenes (kcal mol<sup>-1</sup>)

alkene	<i>n</i> <sub>1</sub>	<i>n</i> <sub>2</sub>	<i>n</i> <sub>3</sub>	<i>n</i> <sub>4</sub>	<i>n</i> <sub>5</sub>	$\Delta_f H^\circ$ , eq 2	$\Delta_f H^\circ$ , lit. <sup>a</sup>
ethylene (ethene)	0	0	0	4	0	12.5	12.54
propene	3	0	0	3	1	5.0	4.88
( <i>E</i> )-2-butene	6	0	0	2	2	-2.6	-2.6
2-methylpropene	6	0	0	2	2	-2.6	-4.3, -3.7 <sup>h,c</sup>
1,4-pentadiene	0	2	0	6	2	25.0	25.4
1-pentene	3	4	0	3	1	-5.0	-5.1, <sup>d</sup> -5.1 <sup>h,e</sup>
( <i>E</i> )-2-pentene	6	2	0	2	2	-7.6	-7.9
2-Me-1-butene	6	2	0	2	2	-7.6	-8.4
3-Me-1-butene	6	0	1	3	1	-6.7	-6.5 <sup>d</sup>
2-Me-2-butene	9	0	0	1	3	-10.2	-9.9, -10.1, <sup>d</sup>
( <i>E</i> )-1,4-hexadiene	3	2	0	5	3	17.5	17.1
1,5-hexadiene	0	4	0	6	2	20.1	20.4
3-Me-1,4-pentadiene	3	0	1	6	2	18.4	19.0, <sup>d</sup> 17.6 <sup>f</sup>
1-hexene	3	6	0	3	1	-10.0	-10.1, -9.7 <sup>h,g</sup>
( <i>E</i> )-2-hexene	6	4	0	2	2	-12.6	-12.3, <sup>h,g</sup> -12.9 <sup>f</sup>
( <i>E</i> )-3-hexene	6	4	0	2	2	-12.6	-12.3, <sup>b</sup> <sup>g</sup> -12.1 <sup>d</sup>
2-Et-1-butene	6	4	0	2	2	-12.6	-13.4, -13.3 <sup>h,g</sup>
3,3-Me <sub>2</sub> -1-butene	9	0	0	3	1	-15.1	-14.5, <sup>d</sup> -14.3 <sup>h,g</sup>
2-Me-1-pentene	6	4	0	2	2	-12.6	-14.2, <sup>d</sup> -13.9, <sup>h,g</sup>
3-Me-1-pentene	6	2	1	3	1	-11.6	-11.8, <sup>d</sup> -11.2 <sup>h,g</sup>
4-Me-1-pentene	6	2	1	3	1	-11.6	-12.0, <sup>d</sup> -11.4 <sup>h,g</sup>
2-Me-2-pentene	9	2	0	1	3	-15.2	-16.0, <sup>d</sup> -15.0, <sup>h,g</sup>
3-ethenyl-1,4-pentadiene	0	0	1	9	3	43.4	46.0, <sup>d</sup> 42.7 <sup>f</sup>
1-heptene	3	8	0	3	1	-15.0	-15.0, <sup>h,h</sup> -14.6 <sup>i</sup>
( <i>E</i> )-2-heptene	6	6	0	2	2	-17.5	-17.6, <sup>h,h</sup> -17.0 <sup>d</sup>
( <i>E</i> )-3-heptene	6	6	0	2	2	-17.5	-17.5, <sup>h,h</sup> -17.6 <sup>d</sup>
2,4-Me <sub>2</sub> -1-pentene	9	2	1	2	2	-19.2	-20.9, <sup>h,j</sup> -20.0 <sup>d</sup>
4,4-Me <sub>2</sub> -1-pentene	9	2	0	3	1	-20.1	-20.0, <sup>h,j</sup> -20.0 <sup>d</sup>
1-octene	3	10	1	3	1	-19.9	-19.8, <sup>h,k</sup> -19.4 <sup>d</sup>
( <i>E</i> )-2-octene	6	8	0	2	2	-22.5	-22.2 <sup>h,k</sup> -23.0 <sup>d</sup>
3-Me-2-hexene	9	4	0	1	3	-20.1	-20.0, <sup>d</sup> -20.3 <sup>f</sup>
( <i>E</i> )-3-Et-3-hexene	9	6	0	1	3	-25.1	-25.0, <sup>d</sup> -24.9 <sup>f</sup>
( <i>E</i> )-2,5-Me <sub>2</sub> -3-hexene <sup>l</sup>	12	0	2	2	2	-25.9	-26.0, <sup>d</sup> -26.5 <sup>f</sup>
2,2,4-Me <sub>3</sub> -1-pentene	12	2	0	2	2	-27.7	-26.4, <sup>d</sup> -28.4 <sup>f</sup>
1-nonene	3	12	0	3	1	-24.5	-25.0, <sup>d</sup> -24.7 <sup>f</sup>
2-nonene	6	10	0	2	2	-27.5	-27.0, <sup>d</sup> -27.6 <sup>f</sup>
1-decene	3	14	0	3	1	-29.9	-29.8, -29.6 <sup>f</sup>
5-decene	6	12	0	2	2	-32.6	-32.0, <sup>d</sup> -30.4 <sup>h,m</sup>
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( <i>Z</i> )-2-butene <sup>n</sup>	6	0	0	2	2	-2.6	-1.8
( <i>Z</i> )-2-pentene <sup>o</sup>	6	2	0	2	2	-7.6	-6.7
( <i>Z</i> )-3-hexene <sup>p</sup>	6	4	0	2	2	-12.6	-11.2 <sup>d</sup>
2,3-Me <sub>2</sub> -2-butene <sup>q</sup>	12	0	0	0	4	-17.7	-18.8
( <i>Z</i> )-cyclopentene <sup>r</sup>	0	6	0	2	2	2.5	8.5
cyclohexene <sup>s</sup>	0	8	0	2	2	-2.5	-1.0 ± 0.2
1,4-cyclohexadiene <sup>t</sup>	0	4	0	4	4	25.0	24.0 ± 0.7
( <i>E</i> )-cyclooctene <sup>u</sup>	0	12	0	2	2	-12.4	4.8
norbornene <sup>v</sup>	0	6	2	2	2	-0.7	21 ± 1
norbornadiene <sup>w</sup>	0	2	2	4	4	26.8	58.4 ± 0.4

<sup>a</sup> From ref 3, unless indicated otherwise. <sup>b</sup> From the experimental enthalpies of formation (Table 1) and of hydrogenation. <sup>c</sup> Ref 15. <sup>d</sup> Ref 4. <sup>e</sup> Ref 16. <sup>f</sup> Estimated by group additivity in ref 4. <sup>g</sup> Ref 17. <sup>h</sup> Ref 18. <sup>i</sup> Ref 19. <sup>j</sup> Ref 20. <sup>k</sup> Ref 21. <sup>l</sup> *trans*-Diisopropylethylene. <sup>m</sup> Ref 22a. <sup>n</sup> Strain = 1.2 kcal mol<sup>-1</sup>. <sup>o</sup> Strain = 0.9. <sup>p</sup> Strain = 1.4. <sup>q</sup> Strain = 0.9. <sup>r</sup> Strain = 6.0 versus reported 6.9 (ref 23). <sup>s</sup> Strain = 1.5 ± 0.2 versus reported 2.6 (ref 23). <sup>t</sup> Strain = 1.0 ± 0.7 versus reported 2.6 (ref 20). <sup>u</sup> Strain = 17.2 versus reported 17.9 (ref 23). <sup>v</sup> Bicyclo[2.2.1]hept-2-ene, strain = 21.7 ± 1.0 versus reported 23.6 (ref 24a) and 21.6 (ref 24b). <sup>w</sup> Bicyclo[2.2.1]hepta-2,5-diene, strain = 31.6 ± 0.4 versus reported 31.6 (ref 24a) and 32.3 (ref 24b).

A recent method for calculating enthalpies of formation of hydrocarbons has been devised by Gronert for unstrained alkanes, alkenes, and alkyl radicals by global fitting to a group of 24 typical molecules.<sup>1a</sup> This method uses seven freely adjustable parameters not derived from enthalpies of formation plus the enthalpy of formation of the hydrogen atom, including terms for 1,3 repulsive interactions (C–C–C, C–C–H, and H–C–H). It successfully reproduces experimental values without any terms accounting for hyperconjugation. There is some experimental evidence of bond angle broadening due to 1,3 repulsive interactions in C–C–C and H–C–C,<sup>1</sup> but the influence on  $\Delta_f H^\circ$  appears to be negligible.

Subsequently Wodrich and Schleyer also proposed a new method for alkanes, alkenes, alkynes, and alkyl radicals using *attractive* 1,3 interactions and terms ascribed to hyperconjugation.<sup>2b</sup> Their method uses experimental enthalpies of formation as the basis for each type of species: methane, ethene, ethyne, 1° radical and 2° radical, values for C–C–C attractive interactions, contributions of hyperconjugation, and adjustable parameters for attenuation of the effect of more than one carbon substituted on carbon. Acceptable fitting of 36 typical species was obtained, and the fact was emphasized that no global fit was used.



**TABLE 4: Calculated by Equation 3 and Literature Enthalpies of Formation of Alkynes (kcal mol<sup>-1</sup>)**

alkyne	<i>n</i> <sub>1</sub>	<i>n</i> <sub>2</sub>	<i>n</i> <sub>3</sub>	<i>n</i> <sub>6</sub>	<i>n</i> <sub>7</sub>	$\Delta_f H^\circ$ , eq 2	$\Delta_f H^\circ$ , lit. <sup>a</sup>
ethyne (acetylene)	0	0	0	1	0	54.4	54.2 ± 0.2
propyne	3	0	0	1	0	44.4	44.3 ± 0.2
1-butyne	3	2	0	1	0	39.4	39.4 ± 0.2
2-butyne	6	0	0	0	1	35.2	34.7 ± 0.2
1-pentyne	3	4	0	1	0	34.4	34.5 ± 0.5
2-pentyne	6	2	0	0	1	30.3	30.8 ± 0.5
3-Me-1-butyne	6	0	1	1	0	32.7	32.6 ± 0.5
1,5-hexadiyne	0	4	0	0	2	98.9	99.0, <sup>b</sup> 99.6, <sup>c</sup> 99.1 <sup>d</sup>
1-hexyne	3	6	0	1	0	29.4	29.2 ± 0.1
2-hexyne	6	4	0	0	1	25.3	25.7 ± 0.6
3-hexyne	6	4	0	0	1	25.3	25.2 ± 0.5
4-Me-1-pentyne	6	2	1	1	0	27.8	28.0, <sup>b</sup> 27.5 <sup>e</sup>
4-Me-2-pentyne	9	0	1	0	1	23.6	23.0, <sup>b</sup> 22.8 <sup>e</sup>
3,3-Me <sub>2</sub> -1-butyne	9	0	0	1	0	24.3	25.4, 24.4, <sup>e</sup> 25.0 ± 0.7 <sup>b</sup>
1,5-heptadiyne	3	4	0	1	1	89.7	90.3 <sup>c</sup>
1,6-heptadiyne	0	6	0	2	0	93.9	94.5 <sup>c</sup>
1-heptyne	3	8	0	1	0	24.4	24.8 ± 0.6
2-heptyne	6	6	0	0	1	20.3	20.3 ± 0.5
3-heptyne	6	6	0	0	1	20.3	19.8 ± 0.6
4,4-Me <sub>2</sub> -2-pentyne	12	0	0	0	1	15.2	14.8 <sup>b</sup>
1,7-octadiyne	0	8	0	2	0	88.9	89.3 <sup>c</sup>
1-octyne	3	10	0	1	0	19.5	19.3 ± 0.9, 19.4 <sup>c</sup>
2-octyne	6	8	0	0	1	15.3	15.2 ± 0.4, 16.6 <sup>c</sup>
3-octyne	6	8	0	0	1	15.3	14.9 ± 0.4, 16.0 <sup>c</sup>
4-octyne	6	8	0	0	1	15.3	14.4 ± 0.5, 15.8 <sup>c</sup>
1-decyne	3	14	0	1	0	9.5	10.0 ± 0.8, 10.0 ± 0.5 <sup>f</sup>
2-decyne	6	12	0	0	1	5.3	5.6 ± 0.6 <sup>f</sup>
5-decyne	6	12	0	0	1	5.3	4.4 ± 0.5 <sup>f</sup>
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1,4-pentadiyne	0	2	0	1	1	103.9	107.8 <sup>g</sup>
1,4-hexadiyne	3	2	0	1	1	94.7	98.1 <sup>g, h</sup>
1,4-heptadiyne	3	4	0	1	1	89.7	93.5 <sup>g, i</sup>
2,5-heptadiyne	6	2	0	0	2	85.6	89.1 <sup>f, j</sup>

<sup>a</sup> From ref 3, unless indicated otherwise. <sup>b</sup> Ref 4. <sup>c</sup> Ref 25b, from the G3(MP2) calculation of enthalpies of hydrogenation and the experimental value<sup>3</sup> of the product alkane. <sup>d</sup> Ref 27, G3 calculation. <sup>e</sup> Estimated by group additivity in ref 4. <sup>f</sup> From the enthalpy of hydrogenation of ref 25b and the experimental<sup>3</sup> value of the product alkane. <sup>g</sup> G3(MP2) calculation (ref 25a), strain = 3.9 kcal mol<sup>-1</sup>. <sup>h</sup> Strain = 3.4. <sup>i</sup> Strain = 3.8. <sup>j</sup> Strain = 3.5.

At issue in these two works is whether hyperconjugation is a significant factor for the stability of the species examined and whether 1,3 interactions are repulsive or attractive. Both works agree that their fitting methods do not provide conclusive evidence either way. Gronert makes his arguments against hyperconjugation on the basis of other evidence: van der Waals radii, bond angles, bending vibration force constants, and EPR<sup>1b</sup> spectra of radicals. He notes the viability of a method that is successful without recourse to hyperconjugation. Other recent publications yielded mixed results for neutral species: against hyperconjugation<sup>32,33</sup> or in favor of it.<sup>34</sup>

The present calculation of enthalpies of formation does not have any adjustable parameters and is not a global fit to the experimental  $\Delta_f H^\circ$  of the compounds treated. Were 1,3 interactions, for example, C—C—C interactions,<sup>1,2</sup> operative to a significant extent, eqs 1–4 would not be as accurate as they are. Equation 1 applies equally well to ethane (no C—C—C

**TABLE 5: Calculated by Equation 4 and Literature Enthalpies of Formation of Alkylbenzenes (kcal mol<sup>-1</sup>)**

alkylbenzene	<i>n</i> <sub>1</sub>	<i>n</i> <sub>2</sub>	<i>n</i> <sub>3</sub>	<i>N</i> <sub>8</sub>	$\Delta_f H^\circ$ , eq 4	$\Delta_f H^\circ$ , lit. <sup>a</sup>
benzene	0	0	0	0	19.8	19.82 ± 0.12
toluene	3	0	0	1	12.0	11.95 ± 0.15
ethylbenzene	3	2	0	1	7.0	7.1 ± 0.2
propylbenzene	3	4	0	1	2.0	1.9 ± 0.2
butylbenzene	3	6	0	1	-3.0	-3.0 ± 0.3
isobutylbenzene	6	2	1	1	-4.7	-5.1 ± 0.3
pentylbenzene	3	8	0	1	-8.0	-7.8 <sup>b</sup>
neopentylbenzene	9	2	0	1	-13.1	-13.0 <sup>b</sup>
1,3-Me <sub>2</sub> -benzene	6	0	0	2	4.1	4.1 ± 0.2
1,4-Me <sub>2</sub> -benzene	6	0	0	2	4.1	4.3 ± 0.2
1,3-Et <sub>2</sub> -benzene	6	4	0	2	-5.9	-5.0 <sup>b</sup>
1,4-Et <sub>2</sub> -benzene	6	4	0	2	-5.9	-5.0 ± 0.5 <sup>b</sup>
1,4-dipropylbenzene	6	8	0	2	-15.8	-16, <sup>b</sup> -15.7 <sup>c</sup>
1-Et-3-Me-benzene	6	2	0	2	-0.9	-0.5 ± 0.3
1-Et-4-Me-benzene	6	2	0	2	-0.9	-0.8 ± 0.4
1,3,5-Me <sub>3</sub> -benzene	9	0	0	3	-3.8	-3.8 ± 0.3 <sup>b</sup>
1,3,5-Et <sub>3</sub> -benzene	9	6	0	3	-18.7	-19.0 <sup>b</sup>
allylbenzene <sup>d</sup>	0	0	0	1	31.0 <sup>d</sup>	32.1 ± 1 <sup>b</sup>
cyclohexylbenzene	0	10	1	1	-4.5	-4.0 ± 0.4
diphenylmethane	0	2	0	2	39.0	39.4 ± 0.4
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isopropylbenzene	6	0	1	1	0.3	0.9 ± 0.3
tert-butylbenzene	12	0	0	1	-8.1	-5.4 ± 0.3
1,2-Me <sub>2</sub> -benzene	6	0	0	2	4.1	4.5 ± 0.3
1-Et-2-Me-benzene	6	2	0	2	-0.9	0.3 ± 0.3
1,2-di- <i>t</i> -Bu-benzene	18	0	0	2	-36.1	-30.8 <sup>c</sup>
4- <i>t</i> -butyltoluene	12	0	0	2	-16.0	-13.6 ± 0.4
1,2,3-Me <sub>3</sub> -benzene	9	0	0	3	-3.8	-2.3 ± 0.3
1,2,4-Me <sub>3</sub> -benzene	9	0	0	3	-3.8	-3.3 ± 0.3
1,2,4,5-Me <sub>4</sub> -benzene	12	0	0	4	-11.6	-11.2 ± 0.5
1,2,3,5-Me <sub>4</sub> -benzene	12	0	0	4	-11.6	-10.3 ± 0.3
Me <sub>5</sub> -benzene	15	0	0	5	-19.1	-16.1 ± 0.5
Me <sub>6</sub> -benzene	18	0	0	6	-27.4	-18.5 ± 0.6, -21 ± 0.7 <sup>b</sup>
Et <sub>6</sub> -benzene	18	12	0	6	-57.3	-53.8 <sup>b</sup>
biphenyl	0	0	0	2	44.0	43.5 ± 0.2
styrene	0	0	0	1	36.9 <sup>e</sup>	35.1 ± 0.2
trans-stilbene <sup>e</sup>	0	0	0	2	61.3 <sup>f</sup>	53.4, 53.0 ± 0.5 <sup>g</sup>
para-terphenyl <sup>h</sup>	0	0	0	4	68.1	66.6 ± 1.5
para-quaterphenyl	0	0	0	6	92.3	91.4 ± 1.8
phenylacetylene	0	0	0	1	76.4 <sup>i</sup>	77.8 ± 0.3, <sup>j</sup> 73.2 ± 0.5 <sup>k</sup>
triphenylmethane	0	0	1	3	64.3	65.0 ± 1 <sup>b</sup>
tetraphenylmethane	0	0	0	6	92.3	95.0 ± 1 <sup>b</sup>
C <sub>14</sub> H <sub>12</sub> <sup>l</sup>	0	4	0	4	38.4	37.1 ± 0.4, 42 ± 2 <sup>b</sup>

<sup>a</sup> From ref 3, unless indicated otherwise. <sup>b</sup> Ref 4. <sup>c</sup> Estimated by group additivity in ref 4. <sup>d</sup> 3-Phenyl-1-propene; calculated with *n*<sub>4</sub> = 3 and *n*<sub>5</sub> = 1. Lit. value is from the enthalpy of hydrogenation<sup>22b</sup> and the enthalpy of formation of product propylbenzene.<sup>8</sup> <sup>e</sup> (*E*)-1,2-diphenylethene. <sup>f</sup> Calculated with *n*<sub>4</sub> = 2, *n*<sub>5</sub> = 2, and 19.82 × 2. <sup>g</sup> From the enthalpy of hydrogenation<sup>28</sup> and of formation of ethylbenzene.<sup>3</sup> <sup>h</sup> 1,4-Diphenylbenzene, using 19.82 × 3. <sup>i</sup> Phenylethyne, *n*<sub>6</sub> = 1. <sup>j</sup> From the enthalpy of hydrogenation<sup>29</sup> and of formation of product ethylbenzene.<sup>3</sup> <sup>k</sup> From the enthalpy of hydrogenation<sup>30</sup> and of formation of product ethylbenzene.<sup>3</sup> <sup>l</sup> 9,10-Dihydrophenanthrene.

interaction) and neopentane (six C—C—C interactions). Neither are hyperconjugative interaction terms, such as those incorporated by Wodrich and Schleyer<sup>2</sup> needed for any of the compounds treated in this work.

The energy released upon hydrogenation of propene is 2.7 kcal mol<sup>-1</sup> smaller than that of ethene. This is commonly quoted as the value of hyperconjugation stabilization by an alkyl group.

Hydrogenation of (*E*)-2-butene releases 5.13 kcal mol<sup>-1</sup> less than that of ethene, and this is given as the value of hyperconjugation stabilization for two *trans*-alkyl groups. Other values are obtained similarly for other patterns of alkyl substitution on the double bond. The rationalization conventionally offered for this effect is ascribed to the interaction of the  $\pi^*$  orbital of the alkene with an occupied orbital of the alkyl substituent on the double bond.

However, this is not the only way to describe the effect of alkyl substitution. The change in  $\Delta_f H^\circ$  in going from H<sub>2</sub>C=CH<sub>2</sub> to H<sub>2</sub>C=CHCH<sub>3</sub> can also be described as

$$\Delta_f H^\circ(\text{H}_2\text{C}=\text{CHCH}_3) = \Delta_f H^\circ(\text{H}_2\text{C}=\text{CH}_2) + (-3.345 \times 3) + k \quad (5)$$

where  $(-3.345 \times 3)$  from eq 1 is the contribution of the three hydrogens of the methyl group to the enthalpy of formation and  $k$  is the effect of the interaction of the alkyl group with the double bond. Substituting known values into the equation yields  $k = 4.88 - 12.54 - (-3.345 \times 3) = 2.38$  kcal mol<sup>-1</sup>, which is destabilizing. Thus, the definition of hyperconjugation (its reference state) determines its value and whether it is stabilizing or destabilizing.

A recently proposed method<sup>2c</sup> that includes hyperconjugation and “protobranching” (1,3 C—C—C attractive interactions) was successful, and this success was reported as proving the existence of hyperconjugation stabilization of 5.5 kcal mol<sup>-1</sup> for one alkyl group on the double bond. Equation 5 for the variously methyl-substituted alkenes of Table 3, however, gives values of  $k_1 = 2.38$  kcal mol<sup>-1</sup> for H<sub>2</sub>C=CHR,  $k_2 = 4.96$  for (*E*)-RHC=CHR,  $k_3 = 3.69$  for R<sub>2</sub>C=CH<sub>2</sub>,  $k_4 = 7.56$  for R<sub>2</sub>C=CHR, and  $k_5 = 10.80$  for R<sub>2</sub>C=CR<sub>2</sub>, all destabilizing. Using these values for the effect of alkyl substitutions on the double bond, we obtain agreement with the experimental enthalpies of formation of Table 3 by eq 6, where the value of  $k_i$  is the one appropriate for the alkyl substitution pattern.

$$\Delta_f H^\circ(\text{alkene}) = \Delta_f H^\circ(\text{ethene}) + (-3.345)n_1 + (-2.490)n_2 + (-1.590)n_3 + k_i \quad (6)$$

The agreement obtained by eq 6<sup>35</sup> is comparable to the one reported in Table 3, which was obtained by a different calculation, eq 3. Success in fitting the regular patterns of the enthalpies of formation of hydrocarbons does not prove the validity of rationalizations proposed for them.

**Alkynes and Alkylbenzenes.** The energy released upon hydrogenation of propyne is 4.9 kcal mol<sup>-1</sup> smaller than that of ethyne. This is commonly quoted as the value of hyperconjugation stabilization by an alkyl group. Postulating hyperconjugation and protobranching has led to the report of hyperconjugative stabilization of 7.7 kcal mol<sup>-1</sup> in propyne.<sup>2c</sup> However, the change in  $\Delta_f H^\circ$  in going from HC≡CH to HC≡CCH<sub>3</sub> can be described by eq 7, a variant of eq 5,

$$\Delta_f H^\circ(\text{HC}\equiv\text{CCH}_3) = \Delta_f H^\circ(\text{HC}\equiv\text{CH}) + (-3.345 \times 3) + k \quad (7)$$

where  $(-3.345 \times 3)$  from eq 1 is the contribution of the three hydrogens on the sp<sup>3</sup> carbon and  $k$  is the effect of the interaction of the alkyl group with the triple bond,  $k = 44.3 - 54.42 - (-3.345 \times 3) = -0.1$  kcal mol<sup>-1</sup>, a negligible effect found by focusing not on hydrogenation of the multiple bond but on the  $\Delta_f H^\circ$  of the entire molecule.

The value  $c_5 - c_4 = 5.600 - 3.135 = 2.47$  is similar but not identical to  $k = 2.38$  in eq 5. Similarly for alkynes, our  $k =$

$-0.1$  in eq 7 is not the same as  $c_7 - c_6 = 55.31 - 54.42 = 0.89$ . These differences are not great, but conceptually, the difference is significant in that the  $k$  values were not derived from the  $c_i$  coefficients, nor are they linearly related to them. Readers who wish to maintain that conventional definitions of hyperconjugation, protobranching, and so forth are preferable to our new alternative should explain why changes in the enthalpies of hydrogenation of double bonds, for example, ethylene versus propylene, are better criteria than corresponding changes in their enthalpies of formation, as in eqs 5–7. In other words, they should show why more complex procedures are preferable to our simpler one, in violation of the logical dictum called Occam’s razor.

Adjacent pairs of methyl groups do not make a substantial contribution to the strain energy of methylbenzenes. In Table 5, the strain-free  $\Delta_f H^\circ$  calculated by eq 4 of *ortho*-xylene (1,2-dimethylbenzene) is almost identical to the experimental value, indicating the lack of strain. The two nonadjacent methyls in 1,2,4-trimethylbenzene, for which the calculated and experimental  $\Delta_f H^\circ$  differ by only  $0.5 \pm 0.3$  kcal mol<sup>-1</sup>, show little strain, and the  $\Delta_f H^\circ$  values for 1,2,4,5-tetramethylbenzene differ by only  $0.4 \pm 0.5$ . Three adjacent methyl groups in 1,2,3-trimethylbenzene produce some strain, 1.5 kcal mol<sup>-1</sup>, as indicated Table 5, and six adjacent methyl groups in hexamethylbenzene produce a substantial strain of about 8 kcal mol<sup>-1</sup>.

Conjugation stabilization in biphenyl is small,  $0.5 \pm 0.2$  kcal mol<sup>-1</sup>, consistent with little or no conjugation reported previously<sup>13</sup> and also consistent with reports that the two phenyl rings are not coplanar (electron diffraction, Raman, NMR) but make a dihedral angle of 30–45°. Coplanarity was reported in the solid, but crystal energy effects are operative there. Little or no conjugation stabilization,  $1.5 \pm 1.5$  kcal mol<sup>-1</sup>, is also found in *p*-terphenyl (1,4-diphenylbenzene), where the dihedral angles between the central and terminal rings are about 45° according to its “3d Mol file” depiction.<sup>3</sup>

Conjugation stabilization in styrene (phenylethene),  $1.8 \pm 0.2$  kcal mol<sup>-1</sup>, is smaller than that in 1,3-butadiene, which is consistent with 1.7 and 1.5 reported previously<sup>13</sup> and also consistent with the fact that the vinyl group is not coplanar with the benzene ring by electron diffraction<sup>37</sup> and NMR<sup>38</sup> studies showing dihedral angles of 27 and 17°, respectively. Coplanarity is attained in *trans*-stilbene, and the thermodynamic conjugation stabilization is 8 kcal mol<sup>-1</sup>, which brings the two rings into conjugation.

The two conflicting experimental results from the enthalpies of hydrogenation  $\Delta_f H^\circ$  of phenylacetylene (phenylethyne) do not allow a definite conclusion from the experimental entries in Table 5. One result indicates destabilization by  $1.4 \pm 0.3$  kcal mol<sup>-1</sup>, and the other indicates stabilization by  $3.2 \pm 0.5$ . To resolve the issue, we performed a full G3 model chemistry calculation of the enthalpy of formation of phenylacetylene. The result of  $\Delta_f H^\circ(\text{C}_6\text{H}_5\text{C}\equiv\text{CH}) = 76.41$  kcal mol<sup>-1</sup> is the same as that obtained by combination of eqs 3 and 4, which do not account for thermodynamic conjugation stabilization. This finding, indicating no conjugation in this case, is not subject to any effects of the possible lack of coplanarity.

**Theoretical Implications.** 1,3-Interaction and hyperconjugation terms, attractive or repulsive, can be postulated and incorporated into eqs 1–4 to produce mathematically equivalent results. However, such terms will be linearly related to the coefficients  $c_1$ – $c_8$ . The success of such procedures does not prove the postulated effects, as has been claimed.<sup>2c</sup>

By combining eqs 1–4, as appropriate, some surprising results are obtained for measurable thermodynamic stabilization by

**TABLE 6: Calculated and Literature Enthalpies of Formation of Conjugated Dienes, Eneynes, Diynes, and Triynes (kcal mol<sup>-1</sup>)**

conjugated molecules	$\Delta_f H^\circ$ , calcd	$\Delta_f H^\circ$ , lit. <sup>a</sup>	conjugation stabilization <sup>b</sup>
1,3-butadiene	29.9	26.0 ± 0.2	-3.9 ± 0.2
(E)-1,3-pentadiene	22.4	18.1 ± 0.2	-4.3 ± 0.2
(E)-1,3-hexadiene	17.4	13.0 ± 0.4	-4.4 ± 0.4
(E,E)-2,4-hexadiene	14.8	10.6 ± 0.4	-4.2 ± 0.4
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1-buten-3-yne	69.4	70.4	+1.0
		70.8 ± 0.5 <sup>c</sup>	+1.5 ± 0.5
(E)-3-penten-1-yne	61.9	61.9	0.0
		61.0 ± 0.7 <sup>d</sup>	-0.9 ± 0.7
		60.9 ± 0.4 <sup>e</sup>	-1.0 ± 0.4
		61.9 ± 0.3 <sup>c</sup>	0.0 ± 0.3
1-penten-3-yne	60.3	60.0 <sup>c</sup>	-0.3
2-Me-1-buten-3-yne	61.9	61.8	-0.1
1-hexen-3-yne	55.3	55.0 <sup>d</sup>	-0.3
2-Me-1-penten-3-yne	52.7	52.0 <sup>d</sup>	-0.7
2-Me-1-hexen-3-yne	47.7	47.0 <sup>d</sup>	-0.7
(E)-3-Et-3-penten-1-yne	49.3	46.0 <sup>d</sup>	-3.3
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butadiyne	108.8	109.0 <sup>f</sup>	+0.2
		109.1 <sup>g</sup>	+0.3
		111 ± 2 <sup>h</sup>	+2.2
		108.8 <sup>i</sup>	0.0
		108.9 <sup>j</sup>	+0.1
1,3-pentadiyne	99.7	98.4 <sup>g</sup>	-1.3
		101 <sup>d</sup>	+1.3
1,3-hexadiyne	94.7	93.9 <sup>g</sup>	-0.8
2,4-hexadiyne	90.6	90.2 <sup>c</sup>	-0.4
		88.3 <sup>g</sup>	-2.3
1,3-heptadiyne	89.7	88.8 <sup>g</sup>	-0.9
2,4-heptadiyne	85.6	83.8 <sup>g</sup>	+1.8
Me <sub>3</sub> CC≡CC≡CCMe <sub>3</sub>	50.4	50 ± 1 <sup>d</sup>	-0.4
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1,3,5-hexatriyne	164.2	163.7 <sup>g</sup>	-0.5
1,3,5-heptatriyne	155.0	152.8 <sup>g</sup>	-2.2
1,3,5-octatriyne	150.0	148.1 <sup>g</sup>	-1.9

<sup>a</sup> Ref 3, unless indicated otherwise. <sup>b</sup>  $\Delta_f H^\circ(\text{lit.}) - \Delta_f H^\circ(\text{calcd.})$ . A positive value indicates destabilization. <sup>c</sup> From the reported<sup>40</sup> heat of hydrogenation and the heat of formation of product butane.<sup>3</sup> <sup>d</sup> Ref 4. <sup>e</sup> From the reported heat of hydrogenation<sup>44</sup> and the heat of formation of pentane.<sup>5</sup> <sup>f</sup> Ref 27, full G3 calculation. <sup>g</sup> Ref 25, G3(MP2) calculation. <sup>h</sup> Ref 45. <sup>i</sup> Ref 46. <sup>j</sup> Ref 47.

conjugation. Table 6 lists results for conjugated dienes, eneynes, diynes, and triynes. It is well-known that experimental  $\Delta_f H^\circ$  values demonstrate that conjugated dienes are more stable than isolated ones and that the heat released upon hydrogenation of the first double bond of 1,3-butadiene is smaller than that of the second (1-butene) by 3.7 kcal mol<sup>-1</sup>, which was defined as the thermodynamic conjugation stabilization by Kistiakowsky et al.<sup>39</sup> The average conjugation stabilization of the four dienes in Table 6 is 4.2 ± 0.3 kcal mol<sup>-1</sup>. Conjugation stabilization in 1,3-butadiene is commonly rationalized in terms of the overlap of the two central *p* orbitals, allowing  $\pi$  electron delocalization.

On the basis of such a *p* orbital overlap, it might be expected that a similar, or even greater, thermodynamic effect would appear in conjugated eneynes, R<sub>2</sub>C=CR-C≡CR, where R is either hydrogen or an alkyl group. Our calculation of the  $\Delta_f H^\circ$  of eneynes indicates very small thermodynamic effects of conjugation, when compared to available experimental values in Table 6. Overall, the unsigned average effect of conjugation is small in the 12 entries for eneynes, which show an average thermodynamic stabilization by 0.0 ± 0.7 kcal mol<sup>-1</sup>. This surprising effect has been previously commented upon regarding (E)-3-penten-1-yne.<sup>40,41</sup>

Similarly, we find small stabilization in conjugated diynes by applying eq 3 (Table 6), even though one might have expected at least the same, if not greater, stabilization than that established for conjugated dienes. For butadiyne, we have reported zero thermodynamic stabilization by G3(MP2) calculations<sup>25,42</sup> on the grounds that the enthalpy of hydrogenation of both triple bonds in butadiyne is just twice that of 1-butyne. By way of confirmation, the ACID (anisotropy of current-induced density) method of quantifying electronic delocalization found a substantial CIV (critical isosurface value) of 0.0744, indicating delocalization in *s-trans*-1,3-butadiene, but a very small, although nonzero, value of CIV = 0.014 in butadiyne.<sup>43</sup>

The surprising finding for butadiyne has been confirmed by the full G3 calculation of Bond<sup>27</sup> ( $\Delta_f H^\circ = 109.0$  kcal mol<sup>-1</sup>).<sup>48</sup> The same finding was confirmed by the full G3 calculation of Jarowski et al.<sup>2a</sup> They, however, took issue with Kistiakowsky's definition of conjugation stabilization, and correcting for an assumed hyperconjugation energy, conjugation stabilization for dienes was reckoned to be 8.2 kcal mol<sup>-1</sup>, and that for diynes was reckoned to be 9.2; subsequently, these two values were revised to 14.8 kcal mol<sup>-1</sup> and 27.1, respectively, by incorporating the additional construct of protobranching.<sup>2c</sup> The claim that conjugation stabilization<sup>2c</sup> of the -C≡CH group with an adjacent *p* orbital is greater than that of the -C=CH<sub>2</sub> group by as much as 12.3 kcal mol<sup>-1</sup> is not consistent with the radical stabilization enthalpy of •CH<sub>2</sub>CH=CH<sub>2</sub>, which is greater than that of •CH<sub>2</sub>C≡CH by about 4 kcal mol<sup>-1</sup>, by G3(MP2)<sup>49</sup> and ROCBS-QB3 and W' calculations.<sup>50</sup>

These hypothetical peregrinations notwithstanding, the facts that we reported<sup>25,42</sup> for stepwise hydrogenation of butadiyne are uncontested. We prefer Kistiakowsky's definition of conjugation stabilization because it is an operational definition, which has the advantage of firm foundation on the measurable or calculable enthalpies of formation and enthalpies of hydrogenation, unencumbered by any rationalizations regarding the causes of the final results. The results of Table 6 follow Kistiakowsky's definition of conjugation stabilization. For 13 entries of conjugated diynes and 3 conjugated triynes in Table 6, the average thermodynamic conjugation stabilization is 0.0 ± 0.9 and 1.5 ± 0.7 kcal mol<sup>-1</sup>, respectively, based on enthalpies of formation and consistent with previously reported values of 0.9 and 1.8 kcal mol<sup>-1</sup>, respectively.<sup>25b</sup> The thermodynamic conjugation stabilization of phenylacetylene appears to be nonexistent, within the uncertainty of the calculation.

## Conclusions

Counting and categorizing hydrogen atoms permits one to obtain the  $\Delta_f H^\circ$  of over 120 typical unstrained hydrocarbons. The results raise doubts regarding the importance of various proposed 1,3 interactions, hyperconjugation, or protobranching in estimating thermodynamically measurable enthalpies of formation. Calculated strain energies of 68 typical hydrocarbons are in agreement with literature values. Thermodynamically measurable or calculable conjugation stabilization is negligible in eneynes, diynes, and phenylacetylene.

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**Supporting Information Available:** Input and output files for phenylacetylene, a short program for converting G3 or similar output to enthalpies of formation, a rationale for selecting the coefficients as we did, and extended hydrogen atom count



matrices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209–1219. Addition and Correction *J. Org. Chem.* **2006**, *71*, 9560. (b) Gronert, S. *Org. Lett.* **2007**, *9*, 2211–2214. (c) Gronert, S. *J. Org. Chem.* **2006**, *71*, 7045–7048.
- (2) (a) Jarowski, P. D.; Wodrich, M. D.; Wannere, C. S.; Schleyer, P. v. R.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 15036–15037. (b) Wodrich, M. D.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 2135–2138. (c) Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; Schleyer, P. v. R. *Chem.—Eur. J.* **2007**, *13*, 7731–7744.
- (3) (a) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry Webbook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899, June, 2005 Release. (<http://webbook.nist.gov>). (b) Compiled by Shimanouchi, T. In NIST No. 69.
- (4) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Standard Reference Database 25, Structures and Properties*, version 2.82; National Institute of Standards and Technology: Gaithersburg, MD 20899, 1994.
- (5) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001–1012.
- (6) DeTar, D. F. *J. Org. Chem.* **1991**, *56*, 1463–1470; designated “formal steric enthalpy”
- (7) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005–8025.
- (8) Chickos, J. S.; Hesse, D. G.; Panshin, S. Y.; Rogers, D. W.; Saunders, M.; Uffer, P. M.; Liebman, J. F. *J. Org. Chem.* **1992**, *57*, 1897–1899.
- (9) (a) DeTar, D. F. *J. Org. Chem.* **1995**, *60*, 7125–7133. (b) Aped, P.; Allinger, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 1–16.
- (10) Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158–3172.
- (11) Winiker, R.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1980**, *113*, 3456–3476; from thermolysis of the compounds with  $\Delta_f H^\circ$  calculated by MM2.
- (12) (a) Flamm-ter Meer, M. A.; Beckhaus, H.-D.; Rüchardt, C. *Thermochim. Acta* **1984**, *80*, 81–89. (b) Verevkin, S. P.; Nölke, M.; Beckhaus, H.-D.; Rüchardt, C. *J. Org. Chem.* **1997**, *62*, 4683–4686; experimental determination of  $\Delta_f H^\circ$
- (13) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975–983.
- (14) Wiberg, K. B.; Carling, J. J.; Matturro, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 5854–5861.
- (15) Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 876–882.
- (16) Rogers, D. W.; Skanupong, S. J. *Phys. Chem.* **1979**, *83*, 2430–2430.
- (17) Rogers, D. W.; Crooks, E.; DeJroongruang, K. *J. Chem. Thermodyn.* **1987**, *19*, 1209–1215.
- (18) Rogers, D. W.; DeJroongruang, K. *J. Chem. Thermodyn.* **1988**, *20*, 675–680.
- (19) Roth, W. R.; Lennartz, H.-D. *Chem. Ber.* **1980**, *113*, 1806–1817.
- (20) Rogers, D. W.; DeJroongruang, K. *J. Chem. Thermodyn.* **1989**, *21*, 1115–1120.
- (21) Rogers, D. W.; DeJroongruang, K.; Samuel, S.; Fang, W.; Zhao, Y. *J. Chem. Thermodyn.* **1992**, *24*, 561–565.
- (22) (a) Rogers, D. W.; Siddiqui, N. A. *J. Phys. Chem.* **1975**, *79*, 574–577. Correction Rogers, D. W. *J. Phys. Chem.* **1979**, *83*, 2430. (b) Rogers, D. W.; McLafferty, F. J. *Tetrahedron* **1971**, *27*, 3765–3775.
- (23) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734–5747.
- (24) (a) Rogers, D. W.; Chol, L. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1810–1814. (b) Khoury, P. R.; Goddard, J. D.; Tam, W. *Tetrahedron* **2004**, *60*, 8103–8112.
- (25) (a) Rogers, D. W.; Matsunaga, N.; McLafferty, F. J.; Zavitsas, A. A.; Liebman, J. F. *J. Org. Chem.* **2004**, *69*, 7143–7147. (b) Rogers, D. W.; Zavitsas, A. A.; Matsunaga, N. *J. Phys. Chem. A* **2005**, *109*, 9169–9173.
- (26) Rogers, D. W.; Dagdagan, O. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1979**, *101*, 671–676.
- (27) Bond, D. *J. Org. Chem.* **2007**, *72*, 5555–5566; full G3 calculation.
- (28) Williams, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 1395–1404.
- (29) Flitcroft, T. L.; Skinner, A. A. *Trans. Faraday Soc.* **1958**, *54*, 47–53.
- (30) Davis, H. E.; Allinger, N. L.; Rogers, D. W. *J. Org. Chem.* **1985**, *50*, 3601–3604.
- (31) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968. Updated by Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419–2438. (b) For another recent refinement of Benson's values, see: Sabbe, M. K.; Saeys, M.; Reyniers, M.-F.; Marin, G. B.; Speybroeck, V. V.; Waroquier, M. *J. Phys. Chem. A* **2005**, *109*, 7466–7480.
- (32) Mitoraj, M.; Zhu, H.; Michalak, A.; Ziegler, T. *J. Org. Chem.* **2006**, *71*, 9208–9211; DFT calculations of bond decomposition energies.
- (33) Grimme, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4460–4464.
- (34) Ingold, K. U.; DiLabio, G. A. *Org. Lett.* **2006**, *8*, 5923–5925; on the basis of the linear correlation between alkyl and allyl C–H bond dissociation energies and the part of the alkyl radical EPR spin on all H's of  $\beta$  CH<sub>3</sub> groups ascribed to hyperconjugation, as opposed to spin polarization. However, Gronert reports<sup>1b</sup> that these spins do not yield a linear correlation with C–CH<sub>3</sub> bonds, as they should.
- (35) For example,  $\Delta_f H^\circ[\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3] = 12.54 + 3(-3.345) + 2(-2.490) + 2.38 = -0.1$  versus  $-0.15$  kcal mol<sup>-1</sup> from experiment;<sup>3</sup>  $\Delta_f H^\circ[\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}_2] = (12.54 \times 2) + (-2.490 \times 2) + (2.38 \times 2) = 24.9$  versus  $25.4 \pm 0.3$  from experiment;<sup>3</sup>  $\Delta_f H^\circ[(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3] = 12.54 + (-3.345 \times 9) + (-2.490 \times 2) + 7.56 = -15.0$  versus  $-15.0 \pm 0.3$  from experiment;<sup>17</sup>  $\Delta_f H^\circ[(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3] = 12.54 + (-3.345 \times 12) + (-2.490 \times 2) + 10.80 = -21.8$  versus  $21.0$  and  $21.8$ ,<sup>4</sup> and so forth.
- (36) (a) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59–76. (b) Almenningen, A.; Bastiansen, O.; Gundersen, S.; Samdal, S.; Skancke, A. *J. Mol. Struct.* **1985**, *128*, 95–114. (c) Pullham, R. J.; Steele, D. J. *Raman Spectrosc.* **1984**, *15*, 211. (d) Chandrakumar, T.; Polson, J. M.; Burnell, E. E. *J. Magn. Reson., Ser. A* **1996**, *118*, 264–271.
- (37) Cochran, J. C.; Hagen, K.; Paulen, G.; Shen, Q.; Tom, S. *J. Mol. Struct.* **1997**, *413*, 313–326.
- (38) Facchine, K. L.; Staley, S. W.; Van Zijl, P. C. M.; Mishra, P. K.; Bothner-By, A. A. *J. Am. Chem. Soc.* **1988**, *110*, 4900–4905.
- (39) (a) Kistiakowsky, G. B.; Ruhoff, K. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 146–153. (b) Conn, J. B.; Kistiakowsky, G. B.; Smith, E. A. *J. Am. Chem. Soc.* **1939**, *61*, 1868–1876.
- (40) Roth, W. R.; Adamczak, O.; Breuckman, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499–2521.
- (41) Rogers, D. W. *Heats of Hydrogenation*; World Scientific Publishing: Hackensack, NJ, 2006; p 27.
- (42) Rogers, D. W.; Matsunaga, N.; Zavitsas, A. A.; McLafferty, F. J.; Liebman, J. F. *Org. Lett.* **2003**, *5*, 2373–2375.
- (43) Geuenich, D.; Hess, K.; Kohler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758–3772.
- (44) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1959**, *55*, 404–407.
- (45) (a) Kiefer, J. H.; Sidhu, S. S.; Kern, R. D.; Xie, K.; Chen, H.; Harding, L. B. *Combust. Sci. Technol.* **1992**, *82*, 101–130. (b) Dorofeeva, O. V. *Thermochim. Acta* **1991**, *178*, 273–286.
- (46) Luk'yanova, V. A.; Pimenova, S. M.; Timofeeva, L. P.; Kosina, M. P.; Kolesov, V. P.; Tarakanova, A. V. *Russ. J. Phys. Chem. (Transl. of Zh. Fiz. Khim.)* **1992**, *66*, 1083–1085; the experimental difficulties in measuring heats of combustion of conjugated diynes are described.
- (47) Bittner, J. D., Ph.D. Thesis, Massachusetts Institute of Technology, Boston, MA, 1981, p 895; <http://dspace.mit.edu/bitstream/1721.1/15917/1/08467819.pdf>.
- (48) From  $\Delta_f H^\circ(\text{butadiyne}) = 109.0$ ,<sup>27</sup>  $\Delta_f H^\circ(1\text{-butyne}) = 39.5$ ,<sup>3</sup> and  $\Delta_f H^\circ(\text{butane}) = -30.0$ ,<sup>3</sup> the enthalpy of hydrogenation of one triple bond of butadiene is  $39.5 - 109.0 = -69.5$ , and that of the second double bond is  $-30.0 - 39.5 = -69.5$  kcal mol<sup>-1</sup>.
- (49) Rogers, D. W.; Matsunaga, N.; Zavitsas, A. A. *J. Org. Chem.* **2006**, *71*, 2214–2219.
- (50) Menon, A. S.; Wood, G. P. F.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 13638–13644.