Group Additive Values for the Gas Phase Standard Enthalpy of Formation of Hydrocarbons and Hydrocarbon Radicals

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A complete and consistent set of 95 Benson group additive values (GAV) for the standard enthalpy of formation of hydrocarbons and hydrocarbon radicals at 298 K and 1 bar is derived from an extensive and accurate database of 233 ab initio standard enthalpies of formation, calculated at the CBS-QB3 level of theory. The accuracy of the database was further improved by adding newly determined bond additive corrections (BAC) to the CBS-QB3 enthalpies. The mean absolute deviation (MAD) for a training set of 51 hydrocarbons is better than 2 kJ mol^{-1}. GAVs for 16 hydrocarbon groups, i.e., $C(C_d)_3(C)$, $C-(C_d)_4$, $C-(C_t)(C_d)(C)_2$, $C-(C_t)(C_d)_2(C)$, $C-(C_t)(C_d)_3$, $C-(C_t)_2(C)_2$, $C-(C_t)_2(C_d)(C)$, $C-(C_t)_2(C_d)_2$, $C-(C_t)_3(C)$, $C-(C_t)_3(C_d)$, $C-(C_t)_4$, $C-(C_b)(C_d)(C)(H)$, $C-(C_b)(C_t)(H)_2$, $C-(C_b)(C_t)(C)(H)$, $C-(C_b)(C_t)(C)_2$, $C_d-(C_b)(C_t)$, for 25 hydrocarbon radical groups, and several ring strain corrections (RSC) are determined for the first time. The new parameters significantly extend the applicability of Benson's group additivity method. The extensive database allowed an evaluation of previously proposed methods to account for non-next-nearest neighbor interactions (NNI). Here, a novel consistent scheme is proposed to account for NNIs in radicals. In addition, hydrogen bond increments (HBI) are determined for the calculation of radical standard enthalpies of formation. In particular for resonance stabilized radicals, the HBI method provides an improvement over Benson's group additivity method.

1. Introduction

An accurate kinetic model for industrial processes proceeding via radical reactions requires a detailed network of elementary reactions.[1−3] The development of such complex reaction networks has progressed significantly over the past decade.[4−13] These reaction networks can consist of thousands of species and reactions. The availability of accurate thermochemical data is of primary importance to solve the kinetic equations and the energy balances. It is practically infeasible to collect all thermodynamic data for the large number of species by experimental means. Especially for free radicals, accurate data are difficult to obtain experimentally. Because of the lack of accurate thermodynamical data, alternative approaches, such as quantum chemical calculations or empirical methods that relate thermochemical data to the molecular structure, have widely been studied.

In principle, quantum chemical methods are able to provide accurate thermochemistry for all the gas phase species appearing in a reaction network.[14,15] In practice, however, accurate calculations for large molecules are computationally extremely intensive. To reduce the amount of experimental data required, Benson developed a group additivity method[16−18] to predict the thermodynamic data for different classes of molecules, based on a limited set of parameters, the so-called group additivity values (GAVs). Benson defined a group as a "polyvalent atom (ligancy > 2) in a molecule together with all of its ligands".[17] For every group, a contribution, the GAV, to the enthalpy of formation is defined. To account for non-bonded interactions, corrections for non-next-nearest neighbor interactions (NNI) and ring strain corrections (RSC) have been introduced. Despite the ever increasing accuracy and computational efficiency of ab initio methods, group additivity methods remain much faster. Group additive methods have proven to predict thermodynamic data with chemical accuracy, i.e., within 4 kJ mol^{-1}, similar to high-level ab initio methods, and they can be easily implemented in computer codes for on-the-fly calculation of thermodynamic properties. Therefore group additivity methods still offer an excellent way to calculate the thermodynamic parameters required in complex reaction networks. Group additivity is based on the group concept and has been extensively discussed in the literature.[15,19,20] This present study illustrates the use of ab initio calculations to determine group additive values in cases where no experimental data on enthalpies of formation are available.

The most widely used group additivity scheme is the group additivity method proposed by Benson,[17] but other additivity schemes have also been developed, e.g., by Platt,[21,22] by Greenshields and Rossini[23] and by Somayajulu and Zwolinski,[24] and methods specific for hydrocarbons by Thinh et al.[25,26] and Joshi.[27] In Benson's method different types of carbon atoms are distinguished, viz. single (C), double (C_d) and triple (C_t)

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bonded carbon atoms; unfused aromatic carbon atoms (C_b) and fused aromatic carbon atoms (C_{bf}); and allenic carbon atoms (C_a or $=C=$). As usual, the corresponding radical atom types are denoted by a dot, i.e., $\dot{C}$, $\dot{C}_d$, $\dot{C}_t$ and $\dot{C}_b$. For radical-specific groups, i.e., groups containing a radical carbon atom, a distinction is made between radical-centered groups and radical-adjacent groups. Radical-centered groups have a central radical atom; radical-adjacent groups have a radical ligand atom.

The accuracy and applicability of group additivity methods depends on the availability and the accuracy of its parameters, the GAVs. For the group additivity method of Benson large sets of GAVs have been determined.[16−18,28−30] Due to their importance, GAVs for hydrocarbons have been updated regularly when new, more accurate experimental data became available. Extensive listings of GAVs can be found in Benson's seminal book *Thermochemical Kinetics*[28] and in Cohen and Benson's 1993 review.[29] In 1996, Cohen has revised the GAVs for gas, liquid and solid phase enthalpies of formation.[30] The GAVs in Cohen's database are derived solely from experimental data, rather than from extrapolated or calculated values, a common practice for some of the earlier databases derived from Rossini et al.[31] or Stull et al.[32] Even in Cohen's detailed review, some of the reported GAVs might not be very reliable, as they were derived from the enthalpy of formation of molecules in which substantial ring strain is present. Despite the fairly large experimental database of hydrocarbon enthalpies of formation, nearly half of the GAVs remains unknown; only 50 out of the 95 GAVs required for stable hydrocarbons have been determined. The total number of 95 GAVs comprises all possible combinations of H, C, C_d, C_t and C_b, excluding fused aromatics. Hydrocarbon radical GAVs have been published by O'Neal and Benson,[33] Ni et al.[34] and Cohen.[35] As discussed, determining accurate enthalpies of formation for hydrocarbon free radicals is experimentally challenging and the number of hydrocarbon radicals for which accurate thermodynamic parameters are available remains rather low as compared to stable molecules. Therefore many radical GAVs remain unknown, only 9 out of 41 GAVs have been reported for radical-centered groups. This lack of GAVs clearly limits the applicability of Benson method for the prediction of thermodynamic parameters in the modeling of hydrocarbon radical chemistry.

In contrast to Benson's group definition, non-next-nearest neighbor interactions (NNI), which are interactions between atoms separated by at least 2 atoms, are not well-defined. Benson's method distinguishes different types of NNIs: alkane 1,4-gauche, alkane 1,5, alkene 1,4-gauche, alkene single and double cis, ene−yne cis and ortho interactions (Figure 1). The cis and ortho interactions are further refined by introducing a distinction between *tert*-butyl and other groups.[17,30] NNI corrections for hydrocarbon radicals were first introduced by Marsi et al.[20] These authors studied non-next-nearest neighbor interactions in alkyl radicals and introduced corrections for two types of NNIs: radical gauche type 1 (RG1) and radical gauche type 2 (RG2), illustrated in Figure 1. From CBS-4 ab initio enthalpies of formation, Marsi et al. determined a stabilizing correction of -0.8 kJ mol^{-1} for the RG1 NNI and found that RG2 interactions can be neglected. Both corrections are thus significantly different from the repulsive gauche alkane correction of 3.3 kJ mol^{-1}. In addition, different counting schemes to determine the number of NNI corrections to be taken into account have been introduced, even for alkanes. For alkanes the number of gauche interactions can be clearly identified. In Benson's original scheme with so-called classical gauche counting each gauche interaction increases the enthalpy of formation of the molecule by the same amount. In 1992, Cohen and Benson[36] revised the gauche counting scheme because it was found that the destabilization energy increases superlinearly with the number of alkane gauche interactions around the same bond. In the revised gauche counting scheme Cohen and Benson[36] therefore propose to assign a higher number of NNI correction terms than the number of alkane−gauche interactions present for highly substituted molecules.

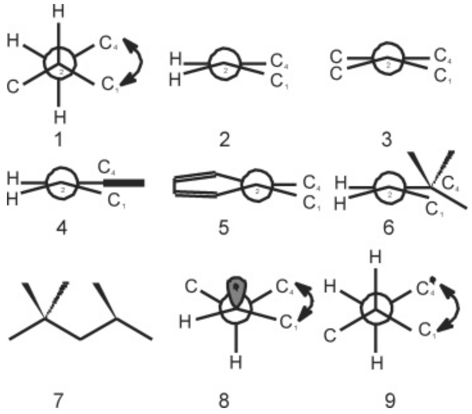


Figure 1. Definitions of non-next-nearest neighbour interactions: (1) 1,4-gauche interaction; (2) single cis interaction; (3) double cis interaction; (4) ene-yne cis interaction; (5) ortho interaction; (6) *tert*-butyl-cis interaction; (7) alkyl 1,5 interaction; (8) radical gauche 1 interaction; (9) radical gauche 2 interaction.

To account for ring strain, ring strain corrections (RSC) were introduced. Because there is no obvious relation between the RSC and the ring structure, a specific RSC is required for every type of ring, taking into account both the ring size and the number of endocyclic double bonds.[29] Cohen later determined separate RSCs for bicyclic and methylene-substituted species.[30]

Recent developments in computational chemistry have made it possible to determine accurate enthalpies of formation from first principles.[37,38] This new development makes it possible to determine some of the missing GAVs, RSCs and NNI corrections from first principles. This approach was first followed by Marsi et al.[20] to determine GAVs and radical gauche interaction corrections from a small database of ab initio CBS-4 enthalpies of formation of $C_{2\leq n\leq 6}$ alkyl radicals. Recently, Sumathi and Green[15] have determined some missing non-radical GAVs from a set of ab initio G2 enthalpies of formation.

Predicting the enthalpy of formation of resonance stabilized radicals by group additive methods is problematic because the resonance effect extends beyond the group region. For resonance stabilized radicals the hydrogen bond increment (HBI) method, introduced by Lay et al.,[39] can provide a valuable alternative to Benson's method. In the HBI method the enthalpy of formation of a radical is derived from the enthalpy of formation of the corresponding parent molecule by adding a so-called HBI to account for the changes that occur upon formation of a radical from the parent molecule. The enthalpy of formation of the parent molecule can either be obtained from group additivity or from experimental databases. The limited availability of radical experimental enthalpies of formation again draws the focus to ab initio databases to determine the Hydrogen Bond Increments.

The aim of this study is (i) to construct a database of accurate standard enthalpies of formation for hydrocarbons, based on high-level CBS-QB3 ab initio calculations, (ii) to derive a consistent and accurate set of GAVs for hydrocarbons and hydrocarbon radicals, (iii) to determine a consistent and accurate set of hydrogen bond increments for hydrocarbon radicals and

(iv) to improve the modeling of non-next-nearest neighbor interactions. A novel, improved counting scheme for radical gauche interaction corrections will be introduced. There are 2 newly reported alkene GAVs, 9 alkyne GAVs, 5 aromatic GAVs, 25 radical GAVs and 13 HBIs. Polycyclic hydrocarbons and radicals are not included in this study. For a discussion on the group additivity method for polycyclic aromatic species we refer to the recent work of Yu et al.[40]

2. Methodology

2.1. Computational Method. All quantum chemical calculations were performed at the CBS-QB3 level of theory[41] using the GAUSSIAN 03 package.[42] The rigid rotor harmonic oscillator approximation was used for all rovibrational modes.

Standard enthalpies of formation were calculated using the atomization energy method. In this method the standard enthalpy of formation is obtained as the difference between the ab initio calculated (AI) atomization enthalpy of a compound and the experimentally determined enthalpy of formation of the gaseous atoms:

$$\Delta_f H^0(C_m H_n) = m\Delta_f H^0_{\mathrm{gas,exp}}(C) + n\Delta_f H^0_{\mathrm{gas,exp}}(H) - [mH^0_{\mathrm{AI}}(C) + nH^0_{\mathrm{AI}}(H) - H_{\mathrm{AI}}{}^0(C_m H_n)] \quad (1)$$

with $\Delta_f H^0_{\mathrm{gas,exp}}(C) = 716.68$ kJ mol^{-1} and $\Delta_f H^0_{\mathrm{gas,exp}}(H) = 218.00$ kJ mol^{-1} at 298 K.[43] This method was used to determine the standard enthalpies of formation for 233 species; see Supporting Information, Table 1S. The thermochemical data reported in this work all pertain to the ideal gaseous state at 1 bar and 298 K.

In this work, standard enthalpies of formation, $\Delta_f H^0$, were calculated for the most stable conformer only, using the rigid rotor/harmonic oscillator (RR/HO) approximation to account for rotational and vibrational contributions to the enthalpy. At 298 K, the most stable conformer is the dominant one in the equilibrium mixture and therefore the higher energy conformers will have a very small contribution to the enthalpy. Only if the energy difference between conformers is on the order of RT, i.e., 2.5 kJ mol^{-1}, will the equilibrium mixture contain a non-negligible amount of the higher energy conformers at $T = 298$ K. The contribution of the different conformers to the enthalpy can be described using Boltzmann mole fractions based on enthalpies of the different conformers as proposed by DeTar.[44] The author reports an increase in enthalpy upon inclusion of all conformers of 1.13 kJ mol^{-1} for *n*-butane at $T = 298$ K. Even in the case of *n*-octane with 273 staggered conformers, the contribution of different conformers to the enthalpy at $T = 298$ K amounts to 4.9 kJ mol^{-1} only.

The enthalpy contribution of different conformers can also be evaluated by comparing the ab initio calculated value of the standard enthalpy of formation based on RR/HO approximation for the most stable conformer with the value calculated on the basis of the hindered rotor formalism as described by Van Speybroeck et al.[45] Using the hindered rotor formalism to calculate the enthalpy of *n*-butane, we found a difference of 1.31 kJ mol^{-1} as compared to the harmonic oscillator approach.

Both approaches indicate that the contribution of different conformers to the enthalpy is much smaller as compared to the mean difference between calculated and experimentally observed standard enthalpies of formation (see Table 1).

The principle aim of the current study is to determine standard enthalpies of formation. As enthalpies are less affected by statistical contributions originating from mixing of conformers than entropy or heat capacity, the RR/HO approximation is suited. Extending the method to determine heat capacities and entropies necessitates explicit accounting for all conformers. Work is in progress to determine GAV for heat capacities and entropy.

The agreement of ab initio calculated standard enthalpies of formation with experimental standard enthalpies of formation was improved using an empirical correction. Two different empirical correction methods were evaluated: atom additive correction (AAC[14]) and the bond additive correction (BAC[46]). The atom additivity scheme was introduced by Saeys et al.[14] to remove the systematic overestimation of the standard enthalpies of formation by the CBS-QB3 method, in particular for larger molecules. This approach was found to reduce the deviations to better than 3 kJ mol^{-1}. The atom additive corrected standard enthalpies of formation are calculated using

$$\Delta_f H^0_{298}(\mathrm{AAC}) = \Delta_f H^0_{298}(\mathrm{CBSQB3}) + \sum_i N_i \mathrm{AAC}_i \quad (2)$$

where $\Delta_f H^0_{298}(\mathrm{CBSQB3})$ is obtained from eq 1 and i runs over the different types of atoms present in the molecule (here C and H), N_i is the number of atoms of type i and AAC_i is the atom additive correction factor for atoms of type i. The bond additive corrected standard enthalpies of formation are calculated using the BAC scheme,[46,47] introduced by Petersson et al. for the CBS-Q method:[46]

$$\Delta_f H^0_{298}(\mathrm{BAC}) = \Delta_f H^0_{298}(\mathrm{CBSQB3}) + \sum_{ij} N_{ij} \mathrm{BAC}_{ij} \quad (3)$$

where i and j run over the different atom types and N_{ij} is the number of bonds between atoms of type i and j. Corresponding to Petersson et al.[46] the BACs applied in this work pertain to the C—H, C—C, C═C, and C≡C bond.

2.2. Estimation of Group Additive Values. The empirically corrected ab initio database has a uniform accuracy and therefore all group additive values are estimated by unweighed linear regression analysis, using the following objective function, in which y_j is the BAC corrected ab initio standard enthalpy of formation of molecule j and $\hat{y}_j$ is the GA calculated enthalpy of formation:

$$\mathrm{SSQ} = \sum_j (y_j - \hat{y}_j)^2 \quad (4)$$

This results in the normal equations

$$\overline{\mathrm{GAV}} = (\mathbf{X}^{\mathbf{T}}\mathbf{X})^{-1}\mathbf{X}^{\mathbf{T}}y \quad (5)$$

in which $\overline{\mathrm{GAV}}$ is the estimation vector of group additive values and $\mathbf{X}$ the matrix in which the elements $\mathbf{X}_{ij}$ specify the number of times group j occurs in molecule i. Each of the columns of the matrix of independent variables $\mathbf{X}$ corresponds to a group, and each row corresponds to a molecule. Because of the definition of a group, each group contains information about the neighboring groups and the columns in $\mathbf{X}$ are linearly dependent for each class of molecules except for alkanes. Therefore, with the exception of alkanes, the $\mathbf{X}^{\mathbf{T}}\mathbf{X}$ matrix is singular and there are multiple solutions for the $\overline{\mathrm{GAV}}$ vector. Note that the linear dependence of the rowspace does not result in a singular $\mathbf{X}^{\mathbf{T}}\mathbf{X}$ matrix.

To illustrate the linear dependence of the columnspace, consider the alkene groups. In the matrix of independent variables $\mathbf{X}$, every column corresponds to an alkene group, from $C-(C_d)(H)_3$ to C_a, and each row corresponds to an alkene in the database. Two categories of groups can be distinguished:

TABLE 1: Training Set for the Determination of Bond Additivity Corrections and for the Assessment of the Accuracy of the Standard Enthalpy of Formation Predicted by the CBS-QB3, CBS-QB3-BAC, and the Group Additivity Method (298 K, kJ mol^{-1})[a]

		deviations from experiment[e]							deviations from experiment[e]				
			BAC[f]		GA[g]					BAC[f]		GA[g]	
name	$\Delta_f H^0$ exp	CBS-QB3	old[f]	new	Cohen[g]	new[g]	name	$\Delta_f H^0$ exp	CBS-QB3	old[f]	new	Cohen[g]	new[g]
Alkanes													
ethane	−83.7[b]	1.8	−2.2	−2.7	0.1	−2.1	*n*-pentane	−146.4[c]	6.6	−4.0	−0.7	0.1	1.5
ethane	−84.7[c]	2.8	−1.2	−1.7	1.1	−1.1	2,3-dimethylbutane	−177.8[c]	9.8	−3.0	1.5	0.5	1.1
propane	−104.7[b]	3.8	−2.4	−1.7	0.2	−1.6	*n*-hexane	−167.2[c]	7.7	−5.1	−0.6	0.0	−0.6
isobutane	−134.4[b]	5.9	−2.5	−0.5	0.2	0.0	2-methylpentane	−174.3[c]	10.9	−2.8	0.8	0.4	0.6
isobutane	−135.6[c]	7.1	−1.3	0.7	1.4	1.0	heptane	−187.8[c]	8.9	−6.0	−0.2	−0.3	−0.5
n-butane	−125.6[c]	5.1	−3.3	−1.3	1.7	0.3	2,2,3-trimethylbutane	−204.8[c]	9.8	−5.1	0.6	1.9	1.8
n-butane	−127.1[c]	6.6	−1.8	0.2	3.2	1.3	octane	−208.4[c]	9.9	−7.2	−0.2	−0.6	−0.4
neopentane	−168.7[b]	8.1	−2.5	0.8	1.1	1.0	2,2,4-trimethylpentane	−224.1[c]	9.9	−7.2	−0.3	0.7	1.9
n-pentane	−146.8[c]	7.0	−3.6	−0.3	0.5	−0.5	2,2,3,3-tetramethylbutane	−225.9[c]	9.3	−7.8	−0.8	0.4	−0.5
n-pentane	−147.1[c]	7.3	−3.3	0.0	0.8	0.5	2,2,4,4-tetramethylpentane	−241.5[c]	8.7	−10.6	−2.3	−4.4	−2.8
Alkenes													
ethene	52.3[b]	3.7	1.5	−1.7	0.5	−1.6	1,3-pentadiene	76.2[b]	12.4	5.6	3.4	1.4	4.0
allene	190.4[b]	4.9	2.4	−2.2	5.5	1.9	1,4-pentadiene	106.3[c]	10.0	3.2	1.0	0.5	1.0
propene	20.1[b]	5.6	1.2	−0.7	0.5	−0.1	2-methyl-1,3-butadiene	75.7[c]	10.5	3.6	1.5	0.6	2.1
1,3-butadiene	110.1[b]	9.7	5.1	1.7	−0.3	0.9	3-methyl-1,2-butadiene	129.1[c]	8.4	1.5	−0.6	−0.5	−4.6
1,3-butadiene	111.9[c]	7.9	3.2	−0.1			3-methyl-1-butene	−27.4[c]	8.0	−0.7	−0.1	−0.9	−0.1
1,2-butadiene	162.4[b]	7.2	2.5	−0.9	1.3	−0.9	2-methyl-2-butene	−41.5[c]	9.1	0.4	1.0	−0.6	−0.2
1,2-butadiene	165.4[c]	4.2	−0.5	−3.9			*trans*-2-pentene	−33.1[c]	11.0	2.3	2.9	1.4	2.7
1-butene	0.0[b]	7.6	2.0	−2.2	0.5	0.3	*cis*-2-pentene	−28.0[c]	11.4	2.7	3.3	0.9	3.7
isobutene	−16.7[b]	7.2	0.6	0.0	2.2	−0.4	1,5-hexadiene	85.0[c]	11.4	2.3	1.4	−0.4	1.4
cis-2-butene	−7.7[c]	9.2	2.7	2.0	0.7	3.0	3,3-dimethyl-1-butene	−59.8[c]	9.8	−1.1	0.7	3.9	1.1
trans-2-butene	−10.8[c]	7.1	0.6	−0.1	−0.8	0.0							
Alkynes													
ethyne	226.9[c]	7.7	4.1	1.9	0.7	0.7	1-butyne	165.2[c]	10.0	2.1	2.4	1.3	3.6
ethyne	228.3[d]	7.3	3.7	1.5	−0.7	−0.7	2-methylbut-1-en-3-yne	259.0[c]	6.0	−3.2	−0.8	−4.2	−0.8
propyne	184.8[b]	7.2	1.4	0.5	1.4	1.7	*cis*-3-penten-1-yne	258.0[c]	6.7	−1.6	−2.7	−8.2	−2.8
propyne	185.4[c]	7.6	1.8	0.9	0.8	1.1	*trans*-3-penten-1-yne	259.0[c]	7.1	−1.2	−2.3	−6.3	−3.5
1,3-butadiyne	464.0[c]	6.8	−0.8	−2.1	−24.6	−2.1	3-methyl-1-butyne	136.4[c]	13.2	3.0	4.6	0.5	4.6
3-buten-1-yne	296.2[b]	2.9	−4.2	−3.0	−11.3	−6.8	3,3-dimethyl-1-butyne	107.0[c]	10.8	−1.5	1.3	1.0	1.3
Aromatic Compounds													
benzene	82.9[c]	8.1	0.5	−0.1	−0.1	0.0	styrene	146.9[c]	12.6	2.6	1.8	1.3	1.8
benzene	82.5[b]	8.5	1.0	0.4	0.3	0.4	ethylbenzene	29.8[c]	9.6	−2.3	−0.4	1.2	−0.4
toluene	50.2[b]	9.5	−0.2	0.4	0.0	0.4	isopropylbenzene	3.9[c]	10.1	−4.0	−0.9	0.3	−0.9
toluene	50.0[c]	9.7	0.0	0.6	0.2	0.6	*tert*-butylbenzene	−22.7[c]	10.5	−5.7	−1.4	1.4	−1.4
styrene	147.8[b]	11.7	1.7	0.9	0.4	0.9	α-methylstyrene	118.3[c]	10.4	−1.8	−1.4	n/a	−1.4
Mean Absolute Deviation													
alkanes		7.4	4.1	0.9	1.0	1.1							
alkenes		8.4	2.2	1.5	1.1	1.4							
alkynes		7.8	2.4	2.0	5.1	2.2							
aromatics		8.4	2.0	0.8	0.6[h]	0.7[h]							
total		8.2	2.8	1.3	1.8[h]	1.4[h]							

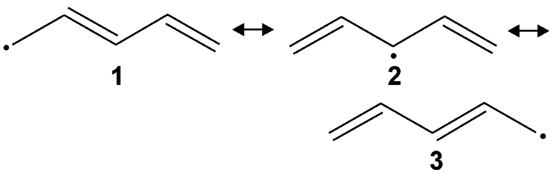
[a] Experimental standard enthalpy of formation and deviation from experimental values. [b] Cioslowski et al.[48] [c] NIST chemistry webbook.[43] [d] Pedley.[49] [e] Deviation $\Delta = \Delta_f H^0 - \Delta_f H^0(\text{exp})$. [f] Bond additive corrected with (old) parameters reported by Petersson et al.[46] and (new) parameters determined in this work; see Table 2. [g] Group additive standard enthalpy of formation, calculated with (Cohen) the GAV reported by Cohen[30] and (new) the GAV determined in this work. [h] α-Methylstyrene was not included in this MAD as there was no $C_d-(C_b)(C)$ GAV reported by Cohen.[30]

groups having a C_d atom as the central atom and groups having one or more C_d atoms as a ligand atom. A C_d carbon atom is, except for terminal C_d-H_2 groups, always bonded to a group that has a C_d atom as a ligand. Hence a group from the first category always occurs together with a group from the second category. For the columns [*i*] in the **X** matrix, the following linear relationship can be found:

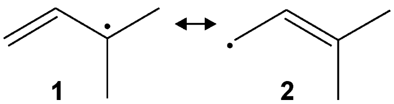
$$[C_d-(C)(H)] + 2[C_d-(C)_2] + [C_d-(C_d)(C)] = [C-(C_d)(H)_3] + [C-(C_d)(C)(H)_2] + [C-(C_d)(C)_2(H)] + [C-(C) + 2[C-(H) + 2[C-(C)(H)] + 2[C-(C_d)_2(C)_2] + 3[C-(C_d)_3H] + 3[C-(C_d)_3C] - 4[C-(C_d)_4]$$

Note that the coefficients are related to the number of C ligands for the left-hand side and to the number of C_d ligands for the right-hand side of the equation. The $C_d-(H)_2$, $C_d-(C_d)(H)$, $C_d-(C_d)_2$ and C_a groups do not appear in the equation because they can be determined independently, i.e., from the enthalpy of formation of ethene, 1,3-butadiene, 2-ethenyl-1,3-butadiene and 1,2-propadiene, respectively. Because of the linear dependence, one of the GAVs can be assigned arbitrarily. Usually, the $C-(C_d)(H)_3$ GAV is chosen equal to the $C-(C)(H)_3$ GAV,[16] which is done in this work as well. Linear dependencies are also found for other molecular classes and are handled in a similar fashion, i.e., by fixing the $C-(C_t)(H)_3$ GAV to the $C-(C)(H)_3$ GAV and the $C_d-(C_t)(H)$ GAV to the $C_d-(C_d)(H)$ GAV.

As discussed, the prediction of the enthalpy of formation of resonance stabilized radicals by Benson's group additivity method is problematic. The enthalpy of formation can be determined unambiguously with the group additivity method only for molecules where the ligands of the radical-centered group include information about all unsaturated bonds that are involved in electron delocalization. This is, e.g., the case for diallylic radicals:



the standard enthalpy of formation of the canonical structure (2) containing the $\mathrm{C{=}C{-}\dot{C}{-}C{=}C}$ sequence can be determined accurately because the $\mathrm{\dot{C}{-}(C_d)_2X}$ (X = H, C) group provides information about all possible delocalization. There is no such a group present in the other canonical structures. To prevent a misestimation of the $\mathrm{\dot{C}{-}(C_d)(H)_2}$ GAV present in the canonical structures (1) and (3), only canonical structures in which the radical-centered group includes information about all unsaturated bonds involved in electron delocalization, are retained in the database. However, even then different equivalent canonical structures are possible, as for, e.g., allylic radicals. The different structures correspond to different group additive enthalpies of formation, whereas the actual enthalpy of formation is equal. An example is the 3-methyl-1-buten-3-yl radical, which is equivalent to the 3-methyl-2-buten-1-yl radical:



Both resonance structures have very different groups leading to different values for the GA enthalpy of formation. To overcome this problem, both resonance structures were initially included in the matrix of dependent variables **X**, and the group additive values were estimated. Subsequently, the resonance structure with the highest GA enthalpy of formation was removed from the matrix **X** and all the GAVs were reevaluated. Therefore, when the GAVs reported in this work are used for on-the-fly calculations of the enthalpy of formation, the enthalpy of formation for all resonance structures should be calculated but only the lowest value should be used.

To assess the reliability of the group additivity approximation, a statistical analysis is performed when possible. The reported significance of regression *F*, mean absolute deviation (MAD), root mean square deviation (RMS) and maximum deviation (MAX) correspond to the differences between the enthalpy of formation predicted by the ab initio group additivity method and the values calculated with the CBS-QB3-BAC ab initio method. The significance of regression *F* is calculated using

$$F = \frac{(\sum_{i=1}^{n} \hat{y}_i^{\,2})/p}{(\sum_{i=1}^{n} (\hat{y}_i - y_i)^2)/(n-p)} \tag{6}$$

where y is the CBS-QB3-BAC ab initio enthalpy of formation, $\hat{y}$ the enthalpy of formation predicted by our ab initio group additivity method, n the number of molecules in the regression and p the number of parameters, i.e., the number of estimated GAVs.

2.3. Hydrogen Bond Increment Method. Lay et al.[39] introduced the hydrogen bond increment (HBI) method to predict thermochemical properties of radicals with a reduced number of parameters. In contrast to Benson's method, the HBI method does not use the group concept and can account for resonance effects that extend beyond the group region. The HBI enthalpy of formation of a radical is calculated from the enthalpy of formation of the corresponding *parent molecule* by adding a HBI to account for the loss of a hydrogen atom. Hence, for standard enthalpies of formation the HBI is defined as

$$\mathrm{R{-}H} \rightleftharpoons \dot{\mathrm{R}} + \dot{\mathrm{H}} \qquad \Delta_r H^0_{298} = \mathrm{BDE(R{-}H)} \tag{7}$$

$$\mathrm{HBI} \equiv \Delta_f H^0_{298}(\dot{\mathrm{R}}) - \Delta_f H^0_{298}(\mathrm{RH}) = \mathrm{BDE(R{-}H)} - \Delta_f H^0_{298}(\dot{\mathrm{H}}) \tag{8}$$

In this study, the enthalpy of formation of the parent molecule is calculated using our ab initio GAVs, but in principle, experimental values could be used where available. Following Lay et al.,[39] the HBIs are denoted by a short-hand structure in which a J indicates the radical character of the preceding carbon atom, such as RCCJ for a primary alkyl radical, or by trivial names such as ALLYL_S for a secondary allylic radical.

Radical-specific NNIs are not accounted for explicitly within the HBI framework. In principle, it is possible to introduce HBIs corresponding to specific structures to implicitly account for NNIs. Clearly, this would lead to a large increase in the number of HBIs and complicate the implementation of the method.

HBIs are not as firmly defined as Benson's group and selecting the correct HBI is sometimes ambiguous. For a radical with a $\mathrm{C{\equiv}CC{=}\dot{C}}$ moiety, the $\mathrm{C{\equiv}CC{=}CJ}$ HBI should be used. If this HBI does not exist, both the $\mathrm{C{=}CC{=}CJ}$ or the VIN HBI (corresponding with the structure $\mathrm{C{=}CJ}$) could be applied.

3. Results and Discussion

3.1. Ab Initio Database. For the determination of the ab initio GAVs, a database of 233 CBS-QB3 standard enthalpies of formation was constructed. The database can be found in Table 1S of the Supporting Information. To assess the accuracy of the ab initio CBS-QB3 method, the enthalpies of formation were benchmarked against a training set of accurate experimental data for 51 hydrocarbons divided into alkanes, alkenes, alkynes and aromatics, Table 1. Experimental standard enthalpies of formation (298 K) were taken from the NIST Webbook,[43] from a compilation by Cioslowski et al.[48] and from Pedley.[49] Only experimental values with a standard deviation smaller than 3.3 kJ mol^{-1} were included in the training set, in agreement with Saeys.[14] Cyclic species and radicals were excluded. For the systematic corrections to the CBS-QB3 enthalpy, no distinction between a C and $\dot{\mathrm{C}}$ carbon atom was made.

It was found that the CBS-QB3 ab initio method systematically overestimates the experimental values in the training set, with the deviation increasing with increasing size of the molecule. The MAD over the training set was 8.2 kJ mol^{-1}, with similar MADs for all four molecular classes (see Table 1). Similar deviations were also noted by Saeys et al.[14] To improve the ab initio enthalpies of formation, Saeys et al. proposed an atom additive correction (AAC) scheme to remove most of the systematic deviations, using eq 2. The AAC parameters are given in Table 2. Although the AAC greatly improves the agreement with the experiment with a MAD of only 2.3 kJ mol^{-1} on the training set, significant deviations still remain for certain molecular classes. Undesirable for the determination of ab initio GAVs is in particularly a mean deviation of −3.3 kJ mol^{-1} for alkanes. Indeed, the experimental data for alkanes are in general highly reliable and the alkane groups also occur in most other molecules.

Therefore, the use of another correction method i.e., the bond additive correction method (BAC) as presented by Peterson,[46]

TABLE 2: Empirical Additivity Corrections for CBS-QB3 Standard Enthalpies of Formation: Atom Additive (AAC) and Bond Additive Corrections (BAC) (298 K, kJ mol^{-1})

	Saeys[a] (CBS-QB3)	Petersson[b] (CBS-Q)	this work (CBS-QB3)
C	−1.29		
H	−0.28		
C—H		−0.46	−0.89
C—C		−1.26	0.84
C═C		−0.33	−1.78
C—C		−2.68	−3.97

[a] Reference 14. [b] Reference 46.

was evaluated, using eq 3. The objective is to develop a method with a MAD better than 2 kJ mol^{-1} for each molecular class and the BAC scheme allows for a greater differentiation between the different molecular classes. Alternatively, an isodesmic reaction scheme, in which the number and formal type of bonds are conserved, could be used. It can easily be shown that an isodesmic reaction scheme based on a limited number of reference species, i.e., one molecule for each bond type, is identical to a BAC scheme if the BAC parameters are obtained from the same reference molecules. Determining the BAC parameters by regression against the complete experimental database leads to optimal values for the BAC parameters however.

Petersson et al.[46] have derived BAC parameters for the CBS-Q method from a training set consisting of 19 hydrocarbons, including 8 cyclo, spiro or bicyclic compounds. Petersson et al. note that "these BAC values should be regarded as preliminary because the BAC are based on a very limited data set".[46] Using Petersson's BAC parameters, given in Table 2, for the CBS-QB3 enthalpies of formation indeed does not lead to an improvement over the CBS-QB3-AAC method and systematic deviations from the experimental data are still found; see Table 1. The MADs for each molecular class are summarized in Table 1, and mean deviations can be found in Figure 2. The mean deviation for the alkane standard enthalpies of formation amounts to −4 kJ mol^{-1}, and the deviations increase with the increasing size of the alkane. For alkenes a mean deviation of +2 kJ mol^{-1} is found and the total MAD over the training set, 2.8 kJ mol^{-1}, is even higher than the MAD for the CBS-QB3-AAC method, 2.3 kJ mol^{-1}. Clearly the CBS-QB3-BAC method using Petersson's parameters does not meet the accuracy criteria put forward. Therefore, new BAC values were estimated (see Table 2). The CBS-QB3 method using the newly estimated BAC parameters was found to be sufficiently accurate with a MAD of 1.3 kJ mol^{-1} and a mean deviation of 0.5 kJ mol^{-1} over the entire training set. The CBS-QB3-BAC method reduces the MAD with a factor 2 as compared to the CBS-QB3-AAC method. In particular, the fact that the MAD for every molecular class is now smaller than 2 kJ mol^{-1} is satisfying. The new BAC parameters differ significantly from the values reported by Petersson.[46] The performance of the BAC method for radicals is evaluated using a test set of 11 radicals, the methyl, ethyl, allyl, *n*-propyl, isopropyl, isobutyl, 2-butyl, *tert*-butyl, neopentyl, 2-methyl-2-butyl and phenyl radical. The mean deviation amounts to 2.9 kJ mol^{-1} and the MAD to 3.6 kJ mol^{-1}.

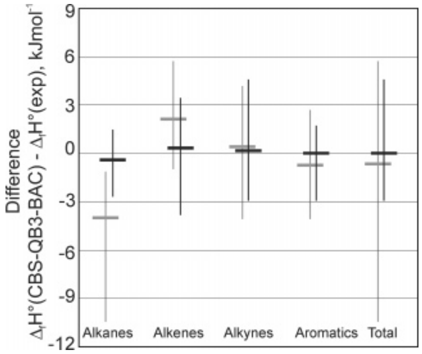


Figure 2. Differences between CBS-QB3-BAC and experimental standard enthalpies of formation for the training set of Table 1. Comparison between the CBS-QB3-BAC method of Petersson et al. (gray)[46] and our new version, Table 2 (black). The crosses indicate the minimum, maximum, and mean deviations.

TABLE 3: Group Additive Values for the Standard Enthalpy of Formation of Alkanes (298 K, kJ mol^{-1})

group	Benson[a]	Cohen[b]	this work[c]
$C-(C)(H)_3$	−42.7	−41.8	**−42.9**
$C-(C)_2(H)_2$	−20.6	−20.9	**−20.5**
$C-(C)_3(H)$	−8.0	−10.0	**−6.9**
$C-(C)_4$	2.1	−0.4	**3.9**
gauche rev	3.3	3.3	**2.9**
1,5	6.3	6.7	**7.1**
F			141000
n/*p*[d]			16/6
MAD[e]			0.4
RMS[e]			0.6
MAX[e]			1.8

[a] Reference 28. [b] Reference 30. [c] Simultaneous estimation of GAVs and NNI corrections, revised gauche counting. [d] *n* data points and *p* regression parameters. [e] MAD = mean absolute deviation, RMS = root mean square deviation, MAX = maximum deviation.

TABLE 4: Number of Gauche Interaction Corrections in the Classical and Revised Gauche Counting Scheme

bond[a]	classical[b]	revised[c]
P−P, S, T or Q	0	0
S−S	0	0
S−T	1	1
S−Q	2	2
T−T	2	**3**
T−Q	4	**5**
Q−Q	6	**8**

[a] P, primary carbon atom; S, secondary carbon atom; T, tertiary carbon atom; Q, quaternary carbon atom. [b] Benson and Buss.[16] [c] Cohen and Benson.[36]

The CBS-QB3-BAC with the newly derived BACs was used to calculate the standard enthalpies of formation of 233 hydrocarbons and hydrocarbon radicals at 298 K. The database, Table 1S, contains 16 alkanes, 34 alkenes, 31 alkynes, 19 cyclic hydrocarbons, 15 aromatics and 118 hydrocarbon radicals. In the next sections this accurate database will be used to estimate GAVs for every class of molecules.

3.2. Alkanes. Benson's method introduces 4 GAVs and 2 NNI corrections for alkanes, Table 3. The six parameters were estimated from the 16 alkane standard enthalpies of formation present in the database, Table 1S. Both classical and revised gauche counting[36] were considered. The revised scheme introduces additional terms for highly substituted bonds and is summarized together with classical gauche counting in Table 4. The difference between classical and revised gauche counting pertains to the interaction between (1) two substituents on adjacent tertiary carbon atoms, for which 3 instead of 2 corrections terms are taken into account, (2) adjacent tertiary and quaternary carbon atoms, for which 5 instead of 4 corrections are counted, and (3) adjacent quaternary carbon atoms, for which 8 instead of 6 corrections are counted.

Two estimation procedures can be followed: the NNI corrections can be estimated either simultaneously with or separately from the 4 GAVs. When the NNI corrections are

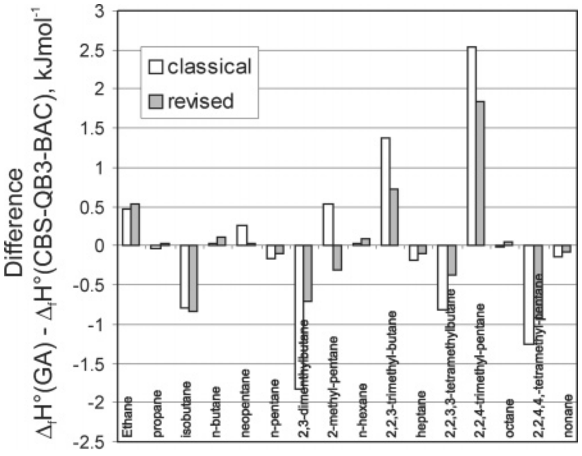


Figure 3. Differences between standard enthalpies of formation for alkanes from group additivity and from the CBS-QB3-BAC method, comparing classical and revised gauche counting. GAV from Table 2S (298 K, kJ mol^{-1}).

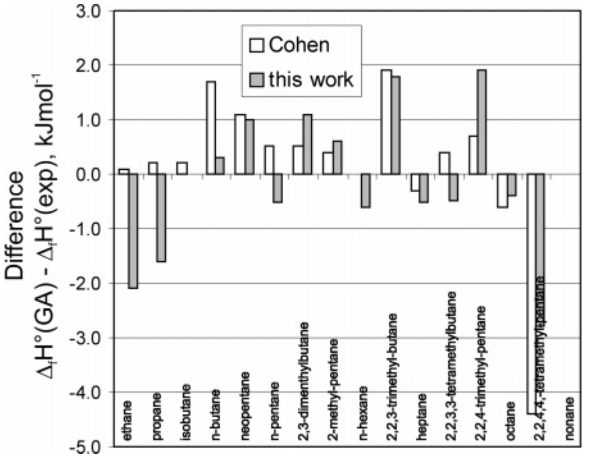


Figure 4. Differences between group additively calculated standard enthalpies of formation and experimental data for alkanes, for enthalpies calculated with the GAV reported by Cohen and the GAV reported in this work (298 K, kJ mol^{-1}).

estimated separately, the GAVs are first determined from a subset of alkanes without NNIs. When the NNI corrections are estimated simultaneously with the GAVs, it is crucial to monitor the correlation between the parameters. If one or more correlation coefficients are large, i.e., larger than 0.9, the values of the NNI corrections will influence the estimated GAVs, and the group additive method will be less accurate for alkanes without gauche interactions. However, the largest correlation was found to be only −0.78 between the GAV for the $C-(C)_4$ group and the gauche NNI correction and all 6 parameters can be estimated simultaneously. The correlation between the alkane GAVs can be found in Table 3S of the Supporting Information. The resulting GAVs and NNI corrections can be found in Table 3. The values reported in Table 3 refer to the revised gauche counting scheme, as this was found to yield more accurate results. Uncertainties on the GAV determined in this work are mentioned in Table 2S of the Supporting Information and typically amount to ±1.3 kJ mol^{-1}. The results for classical and revised gauche counting are compared in Figure 3, in which the deviations between the standard enthalpies of formation predicted by the group additivity method and the ab initio CBS-QB3-BAC values are shown, for both the classical and revised gauche counting scheme. For the revised gauche counting all deviations are less than 1 kJ mol^{-1}, except for the heavily substituted 2,2,3-trimethylpentane. The revised gauche counting offers a clear improvement over the classical gauche counting scheme, in particular when multiple gauche interactions about the same bond are present, e.g., for 2,3-dimethylbutane, 2,2,3,3-tetramethylbutane and 2,2,3-trimethylbutane. In general, the group additivity concept is found to be very accurate for alkanes, with a MAD of only 0.4 kJ mol^{-1} between the ab initio enthalpies of formation and group additivity predictions.

The ab initio GAVs and NNI corrections reported in this work are in very good agreement with the experimental values proposed by Benson and Cohen.[28,30] The deviations with the original values reported by Benson are generally less than 2 kJ mol^{-1}. Comparison with the GAVs reported by Cohen also shows good agreement, the largest difference being 4.3 kJ mol^{-1} for the $C-(C)_4$ group. The slightly high ab initio GAVs for $C-(C)_4$ and $C-(C)_3(H)$ might well be due to the higher value for the gauche correction used by Benson and Cohen because both GAVs are moderately correlated with the gauche correction parameter. Note that in this work the value of the gauche correction was optimized using the revised gauche counting scheme, whereas Cohen and Benson[36] applied the revised counting scheme without reevaluating the gauche correction, keeping it fixed at its classical value. The revised gauche correction determined in this work, 2.9 kJ mol^{-1}, is slightly lower than the value reported by Benson, 3.3 kJ mol^{-1}. In contrast, the 1,5-interaction correction is with 7.1 kJ mol^{-1} somewhat larger than the values reported by Benson and Cohen, 6.3 and 6.7 kJ mol^{-1}, respectively.

The enthalpies of formation calculated with the ab initio GA method and with the experimental GA method using the GAV reported by Cohen[30] are compared with experimental data in Figure 4. The ab initio GA method matches or even outperforms the GA method with the parameters reported by Cohen, except for ethane, propane and 2,2,4-trimethylpentane. For the smaller molecules the group additive standard enthalpy of formation calculated with the GAVs determined in this work underestimates the experimental enthalpy by 1.1−1.6 kJ mol^{-1}, whereas the use of the GAV reported by Cohen[30] yields enthalpies closer to the experimentally observed enthalpy. The deviations for ethane and propane can be traced back to the difference between the CBS-QB3-BAC enthalpy of formation and the experimental value. These deviations fall within the objective of a MAD error of ≤2 kJ mol^{-1} for the CBS-QB3-BAC method. The deviation for 2,2,4-trimethylpentane can be related to the 1,5-interaction. 2,2,4-Trimethylpentane and 2,2,4,4-tetramethylpentane are the only species in our database with 1,5-NNI. For 2,2,4-trimethylpentane the enthalpy is overestimated; for 2,2,4,4-tetramethylpentane it is underestimated. A more refined treatment of 1,5-interactions might further increase the accuracy of the GA method for 1,5-substituted hydrocarbons. However, the scope of this study is on the calculation of the standard enthalpy of formation of a broader range of hydrocarbons and therefore we concentrated our effort on a minimization of the overall deviation from experiment: the total MAD for the GA method with the GAVs determined in this work is 1.4 kJ mol^{-1}, whereas the total MAD using the GAVs reported by Cohen[30] amounts to 1.8 kJ mol^{-1}. A comparison of the MAD values for both methods over the same set of hydrocarbons indicates that the performance of both methods is similar.

3.3. Alkenes. Benson's method requires 17 GAVs for alkene-specific groups and 3 additional NNI corrections in order to calculate the enthalpies of formation of alkenes; see Table 5. Only 13 GAVs have been determined experimentally, 3 of which might not be very reliable ($C-(C_d)(C)_3$, $C-(C_d)_2(C)(H)$ and $C-(C_d)_2(C)_2$). Recently, Sumathi and Green determined GAVs for 2 alkene groups from ab initio G2 enthalpies of formation

TABLE 5: Group Additive Values for the Standard Enthalpy of Formation of Alkenes (298 K, kJ mol^{-1})[a]

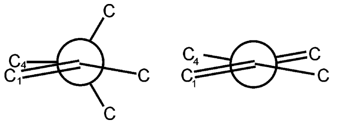
group	Benson[b]	Cohen[c]	this work
$C_d-(H)_2$	26.2	26.4	25.1
$C_d-(C)(H)$	36.0	36.0	37.1
$C_d-(C)_2$	43.3	42.7	45.3
$C_d-(C_d)(H)$	28.4	28.5	30.4
$C_d-(C_d)(C)$	37.2	36.8	40.0
$C_d-(Cd)_2$	19.3[e]	27.6	46.9
Ca (allene)	143.2	143.1	141.3
$C-(C_d)(H)_3$	−42.2	−41.8	(−42.9)
$C-(C_d)(C)(H)_2$	−19.9	−20.1	−18.9
$C-(C_d)(C)_2(H)$	−6.2	−7.1	−3.9
$C-(C_d)(C)_3$	7.0	7.1[g]	7.1
$C-(C_d)_2(H)_2$	−18.0	−18.0	−17.1
$C-(C_d)_2(C)(H)$	−4.6[f]	11.3[h]	0.4
$C-(C_d)_2(C)_2$		28.5[i]	13.8
$C-(C_d)_3(H)$	1.7[f]		4.1
$C-(C_d)_3(C)$			15.3
$C-(C_d)_4$			22.3
cis interaction	4.2	4.6	5.9
2 cis interactions about same bond		13.8	18.3
cis interaction (1 *t*-Bu)		18.4	18.5
F			13235
n/p			34/19
MAD[d]			0.8
RMS[d]			1.4
MAX			4.1

[a] Bracketed values were not estimated, but fixed to the alkane GAV to remove linear dependence; see text. The GAV of boldfaced groups has not been reported before. [b] Reference 28. [c] Reference 30. [d] MAD = mean absolute deviation, RMS = root mean square deviation, MAX = maximum deviation. [e] Suggested by Danner and Daubert.[50] [f] Ab initio values consistent with Benson 1976 GAV, Sumathi and Green.[15] [g] GAV calculated from the standard enthalpy of formation of camphene only. [h] GAV calculated from (*Z*)-5-ethylidene-bicyclo[2.2.1]-2-heptene only. [i] GAV calculated from bicylo[2.2.1]hepta-2,5-diene only.

($C-(C_d)_2(C)(H)$ and $C-(C_d)_3(H)$). Our ab initio database contains 34 alkenes which allows us to determine all alkene GAVs and NNI corrections from first principles.

Alkene groups differ structurally from alkane groups in that some alkene groups implicitly contain information concerning NNI 1,4 interactions.[18] For example, in $C-(C_d)(C)_3$ the ligand atom indicates that the next neighbor of the central carbon atom is also a atom. Hence, the molecule contains at least a $(CH_3)_3C-C_dH{=}C_dH_2$ moiety and at least one 1,4-interaction. This type of 1,4-interaction can be incorporated implicitly into the GAV of the group and therefore does not require an additional NNI correction term. However, not all interactions accross this $C-C_d$ bond can be accounted for by this GAV. In $(CH_3)_3C-(CH_3)C_d{=}C_dH_2$ the 1,4-interaction between one of the methyl groups on the C-atom and the $C_d-(H)_2$ group is implicitly accounted for by the $C-(C_d)(C)_3$ group, but the 1,4-interaction between the 3 methyl substituents and the methyl substituent on the C_d ligand cannot be accounted for implicitly and requires 2 gauche correction terms.

In this work we propose the following procedure to count the number of gauche interaction corrections in alkenes, alkynes and aromatics: across a bond $C_1C_2-C_3C_4$ where the bond between C_1 and C_2 is a double or triple bond, and hence C_2 is a C_d, C_t or C_b type of atom, the 1,4-interaction between C_4 and C_1 does not require a correction term. For example, in 2,3,3-trimethyl-1-butene:



the C_2 is a tertiary carbon atom and C_3 is a quaternary carbon atom. The revised gauche counting scheme would require 5 gauche interaction terms to account for the 1,4-interactions across the C_2-C_3 bond, as discussed for alkanes. However, the 1,4-interaction between C_{d1} and C_4 is implicitly accounted for by the $C-(C_d)(C)_3$ group and the number of gauche interactions for a S−Q bond has to be used, i.e., 2. This yields $\Delta_f H^0 = C_d-(H)_2 + C_d-(C)_2 + 4(C-(C)(H)_3) + C-(C_d)(C)_3 + 2(\text{gauche}) = 25.1 + 45.3 + 4(-42.9) + 7.1 + 2(2.9) = -88.3$ kJ mol^{-1}. For 2,3-dimethyl-1,3-butadiene, with a tertiary−tertiary interaction, 3 correction terms are expected within revised gauche counting. However, both C_d-H_2 groups are neglected resulting in a S−S bond. Hence, no gauche corrections are required ($\Delta_f H^0 = 2(C_d-(H)_2) + 2(C_d-(C_d)(C)) + 2(C-(C_d)(H)_3) = 2(25.1) + 2(40.0) + 2(-42.9) = 44.4$ kJ mol^{-1}).

Gauche interactions between substituents on a $C-C_d$ bond differ from gauche interactions between substituents on a C−C bond and therefore Benson and co-workers[18] introduced a separate alkene gauche interaction correction. Because of the greater separation between the carbon atoms, Benson initially assigned a smaller value of 2.1 kJ mol^{-1} to the alkene gauche correction as compared to the 3.3 kJ mol^{-1} of the alkane gauche interaction correction,[18] but eventually removed the distinction.[29] In this work the value of the alkane gauche correction will be used for both alkane and alkene gauche interactions corrections.

The estimated alkene GAVs and NNI corrections are presented in Table 5. As for the alkanes, the GAVs and the NNI corrections were estimated simultaneously. Because of the linear dependence between the alkene groups discussed as mentioned above, the GAV of the $C-(C_d)(H)_3$ group was set equal to the value for the $C-(C)(H)_3$ group. For alkenes too, the group additivity approximation is found to be very accurate for alkenes with a MAD of only 0.8 kJ mol^{-1} between the GA predictions and the ab initio CBS-QB3-BAC enthalpies. The largest deviation was found for allene and 3-methyl-1,2-butadiene and amounts to 4.1 kJ mol^{-1}. Two alkene GAVs are determined for the first time in this work: $C-(C_d)_3(C)$ and $C-(C_d)_4$. In general, the ab initio based GAVs correspond very well with the experimental values obtained by Cohen.[30] A few GAVs show larger deviations, but the latter are determined out of experimental enthalpies of formation of bicyclic compounds or less reliable experimental data. Examples are the GAVs for the $C-(C_d)_2(C)(H)$, $C-(C_d)_2(C)_2$ and $C-(C_d)(C)_3$ groups. Cohen determined the $C-(C_d)_2(C)(H)$ GAV from the experimental enthalpy of formation of (*Z*)-5-ethylidenebicyclo[2.2.1]-2-heptene, a strained molecule. Here, the $C-(C_d)_2(C)(H)$ GAV was determined from 3-methyl-1,4-pentadiene and 3-ethyl-1,4-pentadiene. Analogously, Cohen determined the $C-(C_d)_2(C)_2$ and $C-(C_d)(C)_3$ GAVs from bicylo[2.2.1]hepta-2,5-diene and camphene, respectively. A large difference is also found for the $C_d-(C_d)_2$ group; Benson took the GAV from Danner and Daubert[50] whereas Cohen does not state explicitly from which species the $C_d-(C_d)_2$ GAV was derived. Here this GAV was derived from 2-vinyl-1,3-butadiene. This molecule was not included in the database applied by Cohen.

A careful study of the alkane and alkene GAVs reveals the influence of replacing a C ligand atom by a C_d ligand atom: in going from $C-(C)_3(H)$ to $C-(C_d)(C)_2(H)$ to $C-(C_d)_2(C)(H)$ and to $C-(C_d)_3(H)$ the GAVs increase from −6.9, to −3.9, 0.4, and 4.1 kJ mol^{-1}, respectively, i.e., an average increase of 3.7 kJ mol^{-1} for each replacement. A similar trend can be found for the GAVs of $C-(C)_2(H)_2$, $C-(C_d)(C)(H)_2$ and $C-(C_d)_2(H)_2$, with an average increase of 1.7 kJ mol^{-1} for each substitution.

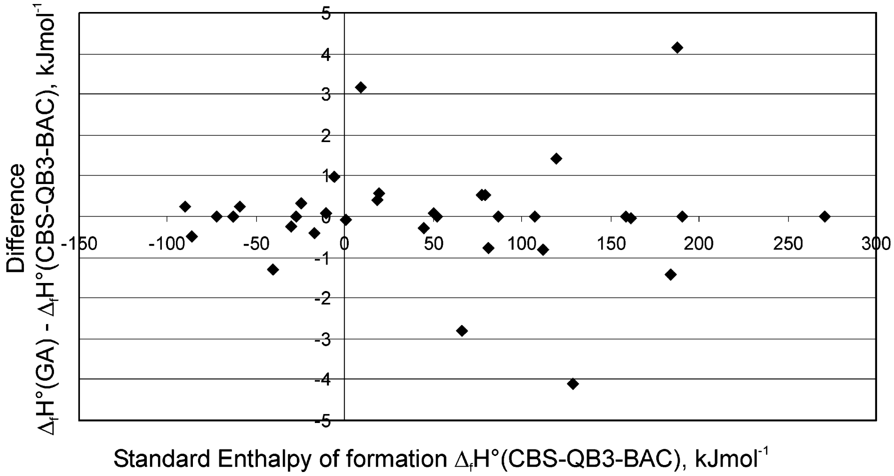


Figure 5. Differences between standard enthalpies of formation for alkenes from group additivity and from the CBS-QB3-BAC method (298 K, kJ mol^{-1}).

The internal consistency of the ab initio GAVs provides further support for their reliability.

The NNI correction for a single cis interaction, 5.9 kJ mol^{-1}, is slightly higher than the values presented by Cohen, 4.6 kJ mol^{-1},[30] and by Benson, 4.2 kJ mol^{-1}. Benson determined the cis correction directly from the enthalpy difference between *cis*- and *trans*-2-butene. In this work the single cis corrections is estimated from 3 different cis alkenes. The *t*-Bu cis correction agrees very well with the value presented by Cohen, whereas the ab initio correction for a double cis interactions about the same bond is 4.5 kJ mol^{-1} higher than the value reported by Cohen. This difference can be traced back to the CBS-QB3-BAC enthalpy of formation of 2,3-dimethyl-2-butene, the only species in the database exhibiting a double cis interaction. Indeed, the ab initio CBS-QB3-BAC value is 7.4 kJ mol^{-1} higher than the experimental enthalpy applied by Cohen.

Deviations between the group additive and the ab initio enthalpies of formation as a function of the CBS-QB3-BAC enthalpies of formation are presented in Figure 5. Over the entire enthalpy range the deviations are in general less than 1 kJ mol^{-1}, consistent with the MAD of 0.8 kJ mol^{-1} in Table 5. Deviations larger than 4 kJ mol^{-1} are found for the allenic compounds allene (+4.1 kJ mol^{-1}) and 3-methyl-1,2-butadiene (−4.0 kJ mol^{-1}), the only allenic compounds in the database. Apparently, the GA approximation is somewhat less reliable for allenic compounds.

3.4. Cycloalkanes and Cycloalkenes. For the prediction of the enthalpies of formation for cycloalkanes and cycloalkenes, the group additivity method introduces ring strain corrections (RSC) depending on the size of the ring and the number of endocyclic double bonds. This leads to a rather large number of RSCs, specific for each type of ring. Our ab initio database contains 7 cycloalkanes, ranging from cyclopropane to cyclooctane, and 12 cycloalkenes, ranging from cyclopropene to *E*- and *Z*-cyclooctene. From the 19 enthalpies of formation 18 RSCs are calculated and hence no statistical analysis is performed.

Ring strain corrections (RSC) for the most common cycloalkanes and cycloalkenes can be found in Table 6. The RSC notation consists of the prefix cyc- followed by the number of atoms in the ring and the number of endocyclic double bonds. For some RSC the position of the double bonds or the *Z*/*E* indication for cis/trans isomerism is indicated. For example, cyc-6-2(1,4) indicates the RSC for a 1,4-cyclohexadiene ring. Note that gauche interactions within the ring are accounted for in the RSC and should not be treated explicitly.

TABLE 6: Ring Strain Corrections (RSC) for the Standard Enthalpy of Formation of Cycloalkanes and Cycloalkenes (298 K, kJ mol^{-1})

RSC[a]	*i*	*j*	Benson[b]	Cohen[c]	this work
cyc-3-0	3	0		115.9	118.6
cyc-3-1	3	1		224.3	230.0
cyc-4-0	4	0	112.2	112.1	112.6
cyc-4-1	4	1		124.7	129.6
cyc-5-0	5	0	29.7	29.7	30.9
cyc-5-1	5	1	24.7	24.7	23.8
cyc-5-2	5	2		23.8	21.0
cyc-6-0	6	0	2.9	2.9	3.2
cyc-6-1	6	1	5.9	2.1	5.3
cyc-6-2(1,3)	6	2	20.1	16.7	15.8
cyc-6-2(1,4)	6	2	2.1	−12.6	−0.7
cyc-7-0	7	0		28.5	31.3
cyc-7-1	7	1		22.6	21.5
cyc-7-2(1,3)	7	2		27.2	24.7
cyc-7-2(1,4)	7	2			28.6
cyc-8-0	8	0		43.1	46.2
cyc-8-1E	8	1			70.6
cyc-8-1Z	8	1		25.1	28.4

[a] cyc-*i*-*j*, where *i* indicates the number of atoms in the ring and *j* the number of endocyclic double bonds; boldface groups have not been reported before. [b] Benson: cycloalkanes;[36] cycloalkenes.[28] [c] Reference 30.

The RSC for cyc-7-2(1,4) and cyc-8-1E are determined for the first time in this work. The ab initio RSC are generally within 4 kJ mol^{-1} of the experimentally based values reported by Cohen and Benson. However, the ab initio value of the cyc-6-2(1,4) correction, −0.6 kJ mol^{-1}, differs significantly from the −12.6 kJ mol^{-1} presented by Cohen.[30] This RSC is derived from the enthalpy of formation of 1,4-cyclohexadiene and a range of experimental values can be found in the literature, ranging from a 109 to 100.4 kJ mol^{-1}. The low value of 100.4 kJ mol^{-1} was used by Cohen[30] to derive the cyc-6-2(1,4) RSC. Our CBS-QB3-BAC standard enthalpy of formation of 113.4 kJ mol^{-1} clearly supports the higher experimental value. Other high-level ab initio calculations also support the higher experimental value. Notario et al.[51] calculated an enthalpy of formation of 111.3 kJ mol^{-1} using the ab initio G3 method, and Saeys et al.[14] reported a value of 111.0 kJ mol^{-1} using CBS-QB3-AAC.[14] The introduction of π-bonds in saturated rings increases the RSC for smaller rings and decreases the RSC for C5−C7 molecules. The only exception is the cyc-6-1 RSC, 5.3 kJ mol^{-1}, which is higher than the cyc-6-0 RSC, 3.2 kJ mol^{-1}.

3.5. Alkynes. Benson's group additivity method requires 28 alkyne-specific GAVs and 1 additional NNI correction for

TABLE 7: Group Additive Values for the Standard Enthalpy of Formation of Alkynes (298 K, kJ mol^{-1})[a]

group	Benson[b]	Cohen[c]	**this work**
$C_t-(H)$	112.8	113.8	**113.8**
$C_t-(C)$	115.4	114.2	**115.6**
$C_t-(C_d)$	122.3	116.7	**120.3**
$C_t-(Ct)$	115.4	105.9	**117.1**
$C-(C_t)(H)_3$	−42.2	−41.8	**(−42.9)**
$C-(C_t)(C)(H)_2$	−19.8	−19.7	**−17.7**
$C-(C_t)(C)_2H$	−7.2	−7.5	**−2.6**
$C-(C_t)(C)_3$	5.5[d]	5.4	**7.6**
$C-(C_t)(C_d)(H)_2$	−14.7[e]		**−15.2**
$C-(C_t)(C_d)(C)(H)$	−28.9[e]		**3.0**
$\mathbf{C}-(C_t)(C_d)(\mathbf{C})_2$			**12.6**
$C-(C_t)(C_d)_2(H)$	7.9[e]		**7.3**
$\mathbf{C}-(C_t)(C_d)_2(\mathbf{C})$			**19.2**
$\mathbf{C}-(C_t)(C_d)_3$			**27.3**
$C-(C_t)_2(H)_2$	−3.4[e]		**−1.8**
$C-(C_t)_2(C)(H)$	7.2[e]		**14.7**
$\mathbf{C}-(C_t)_2(\mathbf{C})_2$			**26.7**
$C-(C_t)_2(C_d)(H)$	19.8[e]		**24.7**
$\mathbf{C}-(C_t)_2(C_d)(\mathbf{C})$			**33.7**
$\mathbf{C}-(C_t)_2(C_d)_2$			**41.5**
$C-(C_t)_3(H)$	42.3[e]		**47.0**
$\mathbf{C}-(C_t)_3(\mathbf{C})$			**56.8**
$\mathbf{C}-(C_t)_3(C_d)$			**69.1**
$\mathbf{C}-(C_t)_4$			**101.9**
$C_d-(C_t)(H)$	28.4	28	**(30.1)**
$C_d-(C_t)(C)$	34.0[e]	39.7	**41.8**
$C_d-(C_t)(C_d)$	31.6[e]		**36.1**
$C_d-(C_t)_2$	36.9[e]		**46.1**
ene-yne cis	−0.4[d]	−2.9	**−3.2**

[a] Boldface groups were determined for the first time in this work. Bracketed values were assigned the corresponding GAV to remove linear dependence; see text. [b] Reference 28 unless stated otherwise. [c] Reference 30. [d] Cohen and Benson 1993;[29] this GAV is not consistent with the Benson 1976 GAVs. [e] Ab initio values consistent with Benson 1976 GAV, Sumathi and Green.[15]

TABLE 8: Group Additive Values for the Standard Enthalpy of Formation of Monocyclic Aromatics (298 K, kJ mol^{-1})[a]

group	Benson[b]	Cohen[c]	**this work**
$C_b-(H)$	13.8	13.8	**13.8**
$C_b-(C)$	23.0	23.0	**24.4**
$C_b-(C_d)$	24.3	24.3	**24.0**
$C_b-(C_t)$		23.8	**16.2**
$C-(C_b)(H)_3$	−42.2	−41.8	**(−42.9)**
$C-(C_b)(C)(H)_2$	−20.4	−19.2	**−21.2**
$C-(C_b)(C)_2(H)$	−4.1	−4.2	**−4.7**
$C-(C_b)(C)_3$	12.3	12.1	**11.1**
$C-(C_b)(C_d)(H)_2$		−10.5	**−19.8**
$\mathbf{C}-(C_b)(C_d)(\mathbf{C})(\mathbf{H})$			**−3.8**
$\mathbf{C}-(C_b)(C_t)(\mathbf{H})_2$			**−15.2**
$\mathbf{C}-(C_b)(C_t)(\mathbf{C})(\mathbf{H})$			**−24.9**
$\mathbf{C}-(C_b)(C_t)(\mathbf{C})_2$			**15.0**
$C_d-(C_b)(H)$	28.5	28.5	**(30.4)**
$C_d-(C_b)(C)$	36.2		**41.5**
$C_d-(C_b)(C_d)$		54.4[d]	**31.6**
$C_d-(C_b)(C_t)$			**40.1**
$C_t-(C_b)$		102.9	**(113.8)**

[a] Boldface groups were determined for the first time in this work. Bracketed values were assigned the corresponding GAV to remove linear dependence; see text. [b] Reference 29. [c] Reference 30. [d] From solid state enthalpy of formation.

alkynes, of which only 10 have been determined on the basis of experimental data. Recently, Sumathi and Green[15] used ab initio G2 calculations to determine 10 of the missing GAVs. In this work all 29 parameters were estimated from our ab initio database. Because the database contains only 31 alkyne species, ranging from ethyne to 3,3-diethenyl-4-penten-1-yne, no statistical analysis was performed. Note that C_t-adjacent groups are capable to take NNIs into account similar to the C_d-adjacent groups. Hence these NNIs should not be treated explicitely.

The ab initio GAVs are presented in Table 7. Nine GAVs are determined for the first time. Because of the linear dependence between the alkyne groups, the GAV of the $C-(C_t)(H)_3$ group was set equal to the value of the $C-(C)(H)_3$ group and the GAV of the $C_d-(C_t)(H)$ group was set equal to the value of the $C_d-(C_d)(H)$ group. The ab initio GAVs agree well with the available experimental values. The agreement with the older values reported by Benson[28] is better than with the more recent values determined by Cohen.[30] For the C_t-centered groups, the deviations from the previously reported GAVs are all smaller than 2 kJ mol^{-1}. Larger deviations are found for the C_t-adjacent groups for which GAV reported by Benson exist, with the ab initio values being higher than the experimental values by 2−5 kJ mol^{-1}. Our ab initio GAVs are significantly higher than the values proposed by Sumathi and Green[15] based on G2 ab initio enthalpies of formation, with differences up to 32 kJ mol^{-1}. Sumathi and Green state that the CBS-Q method is not reliable for triple bonds and attribute the differences between the CBS-Q and G2 enthalpies of formation to problems with the CBS-Q method. However, our ab initio CBS-QB3-BAC enthalpies for alkynes were found to agree very well with available experimental data (Table 1). Even for the standard enthalpy of formation of 2-pentyne the CBS-QB3-BAC value, 128.9 kJ mol^{-1}, matches the experimental value, 128.9 kJ mol^{-1},[43] whereas Sumathi et al. report an extremely low CBS-Q value of 86.4 kJ mol^{-1}.[52]

Only one additional NNI correction is required for the alkyne molecular class, the ene−yne cis correction. This pertains to the cis interaction between an alkyl group and a triple bond, as in *cis*-pent-3-en-1-yne; see Figure 1. The NNI correction is negative, −3.2 kJ mol^{-1}. The ene−yne cis interaction is found to be stabilizing, in agreement with the value reported by Cohen.[30]

The alkyne GAVs are consistent with the alkene and alkane values. Substituting a C-ligand atom by a C_t-ligand atom leads to an increase in GAV of 3−12 kJ mol^{-1} for the first ligand, 16−23 kJ mol^{-1} for the second, 30−36 kJ mol^{-1} for the third and 45 kJ mol^{-1} for the fourth. Substituting a C_d-ligand atom by a C_t-ligand atom increases the GAV by 0−5 kJ mol^{-1} for the first, 12−17 kJ mol^{-1} for the second, 22−28 kJ mol^{-1} for the third and 33 kJ mol^{-1} for the fourth C_t atom. The $C-(C_t)(C_d)(C)(H)$ group for which the GAV reported by Cohen is over 30 kJ mol^{-1} lower than the value determined in this work, fits well into this picture: substitution of the C-ligand in $C-(C_d)(C)_2(H)$ yields 6.9 kJ mol^{-1} difference, and substitution of the C_d-ligand in $C-(C_d)_2(C)(H)$ yields 2.6 kJ mol^{-1}.

In general, the enthalpies of formation for the 31 alkynes in our ab initio database are predicted accurately by the ab initio group additivity method, with a maximal deviation of 3.8 kJ mol^{-1} for the ene−yne conjugated but-1-en-3-yn.

3.6. Monocyclic Aromatics. In this paragraph only groups with one single C_b atom are treated. Polyaromatics involving the fused aromatic carbon atom C_{bf} are not included in this study. For monocyclic aromatics 18 group additive values have been determined, from which 4 are C_b-centered and 14 are C_b-adjacent. Five GAVs have not been reported before. Due to the linear dependence between the groups, 3 GAVs need to be fixed: the $C-(C_b)(H)_3$ GAV is set equal to the $C-(C)(H)_3$ value, the $C_d-(C_b)(H)$ value is set equal to the $C_d-(C_d)(H)$ value and the $C_t-(C_b)$ value is set equal to the $C_t-(C)$ value. Group additive values for monocyclic aromatics are shown in Table 8. In line with C_d- and C_t-adjacent groups, C_b-adjacent groups take NNIs into account. The NNIs concerned should not be treated explicitely.

All GAV agree very well with the experimental values. Except for the $C_d-(C_b)(H)$ and $C_d-(C_b)(C)$ groups the differences with the Benson values[29] are smaller than 1.5 kJ mol^{-1}. Also compared to the GAV reported by Cohen[30] the agreement is excellent with deviations smaller than 2 kJ mol^{-1}, except for the $C_b-(C_t)$, $C-(C_b)(C_d)(H)_2$, $C_t-(C_b)$ and $C_d-(C_b)(C_d)$ groups. Cohen derived the latter GAV from a solid phase standard enthalpy of formation, which could explain the deviation. The $C_b-(C_t)$ and $C_t-(C_b)$ groups always occur together and their GAVs are perfectly correlated. Hence the sum of their GAVs should be compared, not the individual values. The ab initio GAVs yield a sum of 130.0 kJ mol^{-1}, as compared to 126.7 kJ mol^{-1} for the experimental values.

The ab initio GAVs are again consistent with the other values determined in this work. For the C-centered groups the GAVs change by less than 2.5 kJ mol^{-1} when a C-ligand atom is substituted by a C_b-ligand atom. For the $C-(C_b)(C_t)(C)(H)$, the $C-(C_b)(C_t)(C)_2$ and $C-(C_b)(C)_3$ groups the influence is larger, probably because of steric effects.

3.7. Hydrocarbon Radicals. *3.7.1. Group Additivity Method.* In principle, 125 GAVs are required to predict the enthalpies of formation of all hydrocarbon radicals up to monocylic aromatics. The 125 GAVs can be divided into 41 radical-centered and 84 radical-adjacent groups. In addition to the 125 GAVs, a number of radical-specific NNI corrections and RSCs need to be determined. To estimate this large number of parameters and assess the accuracy of the group additivity method, one would require a very large ab initio database of enthalpies of formation. However, the number of parameters can be significantly reduced. Detailed calculations for alkylic, alkenylic, alkynylic and benzylic radicals indicate that the GAVs for the radical-adjacent groups differ very little from the corresponding hydrocarbon group. The radical-adjacent GAVs are on average 1.7 kJ mol^{-1} lower than the corresponding non-radical GAV. The only GAVs with a deviation larger than 6 kJ mol^{-1} are for the $C-(\dot{C})(C_d)(C)_2$, $C-(\dot{C})(C_t)(H)_2$, $C-(\dot{C})(C_t)(C)(H)$ and $C-(\dot{C})(C_t)(C)_2$ groups, all occurring in homoallylic or homopropargylic radicals (see Table 4S). Hence, the number of radical GAVs that needs to be determined can be reduced from 125 to 41 by approximating the radical-adjacent GAVs by the value of the corresponding hydrocarbon group. This approximation only slightly reduces the accuracy of the ab initio group additivity method. Indeed, if the GAV of the radical-adjacent groups are taken equal to the GAV of the corresponding hydrocarbon group, the MAD between the standard enthalpies of formation from the group additivity method and the CBS-QB3-BAC values for the 118 radicals in the database increases only slightly from 1.1 to 1.7 kJ mol^{-1}.

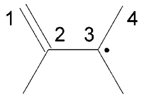
Of the 41 radical-centered GAVs only 9 been determined previously by Benson and O'Neal.[33] Recently, Marsi et al.[20] have published significantly higher GAVs for alkylic radicals. Clearly, the availability of a consistent and accurate set of GAVs would expand the applicability of the group additivity method for the modeling of radical chemistry. On the basis of our ab initio database of 118 radicals, a consistent set of 34 GAVs was determined.

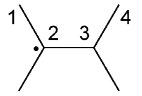
3.7.1.a. Radical NNI: Theory. To account for NNI gauche interactions in hydrocarbon radicals, specific radical gauche interaction corrections need to be introduced. Assigning NNI corrections to radicals is not straightforward. Marsi et al.[20] proposed two types of radical gauche interactions, RG1 and RG2 (Figure 1). However, as their study was restricted to alkyl radicals smaller than C_7, they did not provide a general counting scheme. Here, the following general and consistent counting scheme is proposed:

A. Radical Gauche 1 Corrections ($C_1-\dot{C}_2C_3-C_4$, Figure 1):

1. The number of gauche interaction corrections to be taken into account is determined by neglecting the radical character of C_2 and using the revised alkane gauche counting scheme summarized in Table 4.

2. If one of the central carbon atoms $\dot{C}_2$ or C_3 is a C_d, a C_t or a C_b type of atom, gauche interactions with the adjacent C_d, C_t or C_b atom are implicitly taken into account through the GAV of the other central atom, similar to the procedure described in section 3.3.

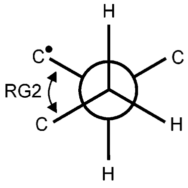




For example, for the 2,3-dimethyl-1-buten-3-yl radical the C_2 carbon atom is of the C_d type. Hence the 1,4-interation with the C_{d1} atom is taken into account by the GAV of the $\dot{C}-(C_d)(C)_2$ group and only 1 RG1 interaction remains (secondary−tertiary type of bond) ($\Delta_f H^0 = C_d-(H)_2 + C_d-(C)_2 + \dot{C}-(C_d)(C)_2 + 3(C-(C)(H)_3) + RG1 = 25.1 + 45.3 + 127.5 + 3(-42.9) + 1.8 = 71.0$ kJ mol^{-1}). For the 2,3-dimethyl-2-butyl radical (tertiary−tertiary), 3 RG1 interactions need to be taken into account according to the revised gauche counting scheme ($\Delta_f H^0 = 4(C-(C)(H)_3) + \dot{C}-(C)_3 + C-(C)_3(H) + 3(RG1) = 4(-42.9) + 184.5-6.9 + 3(1.8) = 11.4$ kJ mol^{-1}).

B. Radical Gauche 2 Corrections ($\dot{C}_1-C_2C_3-C_4$, Figure 1):

Often both alkane gauche (AG, $C_1-C_2C_3-C_4$,) and radical gauche 2 (RG2) interaction occur simultaneously in the same molecule, and rotamers with a different combination of AG and RG2 interactions exist. Because RG2 interactions are found to be less repulsive than AG interactions, the determination of the number of AG and RG2 corrections to be taken into account is based on the rotamer corresponding to the minimal number of AG NNIs. For example, 3 rotamers can be put forward for the 2-methylbut-1-yl radical:



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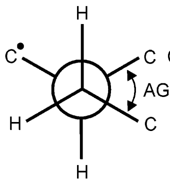

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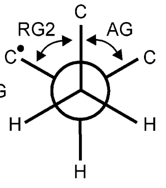


3

respectively having a single RG2 interaction, an AG interaction, or both a RG2 and an AG interaction. The most stable conformation is **1**, with a single RG2 interaction. The following counting procedure is proposed:

1. In the rotamer with the minimum number of gauche interactions, the number of RG2 corrections is determined according to the revised gauche counting scheme (equivalent to classical gauche counting in this case; see Table 4).

2. The number of AG corrections is obtained by subtracting the number of RG2 interactions from the total number of gauche interactions obtained using revised gauche counting. To determine the total number of gauche corrections, the radical character of the $\dot{C}_1$ atom is neglected.

3. If one of the central carbon atoms $\dot{C}_2$ or C_3 is a C_d, C_t or C_b type of atom, gauche interactions with the adjacent C_d, C_t

TABLE 9: Group Additive Values for the Standard Enthalpies of Formation of Radicals: Radical-Centered Groups (298 K, kJ mol^{-1})[a]

radical group	O'Neal Benson[b]	Marsi et al.[c]	**this work**
$\dot{C}-(C)(H)_2$	150.0	162.0	**168.0**
$\dot{C}-(C)_2(H)$	156.8	171.0	**177.3**
$\dot{C}-(C)_3$	159.1	177.3	**184.5**
$\dot{C}-(C_d)(H)_2$	97.1		**107.0**
$\dot{C}-(C_d)(C)(H)$	106.8		**115.2**
$\dot{C}-(C_d)(C)_2$	103.8		**127.5**
$\dot{C}-(C_d)_2(\mathbf{H})$			**76.5**
$\dot{C}-(C_d)_2(\mathbf{C})$			**86.7**
$\dot{C}-(C_d)_3$			**71.4**
$\dot{C}-(C_t)(\mathbf{H})_2$			**121.4**
$\dot{C}-(C_t)(\mathbf{C})(\mathbf{H})$			**133.6**
$\dot{C}-(C_t)(\mathbf{C})_2$			**139.8**
$\dot{C}-(C_t)(C_d)(\mathbf{H})$			**99.5**
$\dot{C}-(C_t)(C_d)(\mathbf{C})$			**108.5**
$\dot{C}-(C_t)(C_d)_2$			**70.7**
$\dot{C}-(C_t)_2(\mathbf{H})$			**116.2**
$\dot{C}-(C_t)_2(\mathbf{C})$			**124.0**
$\dot{C}-(C_t)_3$			**122.8**
$\dot{C}-(C_b)(H)_2$	96.3		**119.1**
$\dot{C}-(C_b)(C)(H)$	103.4		**132.8**
$\dot{C}-(C_b)(C)_2$	106.8		**142.6**
$\dot{C}-(C_b)(C_d)(\mathbf{H})$			**123.6**
$\dot{C}-(C_b)(C_d)(\mathbf{C})$			**98.1**
$\dot{C}-(C_b)(C_d)_2$			**165.7**
$\dot{C}-(C_b)(C_t)(\mathbf{H})$			**126.4**
$\dot{C}-(C_b)(C_t)(\mathbf{C})$			**155.8**
$\dot{C}-(C_b)(C_t)(C_d)$			**87.9**
$\dot{C}_d-(\mathbf{H})$			**275.8**
$\dot{C}_d-(\mathbf{C})$			**273.2**
$\dot{C}_d-(C_d)$			**234.9**
$\dot{C}_d-(C_t)$			**229.8**
$\dot{C}_d-(C_b)$			**246.0**
$\dot{C}_t-$			**454.8**
$\dot{C}_b-$			**276.9**

[a] The GAVs of the radical-adjacent groups were assigned the value of the corresponding non-radical group. Boldface groups were determined for the first time in this work. [b] Reference 33. [c] Reference 20, ab initio values.

or C_b atom are implicitly taken into account through the GAV of the other central atom, similar to the procedure described in section 3.3.

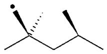
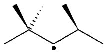
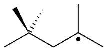
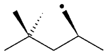
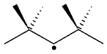
As an example the 2,2,3-trimethyl-1-butyl radical can be considered. Two rotamers exist for this radical. The most stable rotamer has 2 RG2 and 2 AG interactions, the least stable one has 1 RG2 and 3 AG interactions. The revised gauche scheme counts 5 gauche contributions for this radical. Hence, 2 RG2 and 3 AG corrections are taken into account ($\Delta_f H^0 = \dot{C}-(C)(H)_3 + C-(C)_4 + C-(C)_3(H) + 4(C-(C)(H)_3) + 2(RG2) + 3(AG) = 168.0 + 3.9 - 6.9 + 4(-42.9) + 2(1.8) + 3(2.9) = 5.7$ kJ mol^{-1}).

This scheme differs from the scheme proposed by Marsi et al.[20] but is consistent with the approach introduced for stable hydrocarbons. For example, for 2-methyl-1-butyl the new scheme assigns one RG2 correction because the RG2 interaction is more stable than an AG interaction, whereas Marsi et al. assign one AG correction.

Radical 1,5-interactions are in general less destabilizing than alkane 1,5-interactions, except for the interaction in 2,2,4,4-tetramethylpent-3-yl. As the CBS-QB3-BAC results show no obvious correlation among the different types of 1.5-interactions and the destabilization energy, a specific 1,5-interaction correction is introduced for every possible type of interaction.

3.7.1.b. GAVs. Ab initio GAVs for the radical-centered groups can be found in Table 9. NNI corrections, RSCs and a statistical analysis are given in Table 10. All Radical GAVs and NNI corrections are determined simultaneously. There are no linear dependencies because the radical-adjacent GAVs have been set equal to the GAVs of the corresponding non-radical group. The ab initio GAVs in Table 9 are on an average 16.5 kJ mol^{-1} higher than the values reported by O'Neal and Benson,[33] and 6−7 kJ mol^{-1} higher than the ab initio values reported by Marsi et al.[20] In Figure 2 the CBS-QB3-BAC standard enthalpies of formation are on average 3 kJ mol^{-1} higher than experimental values for radicals. However, these deviations cannot account for the difference between the experimental and the ab initio GAV. In particular, the $\dot{C}-(C_b)(C)(H)$ and the $\dot{C}-(C_d)(C)_2$ GAVs are remarkably larger than the corresponding Benson values.

TABLE 10: Non-Neareast Neighbour Interaction (NNI) Corrections and Ring Strain Corrections (RSC) for the Standard Enthalpy of Formation of Radicals (298 K, kJ mol^{-1})

correction	structure	O'Neal Benson[a]	Marsi et al.[b]	**this work**
Gauche corrections				
AG	C−CC−C	3.3	3.3	**(2.9)**
RG1	C−ĊC−C	3.3	−0.8	**1.8**
RG2	Ċ−CC−C	3.3	0.0	**0.7**
1,5-interactions				
type 1				**4.7**
type 2				**3.0**
type 3				**-1.8**
type 4				**2.8**
type 5				**14.9**
Ring Strain Corrections				
cyc-4-1trig				**127.3**
cyc-5-1trig				**19.7**
cyc-5-3trig				**23.2**
cyc-6-1trig				**3.9**
cyc-6-3trig				**3.5**
cyc-6-5trig				**−0.3**
Statistics				
F				10246
n / p [c]				118 / 42
MAD[d]				**1.7**
RMS[d]				**2.4**
MAX[d]				**6.8**

[a] Reference 33. [b] Reference 20, ab initio values. [c] *n* data points and *p* regression parameters, 1,5-interaction corrections were determined separately. [d] MAD = mean absolute deviation, RMS = root mean square deviation, MAC = maximum deviation.

Radical enthalpies of formation are particularly difficult to determine experimentally, however, and the experimental values have been revised since O'Neal and Benson[33] published their GAVs. For example, O'Neal and Benson used an enthalpy of formation of 107.4 kJ mol^{-1} for the ethyl radical, significantly lower than the currently accepted experimental value available in the NIST webbook,[43] 119 ± 2 kJ mol^{-1}, and the ab initio CBS-QB3-BAC value determined in this work, 122.0 kJ mol^{-1}. Similar differences can be found for other radicals: (methyl radical) 142.5 kJ mol^{-1} (O'Neal and Benson[33]), 146.2 kJ mol^{-1}

(CBS-QB3-BAC) and 147 ± 1 kJ mol^{-1} (NIST[43]); (*sec*-propyl radical) 76.1 kJ mol^{-1} (O'Neal and Benson[33]), 90.4 kJ mol^{-1} (CBS-QB3-BAC) and 90 ± 2 kJ mol^{-1} (NIST[43]); (*tert*-butyl radical) 31.8 kJ mol^{-1} (O'Neal and Benson[33]), 54.6 kJ mol^{-1} (CBS-QB3-BAC) and 48 ± 3 kJ mol^{-1} (NIST[43]). Also for the benzyl radical, the enthalpy of formation reported by O'Neal and Benson,[33] 188.5 kJ mol^{-1}, is low as compared to the ab initio value, 212.6 kJ mol^{-1}, and the experimental value,[43] 207 ± 4 kJ mol^{-1}. Clearly, a increase in the GAVs for radical species compared to the values reported by O'Neal and Benson is self-evident.

3.7.1.c. Radical NNI and RSC. The new values for the radical gauche corrections, 1.8 kJ mol^{-1} (RG1) and 0.7 (RG2) kJ mol^{-1}, differ significantly from the value of the AG correction, 3.3 kJ mol^{-1}, illustrating the need to introduce radical-specific gauche corrections. Our values also differ from the corrections proposed by Marsi et al., −0.8 kJ mol^{-1} for RG1 and 0.0 kJ mol^{-1} for RG2[20] based on a lower level CBS-4 ab initio study. In this study both corrections are estimated positive, consistent with the repulsive interactions found from the CBS-QB3 calculations.

The corrections for radical 1,5 interactions can be found in Table 10 as well. Compared to the alkane 1,5-interaction correction of 7.1 kJ mol^{-1}, the corrections for type 1 to 4 are very low, between −1.8 and +4.7 kJ mol^{-1}. The type 5 correction is the total 1,5-correction for the given structure, hence involving 2 1,5-interactions. The destabilization of 14.9 kJ mol^{-1} is comparable to the total destabilization due to 1,5-interactions in 2,2,4,4-tetramethylpentane, i.e., 14.7 kJ mol^{-1}.

Eight cyclic radicals have been included in the database, ranging from cyclobutyl to cyclohexyl. From these, 6 radical ring strain corrections (RSCs) have been determined; see Table 10. The following nomenclature is introduced: cyc-*i*-*j*trig, where *i* indicates size of the ring and *j* indicates the number of trigonal sp_2 carbon atoms in the ring. Radical RSCs differ significantly from the RSCs for the corresponding non-radical rings. The largest difference is found for the cyclopentyl radical, where the radical RSC of 19.7 kJ mol^{-1} is much lower than the non-radical value for cyc-5-0, 30.9 kJ mol^{-1}. For larger rings, the presence of a radical carbon atom has a smaller influence on the ring strain.

Resonance stabilization is difficult to account for within the group additivity approximation, as resonance effects typically extend beyond the group region. Small-scale resonance effects involving only the radical carbon atom and its next neighbors, as in allyl radicals, and the 3-vinyl-1-penten-3-yl radical can be treated well within the group additivity approximation. Larger scale resonance effects cannot be treated within the group additivity approximation, and it advisable to use the hydrogen bond increment method of Lay et al.[39] for these radicals.

In general, the group additivity method as presented in this section is found to be accurate and reliable for hydrocarbon radicals and enthalpies of formation are predicted with a MAD of 1.7 kJ mol^{-1}. Deviations larger than 5 kJ mol^{-1} are found for some extended resonance stabilized radicals and for some homopropargylic radicals. For these radicals an alternative approach might be required to achieve chemical accuracy.

3.7.2. Hydrogen Bond Increment Method. The hydrogen bond increment method of Lay et al.[39] provides an alternative procedure to predict the thermodynamic properties of hydrocarbon radicals. The HBI method calculates the enthalpy of formation by adding a HBI to the enthalpy of formation of the parent molecule; see eq 8. Here we will use the notation introduced by Lay et al., where a J indicates the position of the radical carbon atom; e.g., the CCJ HBI corresponds to the ethyl radical. Because the HBI method is not restricted by the group concept, it can account for the larger molecular structures to account for large scale resonance effects.

TABLE 11: Values for Hydrogen Bond Increments for Acyclic Radicals, Ordered from Least to Most Detailed Structure (298 K, kJ mol^{-1})

HBI[a]	Lay et al.[b]	this work
CCJ	205.3	**207.8**
RCCJ	205.3	**208.9**
ISOBUTYL	205.3	**211.3**
NEOPENTYL	205.3	**212.4**
CCJC	194.2	**196.8**
RCCJC	194.2	**196.5**
RCCJCC	194.2	**199.0**
TERTALKYL	185.2	**189.7**
ALLYL P	151.3	**150.3**
ALLYL S	140.4	**135.4**
ALLYL T	131.2	**130.7**
VIN	247.6	**250.5**
VINS	238.4	**235.9**
C=C=CJ	154.6	
BENZYL P	152.5	**162.0**
BENZYL S	141.7	**154.0**
BENZYL T	132.9	**147.3**
C≡CJ	339.7	**341.0**
C≡CCJ	156.3	**164.3**
C≡CCJC	146.3	**149.9**
C≡CCJC2	135.8	**141.9**
C≡CCJ=C		**199.4**
PHENYL		**263.1**
C=CJC=C	199.8	**189.6**
C=CCJC=C	100.2	**88.3**
C=CC=CCJ	116.9	**120.8**
C=CC=CCJ	121.1	**110.2**
C≡CC=CJ		**255.5**
C≡CC=CJC		**241.9**
C≡CCJC≡C		**113.6**
(C_6H_5)CJ=C		**215.6**
C=CCJ(C_6H_5)		**143.5**
C≡CCJ(C_6H_5)		**141.6**
C=CCJ(C_6H_5)C		**101.9**
C≡CCJ(C_6H_5)C		**180.7**
C=CCJ(C=C)C=C		**67.4**
C=CCJ(C≡C)C=C		**63.4**
C≡CCJ(C≡C)C≡C		**75.7**
F		9738
n/p		110/36
MAD[c]		2.0
RMS[c]		2.8
MAX[c]		9.0

[a] CJ in the HBI group name indicates the radical center. Boldface HBIs were introduced in this work. [b] Reference 39. These authors reported $D(R-H)$ instead of $D(R-H) - \Delta_f H^0(\dot{H})$. Hence, the values reported by Lay et al. are 218 kJ mol^{-1} higher than the values reported here. [c] MAD = mean absolute deviation, RMS = root mean square deviation, MAX = maximum deviation.

Lay et al. have introduced 25 HBIs.[39] While the HBIs were being determined, it became clear that this number is insufficient to describe the variation in the standard enthalpies of formation for the radicals in our database: for some radicals corresponding to the same type of HBI the bond dissociation energies differed by more than 10 kJ mol^{-1}. For example, for most *sec*-vinylic radicals the HBI mounts to about 240 kJ mol^{-1}, but the value for the but-1-en-3-yn-2-yl radical is only 207.0 kJ mol^{-1}. This value is also different from the HBI for *sec*-propargylic radicals, 158.2 kJ mol^{-1}. Hence, 13 additional HBIs were introduced. These new HBIs involve C≡CC=CJ, C≡CC=CJC, C≡CCJC≡C, phenyl, C≡CCJ=C, C≡CCJ(C≡C)C≡C, C=CCJ(C≡C)C=C, C=CCJ(C=C)C=C, (C_6H_5)CJ=C, C≡CCJ(C_6H_5), C=CCJ(C_6H_5), C≡CCJ(C_6H_5)C and C=CCJ(C_6H_5)C.

For all radicals in the database, HBIs were determined using eq 8. The standard enthalpy of formation of the parent molecule was calculated using the previously determined GAVs. Next, the radicals were grouped according to the similarity of their HBI and radical character. When multiple radicals in the database correspond to the same type of HBI, the mean value is reported. HBIs for cyclic radicals were not included. The 38 HBI types that are required to account for the variation in our database are presented in Table 11. Our ab initio HBIs are in general slightly higher than the values reported by Lay et al., in agreement with the rather low experimental values for the standard enthalpies of formation for radical species discussed in the previous section.

Radical gauche corrections are not defined within the HBI framework. Because the radical enthalpy of formation is calculated from the parent molecule, NNIs are accounted for through the parent molecule. However, as was clearly shown in the previous section, radical gauche corrections are significantly smaller than alkane gauche corrections. A possible improvement to the HBI method might therefore be to differentiate between AG and radical gauche interactions. However, preliminary tests indicate the improvement is very small.

As discussed, different HBIs can correspond to the same radical. Indeed, for diallylic radicals, both the C═CCJC═C and the C═CC═CCJ HBI can be used. Because both take the extended resonance effect into account, both HBIs are valid. However, the ALLYL_S HBI does not account for the extended resonance effect and this HBI should not be used for diallylic radicals. To remove any ambiguity in assigning HBIs, the following procedure is proposed. Table 11 is organized so that the most specific HBIs are found at the bottom and the most general HBIs are found at the top of the table. When a HBI is assigned to a given radical, the most specific HBI should be selected, i.e., the lowest in the table.

Using the HBI parameters determined in this work yields a somewhat higher MAD than the HBI values reported by Lay et al.,[39] for all radicals contained in the database for which accurate standard enthalpies of formation are available (see Table 5S in Supporting Information). It was found that the overall accuracy of the HBI method is comparable to the group additivity method with a MAD of 2.0 kJ mol^{-1}. For non-resonance stabilized radicals, the group additivity method is more accurate than the HBI method. For resonance stabilized radicals on the other hand, the HBI method provides an improvement over the group additivity method. We therefore suggest to use the group additivity method for non-resonance stabilized radicals and the HBI method for resonance stabilized radicals.

4. Conclusions

The kinetic modeling of complex radical chemistry requires accurate thermodynamic data for the thousands of molecules involved in the reaction mechanism. Benson's group additivity method and the hydrogen bond increment (HBI) method of Lay et al. provide elegant schemes to accurately determine these thermodynamic parameters, but their applicability is hampered by the lack of parameters, in particular for radical species. In this work, an accurate, internally consistent and complete set of parameters is derived for both methods from state-of-the-art ab initio calculations, extending the applicability of Benson's group additivity method to all hydrocarbon molecules and radicals up to monocyclic aromatics.

The ab initio database contains 233 enthalpies of formation calculated at the CBS-QB3 level of theory. The accuracy was improved to better than 2 kJ mol^{-1} by implementing a bond additive correction with newly derived parameters. From the CBS-QB3-BAC database, 95 GAVs and 38 HBIs were determined and the reliability of the group additivity approximation was assessed. There have been 16 non-radical and 25 radical group additive values (GAVs) determined for the first time. For the well-established alkane GAVs the agreement with experimental values is better than 2 kJ mol^{-1}. To extend the applicability of the HBI method, 13 new parameters were introduced.

To account for non-next-nearest neighbor interactions, the revised gauche counting scheme was found to provide an improvement over the classical gauche counting scheme and was applied throughout this work. A novel, rigorous counting scheme for radical gauche interactions was introduced as a consistent extension of the revised gauche counting scheme.

It was found that the GAVs of the radical-adjacent groups are approximately equal to the GAVs of the corresponding non-radical groups, allowing a 3-fold reduction in the number of GAVs for hydrocarbon radicals.

The hydrogen bond increment method is not restricted by the group concept and allows us to account for electron delocalization in resonance stabilized radicals, providing improved accuracy over the group additivity method for delocalized radicals. A structured list of HBIs is presented, which allows us to assign the best possible HBI to a given radical. However, the HBI method does not include radical-specific non-next-nearest neighbor interactions, slightly affecting its accuracy. Therefore the HBI method is recommended for radicals with electron delocalization, whereas the group additivity method is more accurate for all other radicals.

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List of Symbols

	Symbols
$[i]$	Column vector describing occurrence of group i in a set of molecules
BDE(C−H)	C−H bond dissociation enthalpy (J mol^{-1})
$\Delta_a H^0$	standard atomization enthalpy (J mol^{-1})
$\Delta_f H^0$	standard enthalpy of formation (J mol^{-1})
$\Delta_r H$	standard reaction enthalpy (J mol^{-1})
F	significance
$\overline{\mathrm{GAV}}$	estimation vector of group additive values (J mol^{-1})
$\hat{g}$	estimated vector of group additive values (J mol^{-1})
$\mathbf{y}$	vector of dependent variables (AI enthalpies) (J mol^{-1})
n	number of data points
p	number of parameters
$\mathbf{X}$	matrix of dependent variables
	Acronyms
AI	ab initio
C_a	allenic carbon atom ═C═
C_b	benzene carbon atom, monovalent
C_d	double bonded carbon atom, divalent
C_t	triple bonded carbon atom, monovalent
cyc-i-j	ring strain contribution, i ring atoms and j double bonds (J mol^{-1})

cyc-*i*-*j*trig	ring strain contribution, *i* ring atoms and *j* trigonal atoms (J mol^{-1})
exp	experimental
GAV	group additive value (J mol^{-1})
HBI	hydrogen bond increment (J mol^{-1})
MAD	mean absolute deviation (J mol^{-1})
NNI	non-next-nearest neighbor interaction
P	primary carbon atom
Q	quaternary carbon atom
ref	reference
RMS	root mean square deviation (J mol^{-1})
RSC	ring strain correction (J mol^{-1})
S	secondary carbon atom
T	tertiary carbon atom
trig	trigonal carbon atom

Supporting Information Available: Database with CBS-QB3, CBS-QB3-BAC and GA enthalpies of formation for 233 species, Table 1S. A comparison between alkane GAVs, obtained with the different estimation procedures described in section 3.2, Table 2S. A correlation matrix for the estimation of alkane GAVs en NNI corrections, Table 3S. A comparison between optimized radical-adjacent group additive values and the corresponding non-radical GAVs, Table 4S. Deviations of the calculated standard enthalpy of formation of hydrocarbon radicals with experiment, Table 5S. This material is available free of charge via the Internet at http://pubs.acs.org.

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