

## Accurate and Efficient Method for Predicting Thermochemistry of Polycyclic Aromatic Hydrocarbons – Bond-Centered Group Additivity

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**Abstract:** A self-consistent estimation method for the thermochemical properties of polycyclic aromatic hydrocarbons (PAH) is presented. This method is based on enthalpies of formation ( $\Delta H_f^\circ$ ), entropies ( $S_{298}^\circ$ ), and heat capacities ( $C_p^\circ$ ) obtained from B3LYP/6-31G(d) calculations of the total energies and frequencies for 139 PAHs, including  $C_{60}$  and  $C_{70}$  fullerenes. The enthalpies of formation were calculated using an optimized set of homodesmotic reactions given the available experimental  $\Delta H_f^\circ$  of PAHs. The theoretical entropies were compared with the existing experimental entropies, and some inconsistencies in the experimental data were identified. The estimation method presented here is a systematic extension of the widely employed atom-centered group additivity method originally proposed by Benson. This new method is based on bond-centered groups that define bonds linking two atom-centered groups and specify the size of the rings to which they belong. In addition, a term to describe the resonance energy is included. The thermochemical properties of PAHs up to  $C_{70}$  fullerene are estimated with a mean average deviation of 2.8 kcal mol<sup>-1</sup> in  $\Delta H_f^\circ$ , 0.7 cal K<sup>-1</sup> mol<sup>-1</sup> in  $S_{298}^\circ$ , and about 0.5 cal K<sup>-1</sup> mol<sup>-1</sup> in the  $C_p^\circ$ . This bond-centered group additivity method for the thermochemical properties of PAHs significantly expands both the range of systems that can be estimated and the accuracy of the estimations. The results of this work also allow us to assess the quality of available experimental data. For example, there are strong indications that the literature  $\Delta H_f^\circ$  of benzo[*k*]fluoranthene is about 10 kcal mol<sup>-1</sup> too low.

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have attracted considerable attention in the past few decades. They are formed during the incomplete combustion of hydrocarbon fuels and are precursors of soot. Some PAHs are known carcinogens, and control of their emissions is an important issue. PAH molecules are found in many materials, including coal, fuel oils, lubricants, and carbon black. They are also implicated in the formation of fullerenes,<sup>1</sup> one of the most chemically versatile class of molecules known. Clearly, predictive capability for the formation and growth of PAHs is highly desirable, in order either to minimize their formation or to steer PAH chemistry toward the generation of fullerenes and other desirable carbon nanostructures. The attainment of such a predictive capability involves many aspects, including the enumeration of the important reactions and species in the reaction mechanism, solution of the model's differential equations, and the comparison of the model with experiments.

Thermochemical properties of the species in the model are often the most important parameter, particularly for high-temperature processes such as PAH formation. Thermodynamic consistency requires that reverse rate constants be calculated from the forward rate constants and from the equilibrium

constants. The latter are obtained from the thermochemical properties of reactants and products. Consequently, low-temperature model predictions depend heavily on barrier heights and enthalpy changes of the reactions, while the model predictions at high temperature rely sensitively on entropy change (as  $\Delta S$  is multiplied by  $T$ ). Conventional methods for estimating thermochemical properties<sup>2</sup> rely heavily on experimental data, but very few such data are available. The predictive ability of current kinetic models is significantly limited by the scarcity of thermochemical data.

Recently, automatic reaction mechanism generation software packages have been developed that accomplish the monumental task of enumerating important reactions involved in combustion.<sup>3</sup> However, the applicability and reliability of such automated mechanism generators still rely on the accuracy of the numerical values employed for thermochemical and kinetic data. Moreover, the increase in computing power will allow these automatically generated mechanisms to encompass a previously unimagined number of different molecules, as long as their thermochemical properties and the kinetic rate constants related to their formation and consumption can be accurately estimated. The ability to accurately and consistently estimate thermochemical values for any PAH is an essential step toward building accurate combustion chemistry models that will allow the

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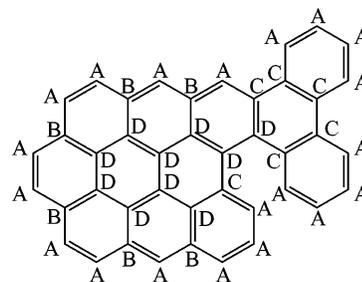
(3) Song, J. *Building Robust Chemical Reaction Mechanisms: Next Generation of Automatic Model Construction Software*, Ph.D. Thesis, MIT, 2004.

prediction of soot and/or fullerene formation using various fuels and various reactor designs.

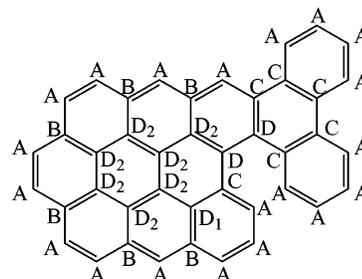
Unfortunately experimental thermochemical data is only available for 16 of the hundreds of Isolated Pentagon Rule (IPR) PAHs with 24 or fewer carbon atoms. No experimental data is available for any larger PAH species (except for the  $C_{60}$  and  $C_{70}$  fullerenes). In the past decade quantum chemical methods were made robust enough to provide accurate thermochemical data for polyatomic molecules. As a result, quantum chemical methods have been used to fill the void for species that are experimentally difficult to synthesize or hard to detect. However, PAHs are in general too large for accurate, but computationally intensive, quantum calculations such as the Gn or CBS-n methods. Lower level quantum chemical calculations for PAHs have been performed by various groups. In the beginning of the '90s Schulman et al. did SCF calculations with various basis sets for many PAHs up to circumcoronene ( $C_{54}H_{18}$ ) to obtain their heats of formation.<sup>4–6</sup> More recently density functional theory (DFT) calculations, mostly at the B3LYP/6-31G(d) level of theory, have been used for the calculation of  $\Delta H_f^\circ$  of PAHs<sup>7,8</sup> and fullerenes<sup>9</sup> as well as  $S_{298}^\circ$  and  $C_p^\circ$  of PAHs.<sup>10</sup> However, many issues remain to be resolved: no general method for the determination of accurate  $\Delta H_f^\circ$  of PAHs from the total energies obtained from density functional calculations has been proposed, and computed low vibrational frequencies are thought to have considerable uncertainties, affecting the calculation of the entropy. More importantly, it is not feasible to do even DFT calculations for the myriad of possible PAH isomers. Thus a rapid, self-consistent and accurate estimation method for their thermochemical properties is needed.

In this paper we present and discuss the results obtained from DFT calculations at the B3LYP/6-31G(d) level as well as the development of our novel estimation method and its results. We start by surveying existing estimation methods for the thermochemical properties of PAHs. In section 3 we present a critical assessment of the available experimental data, against which the quality of any estimation method should be evaluated. The computational methodology employed to arrive at the ab initio thermochemical data needed for the estimation method is described in section 4. This section also compares the  $\Delta H_f^\circ$  calculated through atomization reactions and through isodesmic and homodesmic reactions proposed in this work. The choice of one particular set of homodesmic reactions is discussed. Finally, in section 5 we present the development of our new estimation method and a critical evaluation of its performance with respect to the original ab initio results. We also compare our estimation method with existing methods in the literature with respect to the accuracy and applicability of each of the methods.

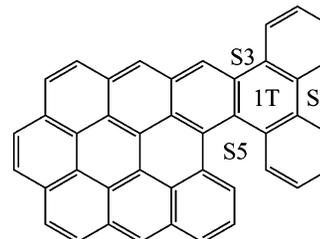
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(a) Groups defined by Stein et al.<sup>11,12</sup>



(b) Groups defined by Moiseeva and Dorofeeva<sup>15</sup>



(c) Bond additivity method for benzenoid PAHs from Herndon et al.<sup>17</sup>

**Figure 1.** Existing additivity methods for benzenoid PAHs.

## 2. Existing Estimation Methods

The most widely used estimation method for the thermochemical properties of PAHs is the one proposed by Stein et al.,<sup>11,12</sup> who extended Benson's group additivity method.<sup>2,13,14</sup> In this method, the  $[C_B-(H)]$  group defined previously by Benson was retained and three new groups were introduced to describe carbons that belong to two or three aromatic rings:  $[C_{BF}-(C_B)_2(C_{BF})]$ ,  $[C_{BF}-(C_B)(C_{BF})_2]$  and  $[C_{BF}-(C_{BF})_3]$ . These groups are illustrated in Figure 1a, where an abbreviated notation is used, in which the groups are named A, B, C, and D, respectively. The  $\Delta H_f^\circ$ ,  $S_{298}^\circ$ , and  $C_p^\circ$  values for the A group had been derived from the corresponding experimental values of benzene. The  $\Delta H_f^\circ$  values for groups B and C were derived from experimental values of other benzenoid PAHs available at that time. The  $S_{298}^\circ$  and  $C_p^\circ$  contributions of groups B and C were assumed to be equivalent. Values for the entropy of these groups were derived from entropies calculated using the third-law method from experimental values of naphthalene, phenanthrene, anthracene, and pyrene. The heat capacities for these groups were obtained from the experimental heat capacities of naphthalene. The  $\Delta H_f^\circ$  and  $S_{298}^\circ$  values for group D were

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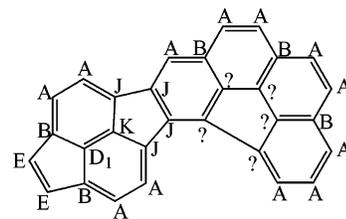
derived from graphite, although the interlayer interactions which are so important in graphite are absent in gas-phase PAHs.

Moiseeva and Dorofeeva<sup>15</sup> noted that entropy values estimated using the group values from Stein et al. and values calculated from vibrational assignment differed by  $2.6 \text{ cal K}^{-1} \text{ mol}^{-1}$  on average for PAHs with more than two D groups. Based on this finding, they proposed dividing the D group from the estimation method of Stein et al. into  $D_1$  and  $D_2$  groups. The  $D_1$  and  $D_2$  groups are defined by Moiseeva et al. as carbon atoms common to three aromatic rings. The  $D_1$  group is attached to two or three B or C groups, whereas the  $D_2$  group is attached to at most one B or C group (see Figure 1b). Moiseeva et al. do not mention the D groups from Stein et al. that belong to only two rings. In Figure 1b these ambiguous and undefined groups are denoted simply as D. The group contributions to  $\Delta H_f^\circ$  were derived based on the experimental enthalpies of formation available in the compilation by Pedley et al.,<sup>16</sup> except for naphthalene, triphenylene, and benzo[*c*]phenanthrene, because the discrepancies between the experimental values and the  $\Delta H_f^\circ$  predicted by the additivity scheme were much larger than the experimental uncertainties. The  $S_{298}^\circ$  and  $C_p^\circ$  contributions for each of the new groups were obtained from statistical mechanics, using the vibrational frequencies calculated from a simple approximate force field.

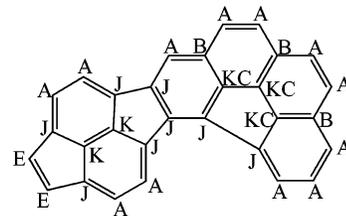
Herndon et al. proposed a bond-additivity method to estimate the heat of formation of benzenoid PAHs,<sup>17</sup> where the parameters are the number of C–H and C–C bonds and the number of bay regions with 3 (S3) or 4 rings (S4). They showed this method to be equivalent to the group additivity method proposed by Stein et al. if the D group is differentiated when it belongs to three ( $D_{\text{int}}$ ) or to two rings ( $D_{\text{per}}$ ). Recognizing that nonplanarity effects increase with the number of rings in the same bay region, they also introduced the groups S5 and S6, for bay regions with 5 and 6 rings, respectively (see Figure 1c for an example of the S5 group). Herndon et al. introduced two additional parameters: T, which accounts for pairs of S3 structures that share a common central ring, and the natural logarithm of the Kekulé structure count  $\ln(K)$  to quantify the resonance energy. Herndon et al.'s estimation method was parametrized against the  $\Delta H_f^\circ$  of 153 benzenoid PAHs calculated from molecular mechanics. The proposed method matches the  $\Delta H_f^\circ$  calculated from molecular mechanics very well, and the  $\ln(K)$  term greatly improves its accuracy. Of course, the accuracy of the molecular mechanics calculation on which these parameters are based is not known; it was probably parametrized to data from a few small PAHs.

All the methods mentioned so far apply only to benzenoid PAHs. However, most of the PAHs, including those involved in the formation of fullerenes, have both five- and six-membered rings. When five-membered rings are taken into account, the complexity of the problem increases considerably. Since five-membered rings introduce strain and curvature to the molecule, the groups in five-membered rings have to be treated differently than those in six-membered rings.

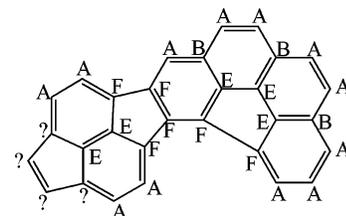
Stein et al. tackled this problem by considering each ring as a group.<sup>18,12</sup> They proposed ring-group values for the benzene



(a) Groups defined by Moiseeva and Dorofeeva<sup>19</sup>



(b) Groups defined by Pope and Howard<sup>20</sup>



(c) Groups defined by Armitage and Bird<sup>21</sup>

**Figure 2.** Existing additivity methods for PAHs containing both five- and six-membered rings.

ring and for the cyclopentadiene ring in structures such as indene and acenaphthalene. They acknowledged that this method is not very accurate but said that the estimations should be suitable for rough equilibrium calculations and suggested that this method could serve as a foundation on which to build more accurate estimation methods as more and more data become available.

The ring-additivity method proposed by Stein et al. has not been pursued further. Instead, researchers have turned to developing specialized groups for carbon atoms that belong to five-membered rings. Moiseeva and Dorofeeva<sup>19</sup> extended their group additivity method for benzenoid PAHs<sup>15</sup> by introducing three new groups for the carbons in five-membered rings of unsaturated PAHs, as shown in Figure 2a. The E group is a  $[C_B-(H)]$  group on a five-membered ring. Analogously, the J group is similar to the six-membered ring C group, and K is similar to the D group as defined by Stein et al. The contribution of the E group to  $\Delta H_f^\circ$  was derived from the experimental values of acenaphthalene, by considering that the five-membered ring is joined to the naphthalene by two B and one  $D_1$  groups, as shown in Figure 2a. The contribution of the J group to  $\Delta H_f^\circ$  was assumed to be the same as the C group, and the value of the enthalpy of formation of the K group was obtained from fluoranthene. The contributions from these groups to  $S_{298}^\circ$  and  $C_p^\circ$  were obtained from molecules with the acenaphthalene and fluoranthene fragments whose thermodynamic properties were calculated by statistical mechanics. Since the J and K group values were derived solely based on fluoranthene fragments, which are all planar, they cannot describe structures where the

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(19) Moiseeva, N. F.; Dorofeeva, O. V. *Thermochim. Acta* **1990**, *168*, 179–186.

five-membered ring is surrounded by three or more consecutive benzene rings, as shown in Figure 2a.

Pope and Howard<sup>20</sup> noting that the method from Moiseeva and Dorofeeva<sup>19</sup> does not capture the curvature introduced by five-membered rings included one more term, which they called KC, that should account for all the curvature. They systematically listed the groups that can be formed with the C<sub>B</sub> atom in a six-membered ring, C<sub>B</sub> atom in a five-membered ring, C<sub>BF</sub> atom that belongs only to six-membered rings, C<sub>BF</sub> atom that belongs to one six-membered and one five-membered ring, and C<sub>BF</sub> atom that belongs to two six-membered and one five-membered ring. Due to the lack of experimental values of the thermochemical properties of the PAHs, they lumped all the possible groups into eight groups (see Figure 2b): A, B, C, and D as defined by Stein et al.,<sup>11</sup> E as defined by Moiseeva and Dorofeeva,<sup>19</sup> J as all the carbon atoms that belong to one five-membered ring and one six-membered ring, K as all the carbon atoms that belong to two six-membered rings and one five-membered ring and that are bonded to two J groups (this group should not introduce curvature in the PAH), and KC as all the other carbon atoms at the junction of two six-membered rings and one five-membered ring. Notice the difference in the definition of the J and the K groups between Moiseeva and Dorofeeva<sup>19</sup> and Pope and Howard.<sup>20</sup> The group values for benzenoid PAHs (groups A, B, C, and D) were taken from Stein et al.<sup>11,12</sup> The values for the groups E, J, and K that Moiseeva derived<sup>19</sup> are used, despite the different definition of the J and K groups. The contribution of the KC value to the  $\Delta H_f^\circ$  was derived from the experimental value of C<sub>60</sub>, and the S<sub>298</sub><sup>o</sup> and C<sub>p</sub><sup>o</sup> group values for KC were derived from statistical mechanics calculations of C<sub>60</sub>. Pope and Howard acknowledge that their method still suffers limitations when capturing H–H repulsion or any curvature effects different than the one present in C<sub>60</sub> fullerenes.

Armitage and Bird derived the value for the [C<sub>BF</sub>–(C<sub>BF</sub>)<sub>3</sub>] group that belongs to one five-membered ring in a different way.<sup>21</sup> They named the group that connects the naphthalene fragment to the benzene fragment in fluoranthene as F (see Figure 2c). Instead of considering its contribution to the  $\Delta H_f^\circ$  to be equivalent to a C group, as done by Moiseeva<sup>19</sup> with their J group, they assumed the contribution of this group to the  $\Delta H_f^\circ$  to be equivalent to the contribution of the C<sub>B</sub>–C<sub>B</sub> group in biphenyl. This assumption is based on the fact that the F–F bond length is close to the bond length of a single bond. The group E, defined as a group that belongs to two six-membered and one five-membered rings, was derived from the experimental  $\Delta H_f^\circ$  of fluoranthene. The resulting method gives good estimates for the  $\Delta H_f^\circ$  of corannulene and C<sub>70</sub> fullerene.

Each of the methods described in this section aimed to solve one specific weakness of the original method proposed by Stein et al.,<sup>11</sup> such as strain caused by nonplanarity arising from steric interactions<sup>17</sup> and strain caused by planar five-membered ring systems.<sup>19</sup> The development of these methods highlighted the difficulties in establishing a comprehensive estimation method for the thermochemical properties of PAHs. First of all, it is evident from the previous works that the thermochemistry of PAH is heavily dependent on its topology. However, the existing definitions of groups in PAHs with five- and six-membered rings

are confusing. Since each of the previous methods dealt only with specific topological characteristics of these PAHs, it is sometimes not clear how wide the definition of a group really is. Another serious difficulty is the insufficient number of experimental values of the thermochemical properties of PAHs. This scarcity hinders the identification of structures that affect the  $\Delta H_f^\circ$ , S<sub>298</sub><sup>o</sup>, and C<sub>p</sub><sup>o</sup> of PAHs. Even when these structures are identified, it is difficult to assess the quality of the estimation method, because there are no values to compare the predictions with. Finally, it has been shown that resonance energy plays an important role in determining the  $\Delta H_f^\circ$  of PAHs. The inclusion of a term to capture resonance energy improved the performance of the method proposed by Herndon et al. considerably.<sup>17</sup> From these considerations it is concluded that an estimation method for PAHs with five- and six-membered rings can be developed based on the topology of these molecules. The definition of groups in this method should be unambiguous and comprehensive. The method should be based on sound values of the thermochemical properties, and finally, it should be able to capture the effects of resonance energy in PAHs with both five- and six-membered rings.

### 3. Experimental Thermochemical Properties

The quality of an estimation method can be assessed only by comparison of its prediction with measured data. Undoubtedly experimental values are the “gold standard”. Unfortunately, there are not many of them available, and in many cases it is not even clear how reliable an experimental value is. This section is a critical survey of the experimental enthalpies and entropies of formation of PAH that can be found in the literature.

**3.1. Experimental Enthalpy of Formation Values.** Gas-phase  $\Delta H_f^\circ$ s of PAHs are usually obtained by adding the heat of formation of the solid state,  $\Delta H_{f(\text{cr})}^\circ$ , and the heat of sublimation,  $\Delta H_{\text{subl}}^\circ$ . For benzene, which is liquid at ambient temperature, the heat of formation of the liquid,  $\Delta H_{f(\text{liq})}^\circ$ , and the heat of vaporization,  $\Delta H_{\text{vap}}^\circ$ , are used. From the heat released by the combustion of the solid PAH, the  $\Delta H_{f(\text{cr})}^\circ$  is calculated, taking into account reduction to the standard state. Usually complete combustion to CO<sub>2</sub> and H<sub>2</sub>O is verified by visual inspection (no formation of soot) or by measurement of the CO<sub>2</sub> formed. Some authors base the results of their combustion experiments on the amount of CO<sub>2</sub> recovered, to minimize the errors arising due to incomplete combustion and impurities in the sample.<sup>22</sup> When soot is formed, its massic energy of combustion also has to be taken into account, as done by Nagano for the combustion of naphthacene.<sup>23</sup>

Enthalpies of sublimation are usually determined either calorimetrically or by vapor-pressure measurements. Since PAHs have very low volatility, torsion-effusion and the Knudsen-effusion methods are most frequently used for their vapor-pressure measurements. When effusion methods are used, the  $\Delta H_{\text{subl}}^\circ$  is calculated from the Clayperon equation:

$$\Delta H_{\text{subl},T_1}^\circ = T_1 \left( \frac{dp}{dT} \right) [V_g - V_{\text{cr}}] \quad (1)$$

Usually the gas phase is considered to be ideal, and V<sub>cr</sub> is assumed to be negligible in comparison to V<sub>g</sub>, in which case eq

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**Table 1.** Group Values for the Estimation of  $C_{p,(cr)}^{est}$  (298.15 K)

Benson's notation	$\text{J K}^{-1} \text{mol}^{-1}$
$C_B-(H)$	17.5
$C_{BF}-(C_B)_2(C_{BF})$ or $C_{BF}-(C_B)(C_{BF})_2$	8.5
$C_{BF}-(C_{BF})_3$	9.1

1 becomes

$$\Delta H_{\text{subl},T_1}^{\circ} = -R \left( \frac{d \ln p}{d(1/T)} \right) \quad (2)$$

When the empirical relation

$$\log p = A - B/T \quad (3)$$

is fitted to the vapor pressure data, the  $\Delta H_{\text{subl}}^{\circ}$  is given by

$$\Delta H_{\text{subl}}^{\circ} = 2.303 \times R \times B \quad (4)$$

where  $R$  is the gas constant. Due to the low volatility of PAH, vapor pressure measurements are usually done at higher temperatures and should be corrected to 298.15 K.

Kirchhoff's equation is used to adjust the heat of sublimation to the desired temperature:

$$\Delta H_{\text{subl}}^{\circ}(298.15 \text{ K}) = \Delta H_{\text{subl}}^{\circ}(T_m) + \int_{298.15}^{T_m} (C_{p,(cr)} - C_{p,(g)}) dT \quad (5)$$

$$\approx \Delta H_{\text{subl}}^{\circ}(T_m) + (C_{p,(cr)} - C_{p,(g)})(T_m - 298.15) \quad (6)$$

Since heat capacities are not always available, many methods have been proposed to account for the second term in eq 6. Some authors adjusted their experimental heat of sublimation and report the value at 298.15 K. When the original authors have not applied any temperature correction to their experimental work, we adjusted the literature enthalpies of sublimation to 298.15 K using the equation proposed by Chickos et al.:<sup>24</sup>

$$(C_{p,(cr)} - C_{p,(g)}) = [0.75(\text{J K}^{-1} \text{mol}^{-1}) + 0.15C_{p,(cr)}^{est}(298.15)] \quad (7)$$

where  $T_m$  is the middle of the temperature interval where the vapor pressure measurements were carried out. The  $\Delta H_{\text{subl}}^{\circ}$  from Wakayama and Inokuchi<sup>25</sup> were corrected using the average temperatures cited by Chickos and Acree.<sup>26</sup> The  $C_{p,(cr)}^{est}$  are evaluated by group additivity. For the PAHs in this study, the group values recommended by Chickos et al.<sup>27,26</sup> are used (Table 1). Equation 7 has been applied successfully to temperatures up to 500 K.<sup>28</sup> The temperature correction to  $\Delta H_{\text{subl}}^{\circ}$  is of the order of 1 kcal mol<sup>-1</sup>, except for  $C_{60}$  and  $C_{70}$ . For these large molecules,  $T_m$  is very high (above 800 K), and the assumption of constant heat capacity is not adequate. However, for the smaller PAHs, since temperature correction of the  $\Delta H_{\text{subl}}^{\circ}$  is comparable to the experimental error, some

authors, especially from earlier works (e.g., Boyd et al.<sup>29</sup>), considered the heat of sublimation to be constant with temperature, introducing small systematic errors to the enthalpies of sublimation.

The compilation of experimental  $\Delta H_{f,(cr)}^{\circ}$ ,  $\Delta H_{\text{subl}}^{\circ}$ , and  $\Delta H_{f,(g)}^{\circ}$  can be found in Table S1 of the Supporting Information. This compilation is not meant to be complete. Rather, this table offers a list of the values that have been most widely cited and should give a good idea of the dispersion among the data. Cox and Pilcher in 1970 published a very careful compilation of  $\Delta H_{f,(cr)}^{\circ}$  and of  $\Delta H_{\text{subl}}^{\circ}$  of organic and organometallic compounds available at that time.<sup>30</sup> When more than one value was available, they made a selection of the "best" value based on the experimental quality of the reported work. Pedley et al. made a later compilation in 1986, following mainly the recommendations made by Cox and Pilcher and adding some new values.<sup>16</sup> The most recent review of the thermochemistry of PAHs was done by Slayden and Liebman.<sup>31</sup> The values from Cox and Pilcher and from Pedley et al. are now widely cited and, in general, accepted. It is appropriate to mention that both references did not apply temperature corrections to the values they compiled. Thus, in some cases, they recommend enthalpies of formation at 298.15 K based on enthalpies of sublimation measured at higher temperature ranges. More recently Chickos and Acree collected most of the published enthalpies of sublimation in an extensive review of the literature from 1910 to 2001.<sup>26</sup>

For many of the PAHs, only one value of  $\Delta H_{f,(cr)}^{\circ}$  or of  $\Delta H_{\text{subl}}^{\circ}$  has been reported, making it difficult to assess the reliability of the experimental value. When more than one value is available in the literature, it is not uncommon that the values reported by different authors differ by a couple of kcal mol<sup>-1</sup>. We do not report here the uncertainties associated with each individual value because often those uncertainties refer to a particular experimental setup. Rather, we assign levels of confidence to each of the  $\Delta H_f^{\circ}$ s that we adopted. Grade "A" refers to values that are well-known and widely used. Their uncertainty should be less than 0.5 kcal mol<sup>-1</sup>. Grade "B" was assigned to values for which many independent experiments have been performed, giving results which are close to each other. The uncertainties for these  $\Delta H_f^{\circ}$ s should be within 2.0 kcal mol<sup>-1</sup>. Grade "C" was given to values that are based on a single measurement or when the measured values (of the  $\Delta H_{f,(cr)}^{\circ}$  or of the  $\Delta H_{\text{subl}}^{\circ}$ ) have a large spread. The uncertainties associated with these values might be as large as 5.0 kcal mol<sup>-1</sup>. Finally grade "D" was assigned to a  $\Delta H_f^{\circ}$  that is suspected to be in error and to the  $\Delta H_f^{\circ}$  of  $C_{60}$  and  $C_{70}$  fullerenes. The experimental  $\Delta H_f^{\circ}$ s for these molecules have uncertainties of 10 kcal mol<sup>-1</sup> or more.

The most widely cited value for the  $\Delta H_f^{\circ}$  of benzene (19.8 kcal mol<sup>-1</sup>) was reported by Prosen et al.<sup>32</sup> Herndon et al.<sup>7</sup> suggest a value that is 0.2 kcal mol<sup>-1</sup> higher, based on an unpublished heat of vaporization value. We chose to use the most widely accepted value. In the case of naphthalene, although Cox and Pilcher<sup>30</sup> cite many  $\Delta H_{f,(cr)}^{\circ}$ 's, ranging from 15.5 to

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19.6 kcal mol<sup>-1</sup>, the value that they recommend (18.6 kcal mol<sup>-1</sup>) is widely used without much controversy. Naphthalene has been classified as a primary reference material for calorimetry and differential thermal analysis with a recommended  $\Delta H_{\text{subl}}^{\circ}$  of 17.35 kcal mol<sup>-1</sup>.<sup>33</sup>

The value of  $\Delta H_f^{\circ}$  of phenanthrene from Nagano<sup>23</sup> was chosen over the value suggested by Pedley et al.<sup>16</sup> While studying the equilibrium of a system with phenanthrene, hydrogen and 9,10-dihydrophenanthrene, Steele et al. noted that the enthalpy of formation of phenanthrene failed to predict the correct equilibrium constant.<sup>34</sup> They then measured the combustion energy of phenanthrene obtaining a value about 1.5 kcal mol<sup>-1</sup> lower than the one suggested by Pedley et al.. This new value predicts a more accurate equilibrium constant for the aforementioned system. More recently Nagano also measured the  $\Delta H_f^{\circ}$  of solid phenanthrene,<sup>23</sup> obtaining a value in accordance with the value obtained by Steele et al..<sup>34</sup> Phenanthrene is evaluated as a tertiary reference material, with a recommended  $\Delta H_{\text{subl}}^{\circ}$  of 21.82 kcal mol<sup>-1</sup>.<sup>33</sup>

The large spread on the earlier heat of sublimation of anthracene has been attributed to the difficulty of ensuring a high level of purity of this substance. Nevertheless, anthracene is evaluated as a primary reference material for calorimetry and differential thermal analysis, with a recommended  $\Delta H_{\text{subl}}^{\circ}$  of 24.7 kcal mol<sup>-1</sup>.<sup>33</sup>

For the larger PAH, the data becomes more scarce, and the dispersions among them are also large. We have as a rule adopted the most recently recommended value. It is worthwhile to mention the debate over the  $\Delta H_f^{\circ}$  of naphthacene. Many authors, comparing the experimental enthalpy of formation of this PAH accepted at the time with values predicted by semiempirical<sup>35</sup> and quantum chemical calculations<sup>7,36</sup> have noticed that the experimental  $\Delta H_f^{\circ}$  of naphthacene was about 10 kcal mol<sup>-1</sup> too low. Recently Nagano measured again the energy of combustion for this PAH obtaining a value about 10 kcal mol<sup>-1</sup> higher than the previously accepted value.<sup>23</sup> Nagano conjectured that the sample for the measurement by Magnus et al.<sup>37</sup> might have been oxidized before the calorimetric measurements. This finding shows that theoretical predictions are now very powerful and can aid experimentalists to determine the quality of a calorimetric measurement.

Experimental values for C<sub>60</sub> and C<sub>70</sub> fullerenes are very abundant due to the interest that these molecules have generated. However, large dispersions among the experimental values are found. The presence of impurities, such as solvents and adsorbed gases, and the use of small samples are commonly cited as the main cause for the discrepancy between the experimental  $\Delta H_{f(\text{cr})}^{\circ}$  values.<sup>39,40</sup> Comparison of results from different groups has led to the conclusion that the history of the samples affect the calorimetric experiments considerably;<sup>39</sup> however, no

standard procedure for the preparation and handling of fullerene samples for thermochemical measurement exists yet. For large molecules such as the fullerenes, the correction of the enthalpy of sublimation from the temperature at which the vapor pressure was measured to 298.15 K is significant.  $\Delta H_{\text{subl}}^{\circ}$  values extrapolated to 298.15 K by different authors using the same experimental vapor pressure measurements can vary by as much as 4 kcal mol<sup>-1</sup>.

In this work we do not consider PAHs with adjacent five-membered rings. To our knowledge, thermochemical data have been deduced for only one PAH with fused five-membered rings, pentalene. Its  $\Delta H_f^{\circ}$  has been estimated from the measured enthalpy of hydrogenation of 1,3,5-tri-*tert*-butylpentalene to be 78.9 kcal mol<sup>-1</sup>.<sup>31</sup>

**3.2. Experimental Entropy Values.** Unfortunately, PAH entropy and heat capacity data are even more rare in the literature than heats of formation. In principle, gas phase entropies can be calculated from the vibrational frequencies (usually of the solid phase) obtained spectroscopically. However, sufficiently reliable vibrational assignments are not available for PAHs, even for those with abundant spectroscopic data such as naphthalene, phenanthrene, and anthracene.<sup>41</sup> Gas-phase entropy can also be obtained by the third-law approach, adding the entropy of the crystal, the entropy of sublimation, and the decrease of entropy due to compression, as given by eq 8:

$$S_{(\text{g})}^{\circ} = S_{(\text{cr})} + \Delta S_{\text{subl}} + S_{\text{comp}} \quad (8)$$

$$= S_{(\text{cr})} + \frac{\Delta H_{\text{subl}}}{T} + R \ln\left(\frac{p}{p^{\circ}}\right) \quad (9)$$

The entropy of the crystal is obtained by measurement of  $C_p^{\circ}$  from 0 K to the temperature of interest. Heat capacity measurements are difficult at temperatures near 0 K, and often the Debye extrapolation for the  $C_p^{\circ}$  is used. In Table 2 we present experimental gas-phase entropies that are available in the literature as well as entropies that we calculated from published experimental data. If equations of the form of eq 3 are used to relate the dependence of the vapor pressure to the temperature, then eq 9 is simplified to

$$S_{(\text{g})}^{\circ} = S_{(\text{cr})} + 2.303 \times R \times A \quad (10)$$

The parameters “A” available in the literature were used in conjunction with experimental  $S_{(\text{cr})}$  to calculate  $S_{(\text{g})}^{\circ}$ . The entropy of the crystal was taken at the average temperature ( $T_m$ ) at which the parameter “A” was obtained, and thus the  $S_{(\text{g})}^{\circ}$  obtained is at  $T_m$ . It was corrected back to 298.15 K by using gas-phase heat capacities obtained from quantum chemical calculations (B3LYP/6-31G(d)). These  $C_p^{\circ}$  are expected to be much more accurate than the entropies because entropies are quite sensitive to uncertainties in low-frequency modes. Gas-imperfection corrections have been assumed negligible for the vapor–solid equilibrium, since the vapor pressure is low. Entropies calculated in this manner are shown in *italics*. Some of the entropies obtained from vibrational assignments are also listed in Table 2. We note that there is a very wide spread in the entropy values for some of the PAHs. This spread is due to differences in the values of vapor pressure over a solid PAH

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**Table 2.** Experimental and Computed (B3LYP/6-31G(d)) Entropies of PAH at 298.15 K<sup>a</sup>

substance	$S_{(cr)}^{\circ}$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	$S_{(g)}^{\circ}$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	ref	$S_{B3LYP,(g)}^{\circ}$ (cal K <sup>-1</sup> mol <sup>-1</sup> )
benzene <sup>b</sup>	41.9		42	64.5 ± 0.2
	41.411	64.457	43	
naphthalene	39.9		42	80.1 ± 0.8
	40.01		44	
		80.22 <sup>c</sup>	45	
		79.67 <sup>d</sup>	46	
phenanthrene	50.6		47	95.2 ± 1.7
	51.40		48	
		93.52 <sup>d</sup>	49	
		97.2	50	
anthracene	49.6	111.6	51	93.6 ± 1.7
	49.51		47	
		93.95 <sup>d</sup>	52	
		89.9	49	
pyrene	53.75	88.1	50	96.0 ± 1.7
			51	
		94.03 <sup>c</sup>	53	
		96.3 <sup>c</sup>	54	
fluoranthene	55.11	100.9	55	
		100.5	50	
		88.6	51	
		88.1	29	
triphenylene	60.87		53	108.5 ± 3.7
		107.9	51	
naphthacene	51.48	97.1	25	
			56	107.0 ± 2.8
perylene		91.0	50	
		95.0	25	
	63.23	117.9	57	112.0 ± 6.0
		117.5	56	
coronene	67.13	115.7	50	
		116.0	51	
		115.3	57	112.6 ± 2.8
		109.0	25	
C <sub>60</sub>	102.1	162.0	58	128.8 ± 3.2
		127.6	59	
		133.8	60	
		133.8	61	
C <sub>70</sub>	108.2	144.6	58	147.8 ± 3.9
		171.4	60	
		171.4	62	
		143.8	61	

<sup>a</sup> The  $S_{(cr)}^{\circ}$  were determined by calorimetric measurements. The  $S_{(g)}^{\circ}$  in italics were calculated in this work from the vapor pressure measurements reported in the reference listed. <sup>b</sup> Values for benzene refer to the liquid, not to the solid crystal. <sup>c</sup> From vibrational assignment. <sup>d</sup> From vapor pressure measurements.

reported by different authors, leading to large differences in the “A” parameter. The last column in Table 2 was calculated from density functional theory (see section 4).

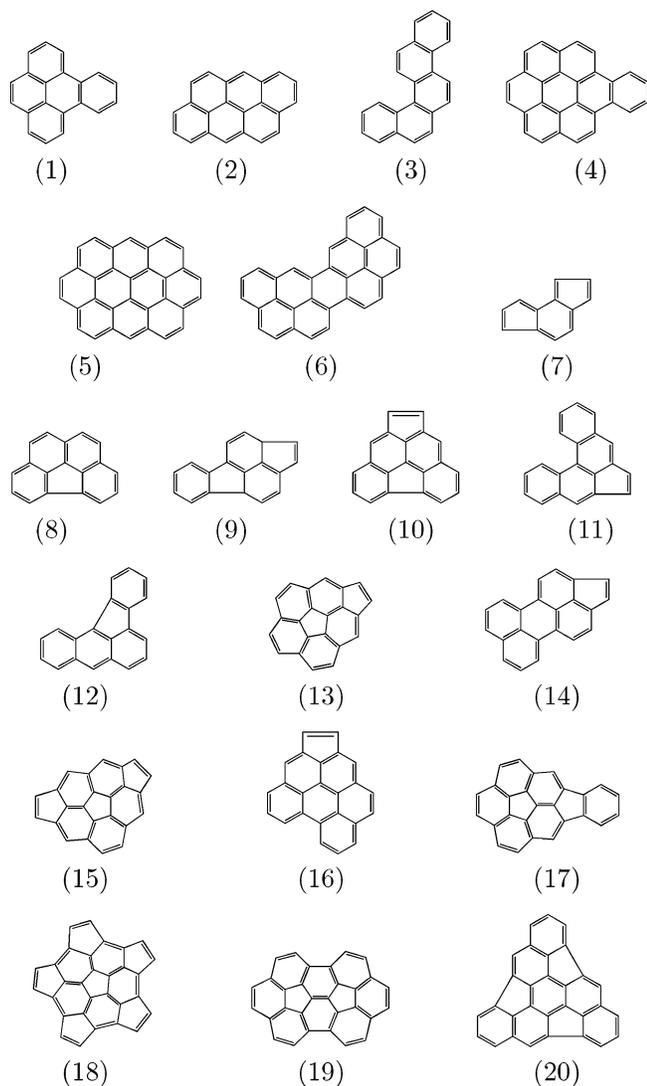
#### 4. Computational Methods

137 PAHs containing both five- and six-membered rings and the C<sub>60</sub> and C<sub>70</sub> fullerenes were considered for the present study. This set of molecules was chosen ensuring that a broad range of structural characteristics in PAHs was represented. 43 of the PAHs contain only six-membered rings, and the largest PAH studied contains 11 rings. All the PAHs considered in this study follow the Isolated Pentagon Rule (IPR); that is, none have fused five-membered rings. Figure 3 shows some typical PAHs included in this work. Quantum chemical calculations were carried out using the Gaussian 98 suite of programs.<sup>63</sup> The geometries were fully optimized at the B3LYP level using the

6-31G(d) basis set, and the stationary points were characterized by computing the second derivatives, namely the force constant matrix, at the same level. B3LYP/6-31G(d) provides accurate geometries, and it has been shown that larger basis sets do not improve the geometries.<sup>64</sup> For C<sub>60</sub> and C<sub>70</sub> fullerenes, the B3LYP/6-31G(d) geometries from Cioslowski<sup>9</sup> and the frequencies calculated at this same level by Schettino et al. were used.<sup>65,66</sup> A frequency scaling factor of 0.9613 has been employed for the calculation of the vibrational partition function, the zero-point energy, entropy, and heat capacities. The scaling factor used for the frequencies of C<sub>60</sub> and C<sub>70</sub> fullerenes was 0.98, as recommended by Schettino et al.<sup>65,66</sup> Uncertainties were assigned to the calculated entropies by assuming an uncertainty of ±20 cm<sup>-1</sup> in all the computed frequencies and making the worst case assumption that all the frequencies are either too high or too low. This assumption is a very conservative estimation of the error in the quantum calculations.

Atomization, isodesmic and homodesmic reactions were tested for the calculation of the  $\Delta H_f^{\circ}$  from the absolute energy. It is known in the literature that the use of such reaction schemes helps in the cancellation of systematic errors that arise in quantum chemical calculations due to the incomplete capture of the electron correlation energy.<sup>67,68</sup> Since the set of species that can be included in the isodesmic/homodesmic reactions

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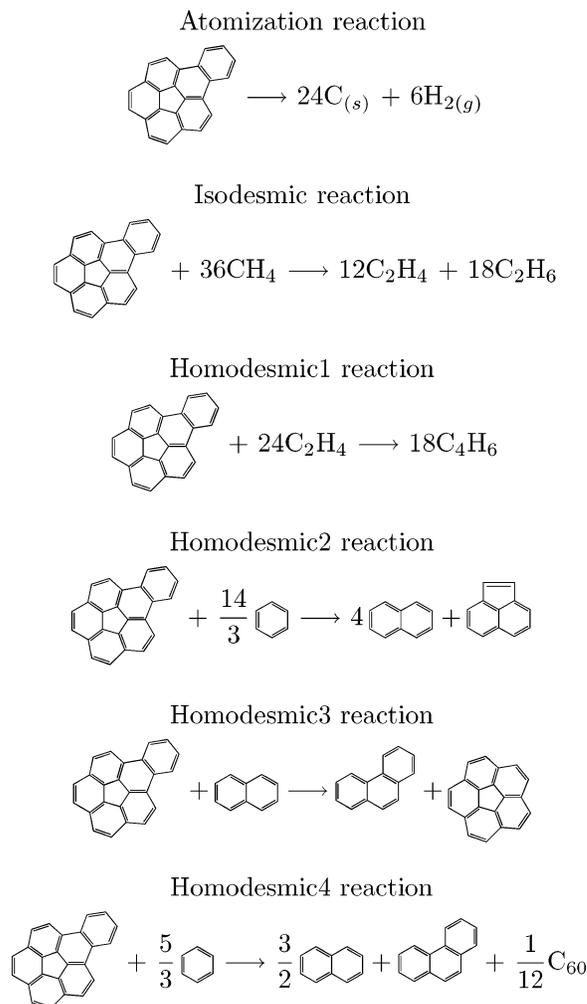


**Figure 3.** Some typical PAHs included in this work.

may vary, these reactions do not lead to unique values for the enthalpy of formation. Given that the aim of this work is to provide a *consistent* method for the estimation of thermochemical properties of PAHs, it is important to establish one standard reaction scheme, through which the  $\Delta H_f^\circ$  of all the PAHs should be calculated. We evaluate the quality of a reaction scheme by comparing its prediction of the  $\Delta H_f^\circ$  of a PAH with known experimental data.

In atomization reactions, the absolute energy of the PAH is compared to the absolute energy of carbon and hydrogen atoms, which have known  $\Delta H_f^\circ$ s. We included bond additivity corrections and spin-orbit corrections.<sup>67</sup> It is expected that if species that are more similar to the molecule whose  $\Delta H_f^\circ$  needs to be calculated were employed in the reaction scheme, a better cancellation of errors would occur. The reason is that the amount of electron correlation energy that is recovered in a quantum calculation should be similar for molecules with similar bonding characteristics.

Isodesmic reactions conserve the number of types of bonds and should thus be an improvement on a simple atomization reaction. In using isodesmic reactions, we treat the PAH as a nondelocalized molecule. Ethane accounts for the C–C single bonds, ethylene, for the double bonds, and methane, for the C–H bonds. Further enhancement in the calculation of  $\Delta H_f^\circ$  should be provided by homodesmic reactions, which, in addition to the types of bonds, also conserve the hybridization of the atoms in the bond (in PAHs all the carbons are  $sp^2$ ). The first set of homodesmic reactions studied (Homodesmic1)



**Figure 4.** Example of each of the reaction schemes tested for the calculation of the  $\Delta H_f^\circ$  from the absolute energy.

uses 1,3-butadiene to account for the single bonds and ethylene for the double bonds. The second set of homodesmic reactions (Homodesmic2) tries to capture the effect of electron delocalization and involves only aromatic molecules, using benzene to account for the carbon atoms that are bonded to a hydrogen, naphthalene to account for the carbons that belong to two or three aromatic rings, and acenaphthalene to account for the carbons that belong to five-membered rings. The third set of homodesmic reactions tested (Homodesmic3) employs phenanthrene and corannulene in addition to the molecules used in Homodesmic2. Phenanthrene accounts for rings that make up the bay region of a PAH, while corannulene accounts for the structure where a five-membered ring is completely surrounded by six-membered rings. Finally, the fourth homodesmic reaction scheme tested employs the same reference molecules as the Homodesmic3 scheme, but uses  $1/12\text{C}_{60}$  instead of corannulene to account for five-membered rings completely surrounded by six-membered rings. Figure 4 exemplifies the isodesmic and homodesmic reactions used.

The comparison between the  $\Delta H_f^\circ$  calculated from total energies by the various reaction schemes and the available experimental data is shown in Table 3, along with the mean average deviation (MAD) and root-mean-square error (RMS) for each reaction scheme. The MAD and RMS do not include the errors of benzo[*k*]fluoranthene.

The atomization reaction scheme provided enthalpies of formation that are remarkably close to the experimental values, except for the  $\text{C}_{60}$  and  $\text{C}_{70}$  fullerenes. We believe that this performance is fortuitous, since previous studies with other delocalized systems showed that atomization reactions do not perform reliably.<sup>69</sup> Among the other

**Table 3.** Comparison of the  $\Delta H_f^\circ$  Predicted by Each of the Reaction Schemes to the Experimental  $\Delta H_f^\circ$  for the 16 PAHs for Which These Values Are Available

	formula	$\Delta H_{f,\text{exp}}^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H_{f,\text{rnscheme}}^\circ - \Delta H_{f,\text{exp}}^\circ$ (kcal mol <sup>-1</sup> )					
			atom.	iso.	homo1	homo2	homo3	homo4
benzene	C <sub>6</sub> H <sub>6</sub>	19.8	1.1	-4.3	-2.0	0 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>
naphthalene	C <sub>10</sub> H <sub>8</sub>	36.0	-0.3	-7.6	-2.9	0 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>
phenanthrene	C <sub>14</sub> H <sub>10</sub>	48.1	2.3	-7.9	-0.8	3.0	0 <sup>a</sup>	0 <sup>a</sup>
anthracene	C <sub>14</sub> H <sub>10</sub>	55.2	-0.3	-10.1	-3.0	0.8	0.8	0.8
pyrene	C <sub>16</sub> H <sub>10</sub>	53.9	-0.4	-10.6	-1.9	2.1	2.1	2.1
triphenylene	C <sub>18</sub> H <sub>12</sub>	65.5	1.7	-11.1	-1.7	3.0	-0.1	-0.1
benzo[ <i>c</i> ]phenanthrene	C <sub>18</sub> H <sub>12</sub>	69.6	2.9	-9.9	0.5	4.3	-1.7	-1.7
benz[ <i>a</i> ]anthracene	C <sub>18</sub> H <sub>12</sub>	69.6	-0.7	-14.2	-4.7	0.0	-3.0	-3.0
chrysene	C <sub>18</sub> H <sub>12</sub>	63.0	3.4	-9.5	0.0	4.7	-1.2	-1.2
naphthacene	C <sub>18</sub> H <sub>12</sub>	79.3	-3.1	-15.9	-6.5	-1.8	-1.8	-1.8
perylene	C <sub>20</sub> H <sub>12</sub>	76.4	-0.5	-13.1	-2.0	2.9	-0.1	-0.1
coronene	C <sub>24</sub> H <sub>12</sub>	73.6	-3.4	-18.2	-4.0	1.4	1.4	1.4
acenaphthalene	C <sub>12</sub> H <sub>8</sub>	61.7	2.1	-6.0	0.3	0 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>
fluoranthene	C <sub>16</sub> H <sub>10</sub>	69.8	-0.6	-12.2	-3.6	-2.9	-2.9	-2.9
corannulene	C <sub>20</sub> H <sub>10</sub>	110.2	9.5	-2.8	9.0	10.2	0 <sup>a</sup>	7.3
benzo[ <i>k</i> ]fluoranthene	C <sub>20</sub> H <sub>12</sub>	(71.0)	(12.0)	(-1.5)	(9.6)	(11.1)	(11.1)	(11.1)
C <sub>60</sub>	C <sub>60</sub>	604.6	40.2	31.5	68.2	40.3	-87.8	0 <sup>a</sup>
C <sub>70</sub>	C <sub>70</sub>	658.5	31.3	21.3	64.0	37.5	-90.5	-2.7
Errors excluding the C <sub>60</sub> and C <sub>70</sub> fullerenes								
MAD <sup>b</sup>			2.1	10.2	2.8	2.4	0.9	1.4
RMS <sup>b</sup>			3.1	11.0	3.7	3.6	1.2	1.2
Errors including the C <sub>60</sub> and C <sub>70</sub> fullerenes								
MAD <sup>b</sup>			6.1	12.1	10.2	6.8	11.3	1.4
RMS <sup>b</sup>			12.7	13.8	22.9	13.7	30.6	2.2

<sup>a</sup> This PAH is a reference molecule for this homodesmic scheme. <sup>b</sup> Does not include errors for benzo[*k*]fluoranthene

reaction schemes, the performance generally improved as the similarity between the molecules involved in the reaction scheme and the PAH with unknown  $\Delta H_f^\circ$  increased. As expected, the  $\Delta H_f^\circ$  calculated through the homodesmic reaction scheme involving only aromatic molecules (Homodesmic2) provided a more extensive error cancellation compared to the isodesmic and the Homodesmic1 reaction scheme. However, Homodesmic2 was not able to capture the stabilization provided by bay areas. It systematically overpredicts the  $\Delta H_f^\circ$  for the benzenoid ring PAHs that contain bay area(s). Moreover, this scheme overpredicts the  $\Delta H_f^\circ$  of corannulene by 10 kcal mol<sup>-1</sup>.

Homodesmic3 and Homodesmic4 reaction schemes both correct for the systematic overprediction of the  $\Delta H_f^\circ$  of PAHs with bay areas by including phenanthrene as a reference molecule. They differ in their handling of structures in which a five-membered ring is completely surrounded by six-membered rings. The  $\Delta H_f^\circ$ s for both C<sub>60</sub> and C<sub>70</sub> predicted by Homodesmic3 are almost 100 kcal mol<sup>-1</sup> too low, indicating that the use of corannulene as a reference structure is not adequate. The use of C<sub>60</sub> rather than corannulene as a reference structure in Homodesmic4 leads to a  $\Delta H_f^\circ$  of C<sub>70</sub> that agrees very well with the experimental value. However, the  $\Delta H_f^\circ$  of corannulene is overpredicted by 7 kcal mol<sup>-1</sup>. We note that there is only one experimental value for the  $\Delta H_f^\circ$  of corannulene, and all the tested reaction schemes (with the exception of the isodesmic scheme) consistently lead to a  $\Delta H_f^\circ$  that is higher than this experimental value (by 7 to 10 kcal mol<sup>-1</sup>). Unfortunately there are no other  $\Delta H_{f,\text{exp}}^\circ$ 's for PAHs similar to corannulene for us to make a definitive judgment of whether the  $\Delta H_{f,\text{exp}}^\circ$  for the latter is in error or not. On the other hand, there are a couple of consistent experimental measurements of the  $\Delta H_f^\circ$  of C<sub>60</sub>. We chose to use the Homodesmic4 reaction scheme to consistently calculate the  $\Delta H_f^\circ$  of all the PAHs included in this study.

The reported experimental  $\Delta H_f^\circ$  of benzo[*k*]fluoranthene is 71.0 kcal mol<sup>-1</sup>.<sup>38</sup> However, all the reaction schemes (again, with the exception of the isodesmic scheme) consistently predict its  $\Delta H_f^\circ$  to be about 10 kcal mol<sup>-1</sup> higher. Furthermore, examination of the experimental enthalpies of formation of the other PAHs made us skeptical

of the  $\Delta H_{f,\text{exp}}^\circ$  of benzo[*k*]fluoranthene. For instance, it is only 1.8 kcal mol<sup>-1</sup> higher than the  $\Delta H_f^\circ$  of fluoranthene, which has one less benzene ring. By comparison, fluoranthene's  $\Delta H_f^\circ$  is in turn 7 kcal mol<sup>-1</sup> higher than the  $\Delta H_f^\circ$  of acenaphthalene, which has one benzene ring less than fluoranthene. This led us to suspect that the experimental  $\Delta H_f^\circ$  of benzo[*k*]fluoranthene is too low and to label it with a "D" (see Table S1 of the Supporting Information).

The choice of the appropriate reaction scheme is crucial, since the  $\Delta H_f^\circ$  calculated using different reference species can disagree considerably. Since high-level quantum chemical calculations for systems containing more than 10 heavy atoms are still very computationally expensive, we must rely on the very scarce experimental data to determine the quality of the homodesmic reaction schemes. By comparisons with the available experimental  $\Delta H_f^\circ$  for PAHs and fullerenes, we determined that, given the currently available experimental data, Homodesmic4 is the most accurate reaction scheme. From now on we will refer to the Homodesmic4 reaction scheme as simply the homodesmic reaction scheme, and  $\Delta H_{f,\text{homo}}^\circ$  refers to the enthalpy of formation calculated through this homodesmic reaction scheme from absolute energies obtained at the B3LYP/6-31G(d) level of theory.

## 5. Estimation Method

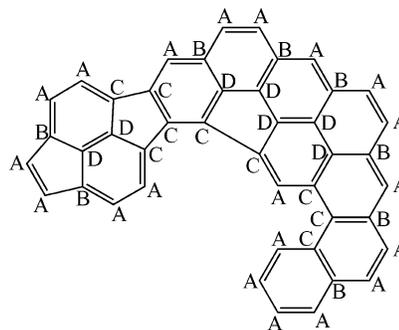
Benson justified the use of additivity laws to estimate properties of molecules due to the empirical finding that forces between atoms are very "short range".<sup>2</sup> In these additivity estimation methods, a molecule is divided into parts, and each part is assigned a portion of the molecular property. The estimation of the property for a new molecule simply requires the addition of the properties of each of its constituent parts, assuming that these have been previously defined. Benson and Buss<sup>13</sup> established a hierarchical system for such additivity laws, in which the "zeroth"-order law would be the additivity of atom properties. This simplest additivity law estimates the molecular weight precisely, but presents obvious limitations for the estimation of the thermochemical properties of the molecule. Augmenting each part into which the molecule is divided allows

the additivity scheme to better capture the short range interactions that occur in the molecule. Thus the first- and second-order approximation are respectively the additivity of bond and of group properties, where a group is defined as a “polyvalent atom in a molecule together with all of its ligands”. We will call this group an atom-centered group. The atom-centered group method performs very well for aliphatic molecules, especially those that are not heavily substituted.  $S_{298}^{\circ}$  and  $C_p^{\circ}$  estimated by this atom-centered group additivity method are typically within  $\pm 0.3 \text{ cal K}^{-1} \text{ mol}^{-1}$  of the measured values, whereas the estimated  $\Delta H_f^{\circ}$ s are typically within  $\pm 1 \text{ kcal mol}^{-1}$ . However, this atom-centered group additivity scheme is not enough to capture all the peculiarities of a PAH molecule. The concept of group additivity is based on the assumption that non-nearest neighbor interactions do not affect significantly the thermochemistry of the molecule. However PAHs are characterized by their delocalized resonance and aromaticity. Moreover, although Benson et al. introduced ring corrections, they are not able to properly account for the strain caused by the presence of five-membered rings in PAHs. As discussed in section 2, previous researchers have tried to capture the effect of five-membered rings by introducing new atom-centered groups but still had difficulties capturing all the nuances of these effects.

We propose a different approach. Instead of introducing more atom-centered groups, we go back and consider the hierarchical system proposed by Benson and Buss,<sup>13</sup> which starts by dividing a molecule first into atoms, then into bonds, and finally into atom-centered groups. If we want to capture properties that are not as local as in aliphatic molecules, the natural extension of Benson and Buss' hierarchical system is to divide the molecule into bond-centered groups. We define a bond-centered group as a bond connecting two of Benson's atom-centered groups. For simplicity, we rename Benson's groups: “A” is defined as the  $C_B\text{-(H)}$  atom-centered group of Benson<sup>2</sup> and “B” is the  $C_{BF}\text{-(C}_B)_2\text{(C}_{BF})$  atom-centered group. “C” is defined as either a  $C_{BF}\text{-(C}_B)_2\text{(C}_{BF})_2$  or  $C_{BF}\text{-(C}_{BF})_3$  atom-centered group with a further restriction that it belongs to only two rings, i.e., it is on the periphery of the PAH. “D” is defined as a  $C_{BF}\text{-(C}_{BF})_3$  atom-centered group in which the center  $C_{BF}$  atom belongs to three rings. Our definition of the “C” and “D” groups is slightly different from Benson's definition (compare Figures 1a and 5). The definition of these atom-centered groups is irrespective of the size of the rings to which these atoms belong. A depiction of these groups for an arbitrary PAH is shown in Figure 5. Possible bond-centered groups between these types of atom-centered groups are as follows: AA, AB, AC, BB, BC, BD, CC, CD, and DD.

Although the bond-centered groups span a larger structure than the atom-centered groups, they still do not completely capture non-neighbor effects, such as the electron delocalization characteristic of aromatic molecules. Carter in 1949 had already recognized that the resonance energy is a function of the logarithm of the number of Kekulé structures in aromatic molecules.<sup>70</sup> We developed an algorithm to count the number of Kekulé structures of PAHs containing both five- and six-membered rings. This algorithm will be described in detail in a subsequent publication.

One notes that five-membered rings introduce strain to the system and that five-membered rings completely surrounded

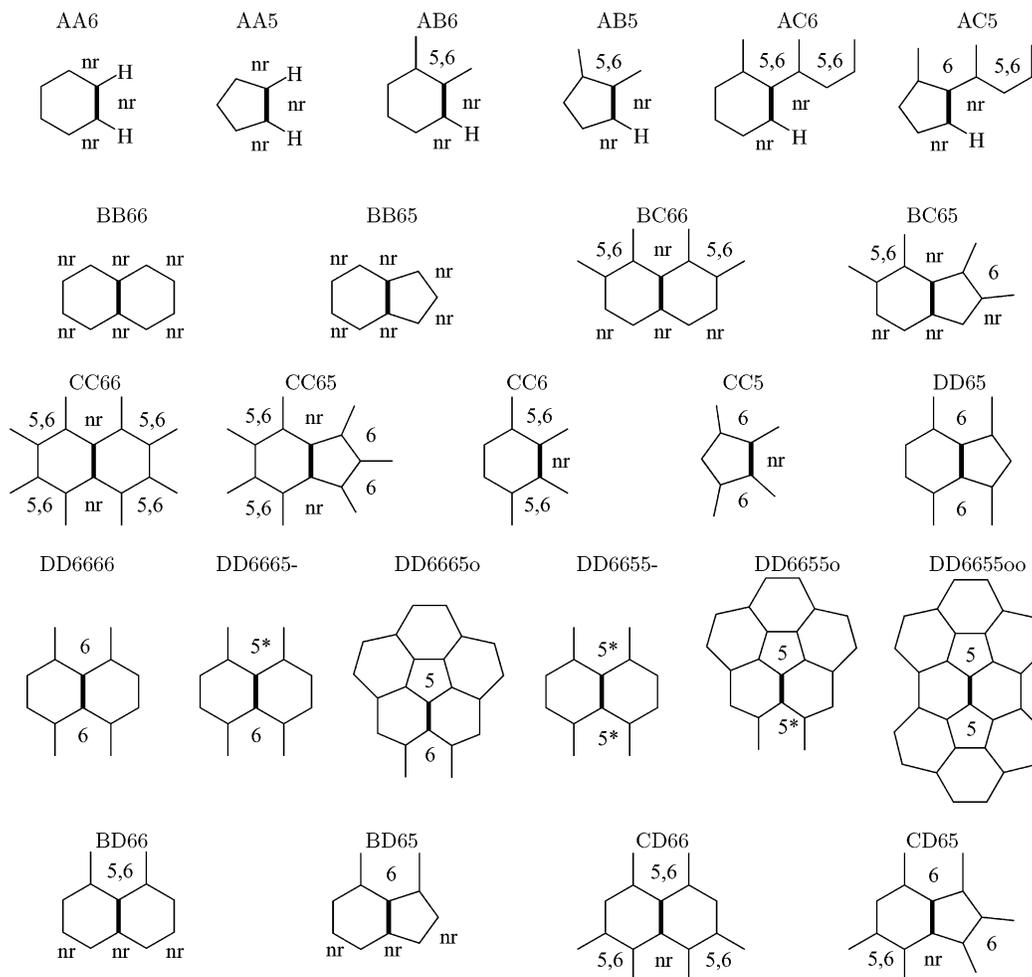


**Figure 5.** Atom-centered groups used for the definition of the bond-centered groups. These atom-centered groups follow basically the definition established by Benson,<sup>2</sup> with a small difference in the definition of the “C” and “D” groups. “A” corresponds to the  $[C_B\text{-(H)}]$  group, “B” corresponds to the  $[C_{BF}\text{-(C}_B)_2\text{(C}_{BF})]$  group, “C” corresponds to a group that is in a bay region. It can be either a  $[C_{BF}\text{-(C}_B)_2\text{(C}_{BF})_2]$  group or a  $[C_{BF}\text{-(C}_{BF})_3]$  group, and “D” corresponds to the  $[C_{BF}\text{-(C}_{BF})_3]$  group that is internal to the PAH.

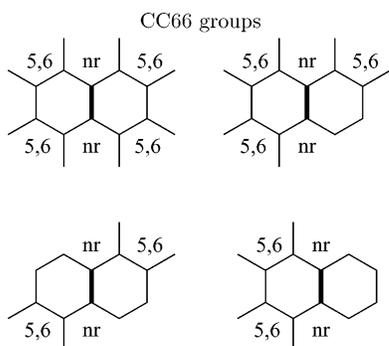
by six-membered rings introduce nonplanarity to the PAH. From these observations one could be inclined to propose a method in which the bond groups would not be differentiated according to the size of the rings. Instead, in such a method, five-membered ring corrections should be included. In the case of IPR PAHs, two ring corrections could be included: one for five-membered rings that are not completely surrounded by six-membered rings and another for five-membered rings that are completely surrounded by six-membered rings. Such a method would have 11 parameters:  $\ln(K)$ , AAx, ABx, ACx, CCx, BB6x, BC6x, CC6x, DD6x, R5, and R5o. The “6” after the name of the bond group indicates the size of the ring to which it belongs, the “x” indicates a ring with either 5 or 6 carbons, and “R5” and “R5o” are the ring corrections. The BD6x and CD6x are linearly dependent to the previous bond groups (see subsequent discussion). However, the errors arising from such a method are unacceptable: RMS is  $14.4 \text{ kcal mol}^{-1}$ , and MAD is  $9.0 \text{ kcal mol}^{-1}$ . The statistics for this method can be found in Table S4 of the Supporting Information. Moreover, it is not clear how further ring corrections should be introduced either to improve the performance of this method or to describe non-IPR PAHs.

It is clear that the simple solution of including two ring corrections is not adequate, and a more detailed definition of the bond groups is necessary. We define bond-centered groups that specify explicitly the size of the ring(s) to which the bond belongs. The diagrams in Figures 6 and 7 should aid in the understanding of these bond-groups. The numbers in the bond group's nomenclature refer to the size of the ring(s) to which the bond belongs. Bonds on the boundary between fused five-membered rings (BB55, BC55, CC55, BD55, CD55, and DD55) were not included, since PAHs with two fused five-membered rings were not included in the model development. The bond group DD66 was further subdivided to capture the different energetic contributions arising when the rings above and below it are six- or five-membered rings. The resulting bonds are DD6666, DD6665, and DD6655. The last two digits in the name of these bonds refer to the size of the rings above and below the bond group. Additionally, the DD6665 and DD6655 bonds were further subdivided according to whether the five-membered ring(s) above the DD bond are completely surrounded by six-membered rings or not. The DD6665 bond was subdivided into the DD6665- and DD6665o, whereas the DD6655 was subdivided into DD6655-, DD6655o, and DD6655oo. A dash

(70) Carter, P. G. *Trans. Faraday Soc.* **1949**, *45*, 597–602.



**Figure 6.** Bond-centered groups defined in this work. Each of the bond-centered group connects two atom-centered groups as defined in Figure 5. In the nomenclature, the numbers following the two letters correspond to the size of the ring that the bond-centered group belong to. In the case of DD66 groups, the two last numbers define the size of the rings that are above and below the DD66 bond-centered group. In each scheme, the bond-centered groups are shown in bold. The numbers in each ring correspond to its size. A ring that can be either five-membered or six-membered is represented by a “5,6”. Positions marked by a “5\*” cannot be completely surrounded by other rings. Positions where no ring is allowed are marked with “nr”. Positions that are not marked might or might not have a ring.



**Figure 7.** All the possible CC66 structures. Figure S1 in the Supporting Information shows all the possible structures for bond groups BC66, BC65, CC66, CC65, CD66, and CD65. For the sake of conciseness, in Figure 6 only the structures with all the possible rings are shown.

(–) at the end of the name of the bond indicates that the five-membered ring(s) is(are) not completely surrounded by six-membered rings, whereas one “o” at the end indicates that one five-membered ring is completely surrounded by six-membered rings. DD665oo represents the case where both five-membered rings above and below the bond are completely surrounded by six-membered rings.

The contributions of each of the bond groups and of the  $\ln(K)$  term to the  $\Delta H_f^\circ$  was derived through a weighted least-squares regression. The weight for each PAH is assigned as the inverse of the uncertainty in the value of the  $\Delta H_{f,\text{hom}}^\circ$ . This uncertainty arises from the uncertainty in the experimental  $\Delta H_f^\circ$  of the reference molecules used in the homodesmic reaction scheme and the uncertainty in the quantum chemical calculation of the heat of reaction ( $\Delta H_{\text{rxn}}$ ) of the homodesmic reaction, as given by eq 11:

$$\epsilon = \epsilon_{\text{exptl}}\Delta H_f^\circ + \epsilon_{\text{quantum}}\Delta H_{\text{rxn}} \quad (11)$$

For example, for the molecule in Figure 4, for which the Homodesmic4 scheme uses  $5/3$  of benzene,  $3/2$  of naphthalene, one phenanthrene, and  $1/12$  of  $C_{60}$ ,

$$\epsilon_{\text{exptl}}\Delta H_f^\circ = \frac{5}{3}\epsilon_{\text{benzene}} + \frac{3}{2}\epsilon_{\text{naphthalene}} + \epsilon_{\text{phenanthrene}} + \frac{1}{12}\epsilon_{C_{60}} \quad (12)$$

The uncertainties of the reference molecules are given by our grading of the experimental values (Table S1 of the Supporting Information). The error in the quantum chemical calculation of  $\Delta H_{\text{rxn}}$  is expected to increase with molecular size and was taken

to be

$$\epsilon_{\text{quantum}\Delta H_{\text{rxn}}} = (\text{number of C atoms}) \times (0.2 \text{ kcal mol}^{-1}) \quad (13)$$

The  $\epsilon$ 's computed using eq 11 are reasonably consistent with the deviations shown in Table 3. For the molecules that form the base of the Homodesmotic4 reaction scheme (i.e., benzene, naphthalene, phenanthrene, acenaphthalene, and  $C_{60}$ ),  $\epsilon_{\text{exptl}\Delta H_f^\circ}$  is considered to be equivalent to the uncertainty that we assigned to its experimental value and  $\epsilon_{\text{quantum}\Delta H_{\text{rxn}}}$  is defined as zero.

Of the 25 bond groups that describe five- and six-membered ring PAHs, only 21 are linearly independent. For example, the number of BD65, BD66, CD65, and CD66 bond groups in a PAH is given by

$$\text{BD65} = \text{AB5} - 2 \times \text{BB65} - \text{BC65} \quad (14)$$

$$\text{BD66} = -0.5 \times \text{AB5} + 0.5 \times \text{AB6} - 2 \times \text{BB66} - \text{BC66} \quad (15)$$

$$\text{CD65} = \text{AC5} + 2 \times \text{CC5} - \text{BC65} - 2 \times \text{CC65} \quad (16)$$

$$\text{CD66} = -0.5 \times \text{AC5} + 0.5 \times \text{AC6} - \text{CC5} + \text{CC6} - \text{BC66} - 2 \times \text{CC66} \quad (17)$$

Similar linear-dependency issues arise in other group additivity schemes, as often discussed in the literature.<sup>2,9,69</sup> The enthalpy contributions of the BD65, BD66, CD65, and CD66 bond groups were assigned to be 4.0 kcal mol<sup>-1</sup>. The entropy and heat capacity contributions from these four groups were assigned to be zero.

When the regression is performed with the ln(K) term and all the linearly independent bond groups, it is found that not all the bond groups are statistically significant. To ensure that all the parameters of the model are statistically significant, the bond group values for BB66 and BB65 were set to be equal. The same was done for the bond groups BC66 and BC65 and for the bond groups CC66 and CC65. Since only six of the PAHs studied have the bond groups DD6665o and/or DD6655oo, we first obtained the contributions of the ln(K) term and of the remaining bond groups by performing a regression without those six PAHs. Next the contributions of the DD6665o and DD6655oo bond groups were determined through a weighted regression of the  $\Delta H_f^\circ$  of the six PAHs that contain these groups, holding the other group values fixed.

A regression diagnostics of the proposed model revealed some collinearity problems. The matrix of the independent variables for the 133 PAHs that do not contain the bonds DD6665o and DD6655oo has a condition number of 33 (see Table S12 of the Supporting Information), which is an indication of moderate dependencies among the variables.<sup>71</sup> Variance inflation factors (VIF) larger than 10 for some of the regression coefficients are also a symptom of collinearity (see Table S9). Principal component analysis<sup>71</sup> was performed, and it was determined that the last four principal components each accounted for less than 1% of the total dispersion of the X-space (see Table S13). Most of the collinearity problem is due to the last principal component, as attested by its condition index. However its relatively large  $t$ -value indicates that this principal component might be significant. Indeed, when principal component #17 is eliminated from the regression, both the mean average deviation

**Table 4.** Cross-validation of the Proposed Bond-Centered Group Additivity Method<sup>a</sup>

	complete set	set 1	set 2
ln(K)	-19.59 ± 1.1	-16.54	-17.74
AA5	10.39 ± 0.7	8.93	10.30
AA6	5.54 ± 0.1	5.21	5.90
AB5	8.72 ± 0.4	9.15	8.65
AB6	5.10 ± 0.2	4.60	5.25
AC5	4.70 ± 0.6	4.48	5.17
AC6	2.32 ± 0.3	1.42	2.15
CC5	11.87 ± 0.8	11.64	12.49
CC6	9.15 ± 0.7	9.39	9.29
BB65	4.10 ± 0.5	6.16	3.96
BB66	4.10 ± 0.5	6.16	3.96
BC65	3.26 ± 0.3	3.78	2.56
BC66	3.26 ± 0.3	3.78	2.56
CC65	5.71 ± 0.5	5.82	5.72
CC66	5.71 ± 0.5	5.82	5.72
DD65	13.24 ± 0.4	14.15	12.40
DD6666	2.71 ± 0.3	2.68	1.88
DD6665-	7.20 ± 0.7	7.98	5.32
DD6655-	20.43 ± 1.2	22.21	18.95
DD6655o	16.40 ± 1.0	13.76	16.19
BD65 <sup>a</sup>	4.00 ± -	4.00	4.00
BD66 <sup>a</sup>	4.00 ± -	4.00	4.00
CD65 <sup>a</sup>	4.00 ± -	4.00	4.00
CD66 <sup>a</sup>	4.00 ± -	4.00	4.00
MAD	2.54	3.16	2.75
RMS	3.64	5.53	4.30

<sup>a</sup> The coefficients obtained by regressing  $\Delta H_f^\circ$  over the entire set of 133 PAHs are shown (in kcal mol<sup>-1</sup>), along with the coefficients from the regression over two distinct sets of PAHs. The RMS and MAD given for Set 1 refer to the errors obtained by using the coefficients obtained through Set 1 to predict the  $\Delta H_f^\circ$  of the PAHs in Set 2 and vice versa. The DD6665o and DD6655oo bond groups were omitted in the cross-validation.

(MAD) and the root-mean-square error (RMS) increase significantly (see Table S14). On the other hand, principal components #16 and #15 have very small  $t$ -values, and elimination of these principal components increases MAD and RMS only slightly. However, the elimination of these two principal components does not alleviate the collinearity problem significantly, as indicated by the small change in the largest VIFs (see Table S14). Since the exclusion of these principal components does not alleviate the collinearity problem while causing the MAD and RMS to increase slightly (for the elimination of principal components #16 and #15, the MAD and RMS increase from 2.54 to 3.17 and from 3.64 to 4.60, respectively), we chose to adopt the coefficients obtained by the ordinary least-squares regression. The collinearity present in this model is a reflection of the structure of the X-space. For example, PAHs with five-membered rings usually have fewer resonance structures than PAHs of the same size that only have six-membered rings. To the extent that the training set of 133 PAHs is representative, the partial collinearity should not cause problems in the prediction of the thermochemical properties of PAHs not included in the training set. The coefficients involved in the collinearity are identified by their large VIF, and the most prominent is the ln(K) term. Other terms that show strong correlation are the AA6, AB6, AC6, CC6, BB65, and BB66 bonds.

A cross-validation of the proposed estimation method was performed in order to test its predictive capability. The set of 133 PAHs (the original 139 excluding the 6 PAHs containing DD6665o and/or DD6655oo bond-groups) was divided into two subsets, by assigning the SIX-(*odd number*) PAHs to Set 1 and the SIX-(*even number*) PAHs to Set 2. Similarly, the FIVE-

(71) Rawlings, J. O. *Applied Regression Analysis*; Wadsworth & Brooks/Cole: Pacific Grove, CA, 1988.

**Table 5.** Values for Bond Groups and the ln(K) Term for the Estimation of Thermochemical Properties

	$\Delta H_f^\circ$ (kcal mol <sup>-1</sup> )	$\Delta S_{298}^\circ$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	$C_p^{\circ T}$ (cal K <sup>-1</sup> mol <sup>-1</sup> )						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
ln(K)	-19.59 ± 1.1								
AA5	10.39 ± 0.7	-13.0 ± 0.2	3.4	4.6	5.6	6.4	7.5	8.3	9.3
AA6	5.54 ± 0.1	11.6 ± <0.1	3.4	4.6	5.6	6.4	7.6	8.3	9.5
AB5	8.72 ± 0.4	6.5 ± 0.1	3.4	4.6	5.5	6.2	7.2	7.8	8.6
AB6	5.10 ± 0.2	3.6 ± <0.1	3.4	4.6	5.5	6.2	7.3	7.9	8.8
AC5	4.70 ± 0.6	7.0 ± 0.2	3.5	4.6	5.5	6.2	7.1	7.7	8.6
AC6	2.32 ± 0.3	4.3 ± 0.1	3.5	4.6	5.5	6.2	7.2	7.9	8.8
CC5	11.87 ± 0.8	-1.9 ± 0.2	3.3	4.4	5.2	5.9	6.8	7.3	7.9
CC6	9.15 ± 0.7	-5.3 ± 0.2	3.4	4.5	5.4	6.1	7.0	7.6	8.4
BB65	4.10 ± 0.5	-1.1 ± 0.1	-1.3	-1.9	-2.3	-2.6	-3.1	-3.3	-3.6
BB66	4.10 ± 0.5	-1.1 ± 0.1	-1.3	-1.9	-2.3	-2.6	-3.1	-3.3	-3.6
BC65	3.26 ± 0.3	-1.2 ± 0.1	-1.4	-1.9	-2.3	-2.7	-3.1	-3.4	-3.7
BC66	3.26 ± 0.3	-1.2 ± 0.1	-1.4	-1.9	-2.3	-2.7	-3.1	-3.4	-3.7
CC65	5.71 ± 0.5	-1.0 ± 0.2	-1.4	-1.9	-2.4	-2.7	-3.1	-3.4	-3.7
CC66	5.71 ± 0.5	-1.0 ± 0.2	-1.4	-1.9	-2.3	-2.7	-3.1	-3.4	-3.7
DD65	13.24 ± 0.4	2.3 ± 0.1	1.4	1.9	2.4	2.7	3.1	3.4	3.7
DD6666	2.71 ± 0.3	0.8 ± 0.1	1.5	2.0	2.4	2.7	3.2	3.4	3.8
DD6665-	7.20 ± 0.7	1.4 ± 0.2	1.4	1.9	2.4	2.7	3.1	3.3	3.6
DD6665o <sup>a</sup>	(3.44 ± 0.7)	(0.5 ± <0.1)	(1.3)	(1.8)	(2.3)	(2.6)	(3.1)	(3.3)	(3.6)
DD6655-	20.43 ± 1.2	1.8 ± 0.4	1.3	1.9	2.3	2.7	3.1	3.4	3.7
DD6655o	16.40 ± 1.0	0.8 ± 0.3	1.2	1.8	2.2	2.6	3.1	3.3	3.6
DD6655oo <sup>a</sup>	(-0.24 ± 0.7)	(0.0 ± <0.1)	(1.3)	(1.8)	(2.3)	(2.6)	(3.1)	(3.3)	(3.5)
BD66 <sup>b</sup>	4.00 ± -	0.0 ± -	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BD65 <sup>b</sup>	4.00 ± -	0.0 ± -	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CD66 <sup>b</sup>	4.00 ± -	0.0 ± -	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CD65 <sup>b</sup>	4.00 ± -	0.0 ± -	0.0	0.0	0.0	0.0	0.0	0.0	0.0

<sup>a</sup> Values for these two bonds were derived from only 6 PAHs. <sup>b</sup> Values for these bonds were assigned (see text).

(*odd number*) were assigned to Set 2 and the FIVE-(*even number*) were assigned to Set 1. See Tables S2 and S3 for the definition of the PAHs. This splitting ensures that both sets cover approximately the same region, as required by data splitting validation procedures.<sup>72</sup> The coefficients for the ln(K) term and for the bond groups were obtained for each of the subsets and are shown in Table 4. One notices that the coefficients obtained from both subsets of PAHs are very close to the coefficients obtained from the entire set. The differences in the values of each of the coefficients are comparable to their standard errors, indicating that the latter are good estimates of the uncertainty of the coefficients. The RMS and MAD obtained when the coefficients derived from Set 1 are used to predict the  $\Delta H_f^\circ$  of the PAHs contained in Set 2 and vice versa are also shown in Table 4. These errors are comparable to the errors obtained from the complete set, indicating that the proposed bond-centered group additivity method has very good predictive capabilities. Since only six of the PAHs studied contain the DD6665o and/or DD6655oo bond groups, no cross-validation was performed for these bond groups. The uncertainty in these group values may be considerably higher than in the others.

Additionally, the model for the 133 PAHs was also validated by the “leave one out” procedure. The discrepancy between the  $\Delta H_f^\circ$  for each observation and its prediction from the regression equation obtained by leaving that observation out was calculated. Results are found in Table S5 of the Supporting Information. The MAD and RMS for these residuals are 2.95 and 4.35 kcal mol<sup>-1</sup>, respectively. These values are only slightly higher than the MAD and RMS for the complete set, as reported in Table 4. No anomalous outliers were found.

The intrinsic entropy ( $S_{\text{int}}^\circ$ ) was used to derive the bond groups, as in Benson’s method.<sup>2</sup> These bond group values do

not contain information about the symmetry of the molecule, so that, in order to calculate the  $S_{298}^\circ$  of a PAH, a correction due to the symmetry has to be added to  $S_{\text{int}}^\circ$  calculated from the bond group values:

$$S_{298}^\circ = S_{\text{int}}^\circ - R \ln(\sigma) \quad (18)$$

The  $S_{\text{int}}^\circ$  and  $C_p^\circ$  at 300, 400, 500, 600, 800, 1000, and 1500 K were fitted through a weighted linear regression to the same bond groups used for the  $\Delta H_f^\circ$ . The inclusion of the ln(K) term did not improve the estimation method for  $S_{\text{int}}^\circ$  or the  $C_p^\circ$ , and thus the estimation method for these thermochemical properties does not include the ln(K) term. The ln(K) was the term that was causing most of the collinearity problem in the regression of the  $\Delta H_f^\circ$ , thus the models for  $S_{\text{int}}^\circ$  and  $C_p^\circ$  show virtually no collinearity as attested by the VIF values of their coefficients (see Table S10). The weights used were the same as the ones used for the derivation of the bond-group values of  $\Delta H_f^\circ$ .

The contributions from each bond group and the ln(K) term to the  $\Delta H_f^\circ$ ,  $S_{298}^\circ$ , and  $C_p^\circ$  are listed in Table 5 along with their standard deviations. The standard deviations for the  $C_p^\circ$  were less than 0.1 K. Since the level of confidence on the values for the bond groups DD6665o and DD6655oo is not as high as for the other bond groups, the values for these groups are given in parentheses.

The statistics for the regression can be found in Table 6 and were calculated considering the complete set of 139 PAHs. The statistics for  $\Delta H_f^\circ$  and  $S_{298}^\circ$  related to the set of 133 PAHs that do not contain the DD6665o and the DD6655oo bond groups are given in parentheses. All the mean average deviation (MAD) and root-mean-square errors (RMS) are in relation to the homodesmic B3LYP/6-31G(d) values and have not been weighted.

The thermochemical properties of PAHs are estimated by summing the contribution of each of its bonds, as given in Table

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**Table 6.** Statistics for the Estimation Method<sup>a</sup>

	$\Delta H_f^\circ$ (kcal mol <sup>-1</sup> )	$\Delta S_{298}^\circ$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	$C_{p,T}^\circ$ (cal K <sup>-1</sup> mol <sup>-1</sup> )							
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	
N	139 (133)	139 (133)				139				
parameters	19 (17)	18 (16)				18				
MAD	2.78 (2.54)	0.71 (0.67)	0.33	0.73	0.31	0.20	0.49	0.50	0.31	
RMS	4.25 (3.64)	1.04 (1.02)	0.45	1.18	0.62	0.30	0.58	0.63	0.45	

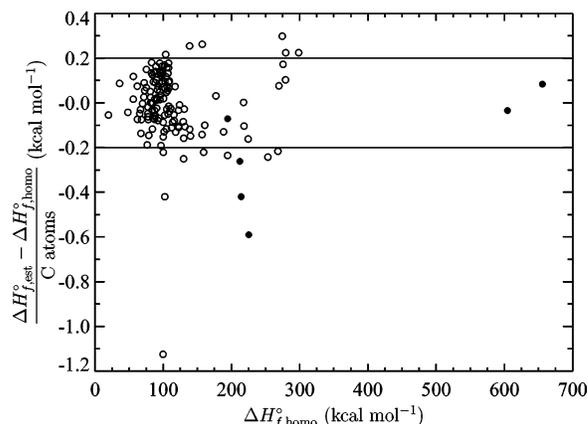
<sup>a</sup> The errors were calculated for the complete set of 139 PAHs and were not weighted. For  $\Delta H_f^\circ$  and  $S_{298}^\circ$ , the statistics related to the set of 133 molecules that do not contain the DD6665o and the DD6655oo bond groups are given in parentheses.

4.  $\Delta H_{f,est}^\circ$  has an additional term related to the resonance energy ( $-16.95 \ln(K)$ ). Sample calculations were made for the PAHs in Figure 3 and are found in Table S6 of the Supporting Information.

## 6. Results and Discussion

The estimation method for the thermochemical properties developed in this work was based on the  $\Delta H_{f,homo}^\circ$ ,  $S_{298}^\circ$ , and  $C_p^\circ$  obtained from DFT calculations. As a comparison with the experimental values, the entropies calculated from the B3LYP/6-31G(d) are listed in the last column of Table 2. Except for naphthalene, the entropy calculated from quantum chemistry is within the uncertainty of the entropy calculated from the third law method based on experimental heat capacity and vapor pressure data. We conclude that the  $S_{298}^\circ$ 's calculated at the B3LYP/6-31G(d) level and with our bond-centered group additivity method are at least as reliable as the available experimental values. We developed a homodesmotic reaction scheme that closely emulates the experimental  $\Delta H_f^\circ$  of the PAHs. The estimation method for the enthalpy of formation that we propose can at best be as good as the  $\Delta H_{f,homo}^\circ$  given by the homodesmotic reaction scheme.

The bond-centered group values reported in Table 4 allow the estimation of the thermochemical properties of any PAH containing both five- and six-membered rings that follows the Isolated Pentagon Rule. The deliberate subdivision of certain groups into more specific substructures is a straightforward and powerful way to improve group additivity methods to meet the needs of a specific application, as done by Bozzelli and co-workers in defining Hydrogen-Bond Increment (HBI) groups for radicals,<sup>73</sup> and Sumathi and Green<sup>69</sup> for ketene species. In this bond-centered group additivity scheme for the estimation of the thermochemical properties of PAHs, it was verified that, in order to estimate accurately the  $\Delta H_f^\circ$  of PAHs up to  $C_{60}$  and  $C_{70}$  fullerenes, it was necessary to subdivide the DD66 group into DD6666, DD6665, and DD6655, according to the size of the ring that is above and below the DD66 bond. Proceeding in this manner, the further subdivision of the DD6665 group into the DD6665- and DD6665o groups and of the DD6655 group into the DD6655-, DD6655o, and DD6655oo groups, according to whether the five-membered rings above and below the DD66 bond are completely surrounded by six-membered rings or not, improves the estimation method significantly for the PAHs studied. Each of these bond groups indeed describe different environments as evidenced by the very different contributions to the  $\Delta H_f^\circ$  from each of these groups. The DD6655- bond, as it occurs in pyracylene introduces considerable strain to the molecule, and thus its contribution to the  $\Delta H_f^\circ$  of a PAH is very



**Figure 8.** Error per carbon atom between  $\Delta H_{f,homo}^\circ$  and  $\Delta H_{f,est}^\circ$  versus the  $\Delta H_{f,homo}^\circ$ . The filled circles correspond to PAHs that contain the bond group(s) DD6665o and/or DD6655oo.

high (20.43 kcal mol<sup>-1</sup>). Incidentally the  $\Delta H_{f,est}^\circ$  for pyracylene estimated by the bond-centered group additivity method (96.4 kcal mol<sup>-1</sup>) agrees very well with the value obtained by Diogo et al.<sup>74</sup> (97.8 kcal mol<sup>-1</sup>) from a measured energy of combustion and an estimated  $\Delta H_{f,subl}^\circ$ . Completely surrounding a five-membered ring with six-membered rings provides stability to the PAH, as is attested by the contributions of the DD6655o and DD6655oo bonds to the  $\Delta H_f^\circ$ . Also the comparison of bond groups DD6665- and DD6665o shows this trend. If the  $\Delta H_f^\circ$  of larger fullerenes is to be estimated with more accuracy, then the DD6655 and DD6665 bond groups may need to be subdivided even further. A method similar to the “structural motifs scheme” developed by Cioslowski<sup>9</sup> for the estimation of the  $\Delta H_f^\circ$  fullerenes would result.

In Figure 8 the difference between the  $\Delta H_{f,homo}^\circ$  and the estimated enthalpy of formation ( $\Delta H_{f,est}^\circ$ ) per carbon atom is plotted against  $\Delta H_{f,homo}^\circ$ . For the majority of the  $\Delta H_{f,est}^\circ$ , including the estimated  $\Delta H_{f,est}^\circ$  for  $C_{60}$  and  $C_{70}$ , the error per carbon atom is less than 0.2 kcal mol<sup>-1</sup>. The errors of the PAHs that contain the bond group(s) DD6665o and DD6655oo are shown with a filled circle. The most obvious outlier, with an absolute error of more than 1 kcal mol<sup>-1</sup> per carbon is as-indacene (PAH (7) in Figure 3). This is the only PAH in which the rings above and below the CC6 bond are both five-membered. The current bond-centered group model is not able to capture the strain that this relatively unstable structure has. Perhaps in the future the CC6 group should be subdivided as we have done with the DD66 group. The three filled circles that are below the  $-0.2$  kcal mol<sup>-1</sup> per carbon error line correspond to PAHs that contain the DD6665o bond group. The

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**Table 7.** Comparison between the Atom-Centered Group Additivity Methods and the Bond-Centered Group Additivity Method (BCGA) Presented in This Work for the PAHs with Known Experimental  $\Delta H_f^\circ$ 

PAH	$\Delta H_{f,\text{exp}}^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H_{f,\text{homo}}^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H_{f,\text{est}}^\circ - \Delta H_{f,\text{exp}}^\circ$ (kcal mol <sup>-1</sup> )				
			Benson	Moiseeva	Armitage	BCGA	
benzene	C <sub>6</sub> H <sub>6</sub>	19.8	19.8	0.0	-3.2	0.0	-0.1
naphthalene	C <sub>10</sub> H <sub>8</sub>	36.0	36.0	0.0	-0.1	0.0	0.2
phenanthrene	C <sub>14</sub> H <sub>10</sub>	48.1	48.1	1.9	1.5	1.9	-0.1
anthracene	C <sub>14</sub> H <sub>10</sub>	55.2	56.1	-3.0	0.0	-3.0	-0.1
pyrene	C <sub>16</sub> H <sub>10</sub>	53.9	56.2	1.3	8.2	1.2	3.7
triphenylene	C <sub>18</sub> H <sub>12</sub>	65.5	65.7	-3.7	-7.8	-3.7	-0.2
benzo[ <i>c</i> ]phenanthrene	C <sub>18</sub> H <sub>12</sub>	69.6	68.0	-4.5	-3.5	-4.5	-2.7
benz[ <i>a</i> ]anthracene	C <sub>18</sub> H <sub>12</sub>	69.6	66.7	-3.4	-0.7	-3.4	-3.7
chrysene	C <sub>18</sub> H <sub>12</sub>	63.0	61.9	1.0	-0.3	1.0	0.8
naphthacene	C <sub>18</sub> H <sub>12</sub>	79.3	77.6	-10.9	-4.8	-10.9	-4.1
perylene	C <sub>18</sub> H <sub>12</sub>	76.4	76.5	-9.4	-6.2	-9.5	-3.1
coronene	C <sub>24</sub> H <sub>12</sub>	73.6	75.2	3.8	-2.9	3.5	2.4
acenaphthalene	C <sub>12</sub> H <sub>8</sub>	62.1	62.1	-	-4.1	-	-1.2
fluoranthene	C <sub>16</sub> H <sub>10</sub>	69.8	67.3	-	-0.7	-0.7	-5.2
corannulene	C <sub>20</sub> H <sub>10</sub>	110.1	117.4	-	-	-0.3	7.7
benzo[ <i>k</i> ]fluoranthene <sup>a</sup>	C <sub>20</sub> H <sub>12</sub>	(71.0)	82.6	-	(17.4)	(14.3)	(10.2)
C <sub>60</sub>	C <sub>60</sub>	604.6	604.6	-	-	-29.5	-2.2
C <sub>70</sub>	C <sub>70</sub>	658.5	655.8	-	-	-9.9	0.7
MAD				3.6	3.1	5.5	2.7

<sup>a</sup> The experimental  $\Delta H_f^\circ$  of benzo[*k*]fluoranthene is suspected to be in error. Values not included in the calculation of the MAD.

only other PAH that contains this bond group is C<sub>70</sub>. Since C<sub>70</sub> contains 20 of this group, the value of DD6665o is strongly influenced by this molecule. As of now it is not possible to conclude whether (1) inclusion of more PAHs containing the DD6665o group would lead to a value of DD6665o that would give acceptable errors for C<sub>70</sub> and the other PAHs with this bond group, (2) the DD6665o bond group needs to be subdivided, or (3) the homodesmotic reaction scheme used to obtain the  $\Delta H_{f,\text{homo}}^\circ$  is not adequate for PAHs with the structural feature described by the DD6665o group.

The inclusion of the term that describes the resonance energy does not improve the estimation of the  $S_{\text{int}}^\circ$  nor of the  $C_p^\circ$ , and thus the method proposed here for the estimation of these thermochemical properties does not include the ln(K) term. Examining the contributions of each of the bond groups to  $C_p^\circ$ , one concludes that the groups can be divided into three categories. The first category includes the bond groups that are in the periphery of the PAH (they include always an "A" group). The second is composed of the bond groups that link two atom groups that are in the periphery of the PAH but that belong to two rings. Finally the last category is composed of the bond groups that link two D groups. Entropies and heat capacities are much more amenable to a description by additivity methods than  $\Delta H_f^\circ$ .

Differences between the experimental  $\Delta H_f^\circ$  and values estimated by some of the previous methods and by the bond-centered group additivity method (BCGA) presented in this paper are given in Table 7. The difference between  $\Delta H_{f,\text{est}}^\circ$  and  $\Delta H_{f,\text{homo}}^\circ$  for some PAHs whose experimental  $\Delta H_f^\circ$  are not available are shown in Table 8. Benson's group additivity method<sup>11</sup> applies to PAHs with six-membered rings only. The other two atom-centered group additivity methods are extensions of Benson's method to include five-membered rings. Moiseeva and Dorofeeva<sup>15</sup> derived new groups for benzenoid PAHs, while Armitage and Bird<sup>21</sup> use essentially the same values suggested by Benson for the six-membered rings in their PAHs. The new bond-centered group additivity method is in much better agreement with the experimental and quantum chemical  $\Delta H_f^\circ$ s

and also is applicable to a broader range of PAHs than any existing method.

The previous atom-centered group additivity methods for PAHs with five-membered rings describe only specific structures, as shown in Figure 2. To enrich the comparison of the performance of the bond-centered group additivity method, the method proposed by Armitage and Bird was extended to describe acenaphthalene structures. The value for the missing group was derived from the experimental  $\Delta H_f^\circ$  of acenaphthalene. The  $\Delta H_f^\circ$ s calculated from this extended Armitage and Bird method are listed in Table 8. The bond-centered group additivity scheme presented here is able to provide thermochemical properties for any IPR PAH. The  $\Delta H_f^\circ$  of corannulene and C<sub>70</sub> fullerene estimated by the Bird and Armitage method agrees well with the  $\Delta H_{f,\text{exp}}^\circ$ . However, it is not uncommon for the  $\Delta H_f^\circ$  estimated by this method to deviate by 10 kcal mol<sup>-1</sup> or more from the  $\Delta H_{f,\text{homo}}^\circ$  for smaller PAHs. The group additivity method of Armitage and Bird usually underestimates  $\Delta H_f^\circ$ . The bond-centered group additivity method has a considerably smaller MAD for the PAHs listed in Table 7 than the other methods. All the group additivity methods estimate the  $\Delta H_f^\circ$  of benzo[*k*]fluoranthene to be about 10 kcal mol<sup>-1</sup> higher than the available experimental value. The unusually large discrepancies between literature values and the present calculations suggest that the  $\Delta H_f^\circ$  of benzo[*k*]fluoranthene and the  $S_{298}^\circ$  of naphthacene should be remeasured.

Finally, a word of caution is due. As in any method of additivity of molecular substructures, the independent variables of the bond-centered group additivity method are mildly correlated. For example, the presence of an AB6 bond will usually (but not always) mean the presence of an AA6 bond. The resulting collinearity is inherent to the X-space and should not present a serious problem, since a wide variety of PAHs structures (up to the C<sub>60</sub> and C<sub>70</sub> fullerenes) has been included in this study, encompassing most of the X-space spanned by PAHs of practical interest.

**Table 8.** Comparison between the Atom-Centered Group Additivity Methods and the Bond-Centered Group Additivity Method (BCGA) Presented in This Work for Some PAHs Whose Experimental  $\Delta H_f^\circ$ 's Are Not Known (These PAHs Are Shown in Figure 3)

PAH	$\Delta H_{f,\text{homo}}^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H_{f,\text{est}}^\circ - \Delta H_{f,\text{homo}}^\circ$ (kcal mol <sup>-1</sup> )				
		Benson	Moiseeva	Armitage <sup>a</sup>	BCGA	
benzo[e]pyrene (1)	C <sub>20</sub> H <sub>12</sub>	69.7	-2.7	0.5	-2.8	0.0
anthanthrene (2)	C <sub>22</sub> H <sub>12</sub>	81.5	-7.1	-1.4	-7.3	0.0
benzo[c]chrysene (3)	C <sub>22</sub> H <sub>14</sub>	81.5	-2.4	-	-2.4	0.9
benzo[a]coronene (4)	C <sub>28</sub> H <sub>14</sub>	90.4	-1.2	-11.6	-1.5	-0.8
ovalene (5)	C <sub>32</sub> H <sub>14</sub>	102.2	-2.6	-12.2	-3.1	-2.2
(6)	C <sub>32</sub> H <sub>16</sub>	116.0	-10.6	-1.6	-10.9	-2.3
benzo[ghi]fluoranthene (8)	C <sub>18</sub> H <sub>10</sub>	87.4	-	-2.1	-1.3	-
cyclopenta[cd]fluoranthene (9)	C <sub>18</sub> H <sub>10</sub>	104.7	-	-5.4	-9.5	-1.9
(10)	C <sub>20</sub> H <sub>10</sub>	130.0	-	-	-14.4	-2.7
benz[a]acephenanthrylene (11)	C <sub>20</sub> H <sub>12</sub>	89.4	-	-7.0	1.8	3.0
benz[a]aceanthrylene (12)	C <sub>20</sub> H <sub>12</sub>	85.4	-	-0.2	-1.2	1.7
cyclopenta[bc]corannulene (13)	C <sub>22</sub> H <sub>10</sub>	156.8	-	-	-13.5	-3.4
cyclopenta[cd]perylene (14)	C <sub>22</sub> H <sub>12</sub>	100.6	-	-0.2	-7.6	0.6
dicyclopenta[bc,hi]corannulene (15)	C <sub>24</sub> H <sub>10</sub>	194.3	-	-	-24.9	-5.3
indeno[5,6,7,1-pqra]perylene (16)	C <sub>24</sub> H <sub>12</sub>	99.1	-	-6.3	-1.0	2.7
(17)	C <sub>26</sub> H <sub>12</sub>	161.0	-	-	-10.7	-3.1
(18)	C <sub>30</sub> H <sub>10</sub>	269.5	-	-	-	-2.8
(19)	C <sub>30</sub> H <sub>12</sub>	194.3	-	-	-7.0	-2.7
(20)	C <sub>30</sub> H <sub>12</sub>	217.7	-	-	-37.5	2.8
MAD			5.3	5.1	11.5	2.1

<sup>a</sup> Extended to include PAHs with acenaphthalene structures (see text).

## 7. Conclusions

A bond-centered group additivity method for the estimation of the thermochemical properties of PAHs has been derived based on thermochemical properties calculated at the B3LYP/6-31G(d) level.  $\Delta H_f^\circ$  were obtained through a set of homodesmic reactions that uses only aromatic molecules. This carefully chosen set of reference molecules corrects for effects that were not completely captured by the quantum chemical calculations. Resonance energy is described through the natural logarithm of the number of Kekulé structures. An algorithm has been developed to count the number of Kekulé structures in PAHs with both six- and five-membered rings. The new bond-centered group additivity method can be easily coupled with Benson's atom-centered group additivity method for aliphatic molecules. All the bond-centered groups are clearly defined and extendable. Extendability means that if the thermochemical properties of a certain class of species need to be estimated with more accuracy, the bond groups can be differentiated and more specific values derived for them. The bond-centered group additivity method for the estimation of the thermochemical properties of PAHs described in this paper captures the structural particularities that determine the  $\Delta H_f^\circ$  of PAHs up to fullerenes. This new method allows the rapid estimation of  $\Delta H_f^\circ$ ,  $S_{298}^\circ$ , and  $C_p^\circ$  values that are practically as good as B3LYP calculations or experimental measurements.

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**Supporting Information Available:** Table S1 is a compilation of available experimental  $\Delta H_f^\circ$  for PAHs and the  $\Delta H_{f,\text{exp}}^\circ$  adopted in this work. A list of the PAHs included in the development of the estimation method can be found in Tables S2 and S3, along with the structure and number of Kekulé structures of each PAH, its  $\Delta H_{f,\text{homo}}^\circ$ , and its  $\Delta H_{f,\text{est}}^\circ$ . The regression coefficients for an alternative method are shown in Table S4. The discrepancies between the  $\Delta H_f^\circ$  calculated through the "leave one out" regression cross-validation procedure and the  $\Delta H_{f,\text{homo}}^\circ$  are listed in Table S5. Figure S1 shows all the possible structures for bond groups BC66, BC65, CC66, CC65, CD66, and CD65. As an example of the use of the bond-centered group additivity method, the bonds forming the PAHs from Figure 3 are given in Table S6 together with the estimation of their  $\Delta H_f^\circ$ ,  $S_{298}^\circ$ , and  $\Delta H_{p,300}^\circ$ . The intrinsic entropies ( $S_{\text{int}}^\circ$ ) and heat capacities at the B3LYP/6-31G(d) level for the 139 PAHs included in this study are given in Table S7. Table S7 also contain the weights used in the regression. Table S8 lists the value of ln(K) and the number of each bond group for all the PAHs included in this study. Tables S9 to S15 contain data related to the treatment of the collinearity in the regression. Tables with the optimized geometries and vibrational frequencies for all the PAHs included in this study are also available as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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