RESEARCH ARTICLE

# High-precision standard enthalpy of formation for polycyclic aromatic hydrocarbons predicting from general connectivity based hierarchy with discrete correction of atomization energy

Zihan Xu[1], Huajie Xu[1], Lu Liu[1], Rongpei Jiang[2], Haisheng Ren (✉)[1,3], Xiangyuan Li[1,3]

1 School of Chemical Engineering, Sichuan University, Chengdu 610065, China
2 Beijing Institute of Aerospace Testing Technology, Beijing 100074, China
3 Engineering Research Center of Combustion and Cooling for Aerospace Power Ministry of Education, Chengdu 610065, China

**Abstract** The standard enthalpy of formation is an important predictor of the reaction heat of a chemical reaction. In this work, a high-precision method was developed to calculate accurate standard enthalpies of formation for polycyclic aromatic hydrocarbons based on the general connectivity based hierarchy (CBH) with the discrete correction of atomization energy. Through a comparison with available experimental findings and other high-precision computational results, it was found that the present method can give a good description of enthalpy of formation for polycyclic aromatic hydrocarbons. Since CBH schemes can broaden the scope of application, this method can be used to investigate the energetic properties of larger polycyclic aromatic hydrocarbons to achieve a high-precision calculation at the CCSD(T)/CBS level. In addition, the energetic properties of CBH fragments can be accurately calculated and integrated into a database for future use, which will increase computational efficiency. We hope this work can give new insights into the energetic properties of larger systems.

**Keywords** standard enthalpy of formation, polycyclic aromatic hydrocarbons, connectivity based hierarchy, high-precision calculation

## 1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the principal components of aviation fuels [1], accounting for

15%–20% of their wt % [2]. A detailed understanding of the properties of PAHs is very important for improving the fuel combustion efficiency [3], reducing the pollution [4,5] and synthesizing hydrocarbons [6]. The incomplete combustion of PAHs can produce soot, which is a significant air pollutant [7,8], making PAHs an ideal material to use to study the mechanism of soot formation [9,10]. Making an accurate prediction of the enthalpy of formation is an important element in the study of the soot formation mechanism [11].

The standard enthalpy of formation is the change of enthalpy during the formation of 1 mole of the substance from its constituent elements, with all substances in their standard states. It is an important thermodynamic property and the basic characteristic data of a species. The standard enthalpy of formation can be used to describe the relative stability of a species and to predict the energy changes in chemical reactions, such as the standard Gibbs energy, which is very important for understanding, controlling and utilizing chemical reactions [12]. Therefore, obtaining accurate standard enthalpies of formation is of critical importance.

Experimentally, the most widely used method for measuring the standard enthalpy of formation of gases is calorimetry, using either the rotating bomb calorimetry [13] or static bomb calorimetry approach [14]. But it is difficult to obtain the standard enthalpy of formation of a condensed phase due to its incomplete combustion and the difficulty of measuring the heat of vaporization. Several theoretical approaches have been developed to calculate standard enthalpies of formation of the organic compounds, namely, group additivity (GA) [15], bond separation (BS) isodesmic reactions [16], and atomization reactions [17]. With the GA method, the target molecule

is decomposed into several groups according to the structural unit based on the additivity of each group. The additivity means that the total properties of a molecule are equal to the sum of the contributions of all the structural units that make up the molecule. The GA method was used to predict the standard enthalpy of formation of 11 PAHs species with a mean absolute error of less than 2.0 kcal·mol$^{-1}$ compared to experimental findings [18]. However, the structural-unit groups of the GA method are unable to completely take into account of proximity effects or isomer differences [19], which, for example, results in the same values of the standard enthalpies of formation for chrysene and benz[a]anthracene.

Unlike the GA method, the BS isodesmic reaction approach is based on the reaction schemes, with the complete hydrogenation of the organic compound under study being separated into two processes. In the first step, the molecule is separated into its simplest parts containing the same component bonds. The energy associated with this reaction arises from the heat of BS. The second step consists of full hydrogenation of the BS products. Compared with the GA method, the BS isodesmic reaction approach is more efficient at cancelling errors in computing the standard enthalpy of formation [20]. But for the large molecules such as PAHs, it leads to excessively large errors in the computed standard enthalpy of formation due to the large number of molecules involved in the BS isodesmic reaction approach [21]. To reduce the errors in calculated standard enthalpy of formation of PAHs, the ring conserved isodesmic reaction scheme, which is based on the BS isodesmic reaction approach, was proposed [20]. In this scheme, the large PAHs are divided into multiple benzene rings according to their delocalization energies and the number of double bonds in the resonance structures. The standard enthalpies of formation of large PAHs are then extrapolated from these components. Sivaramakrishnan et al. [20] used the ring conserved isodesmic reaction approach to calculate the standard enthalpies of formation of 42 PAHs species (up to $C_{24}H_{18}$). They found that the mean absolute error reduced from 8.18 kcal·mol$^{-1}$ of BS isodesmic reaction approach to as low as 1.39 kcal·mol$^{-1}$ when compared with available experimental results. But for some species, the errors are still more than 4.00 kcal·mol$^{-1}$ [20]. This is because the ring conserved isodesmic reaction approach cannot well preserve the chemical environment of PAHs. With an increase of the number of aromatic rings, the effect of large conjugation is more obvious and the properties of the aromatic rings in PAHs differ greatly from those of the discrete benzene ring.

In the atomization−reaction approach, the standard enthalpy of formation for a specific molecule is calculated using the gasification enthalpy of the pure elements combined with the molecular single-point energies and vibration analysis. It can be used to directly calculate reasonably accurate estimates of the standard enthalpies of formation for small molecules, but there is an accumulation of errors for larger molecules [21]. These errors can usually be eliminated through the use of high-precision theoretical methods, such as Gaussian-n series (G2, G3, and G4) [22] and the golden standard, CCSD(T) [23]. However, these high-precision methods require expensive computational resources, which limit the size of molecules that can be solved in this way.

To reduce the computational cost of the high-precision methods while retaining their accuracy, Ramabhadran and Raghavachari [24] proposed a simple, efficient, and user-friendly protocol called the connectivity based hierarchy (CBH), which they used to accurately obtain the CCSD(T) level energies for a large number of substances other than PAHs [25]. The CBH method depends on preserving the environment of molecules to balance the reaction energies [24], but appropriately preserving the environment of PAHs is a great challenge when trying to obtain accurate energetic properties.

In this work, we will explore a high-precision and efficient thermochemistry protocol based on the CBH strategy to obtain accurate standard enthalpies of formation for aromatic molecules.

## 2　Theoretical method

### 2.1　Standard enthalpy of formation calculation

The standard enthalpy of formation can be directly estimated by Eq. (1) based on the atomization reaction [17]:

$$\Delta_f H^\circ = E + ZPVE + \Delta_0^T H - \sum_i^N n_i h_i, \qquad (1)$$

where, $E$ is the single point energy for the parent molecular, $ZPVE$ is its zero-point vibration energy, $\Delta_0^T H$ is the heat increase from 0 K to the target temperature $T$, and $\sum_i^N n_i h_i$ is the summation of all chemical elements that make up the parent molecule. For PAHs, $N$ equals to 2, which stands for C and H elements. $n_i$ is the number of atoms for the $i$th element, and $h_i$ is the element specific constant for each individual atom defined by [17]:

$$h_i = \Delta_f H_i^\circ - E_i - \Delta_0^T H_i, \qquad (2)$$

where the subscript $i$ represents the $i$th element of the molecule, $\Delta_f H_i^\circ$ is the reference standard enthalpy of formation, $E_i$ is the atomic electronic energy, and $\Delta_0^T H_i$ is the reference enthalpy change for individual atomic specie. Since a single atom is an open-shell system, the direct calculation of $h_i$ based on Eq. (2) depends on the accuracy of the theoretical methods as shown in Table 1. To eliminate the errors arising from different theoretical methods, the discrete analysis method was developed to determine the values of $h_i$ in this work.

The discrete values of theoretical calculation ($\Delta_f H_{cal}^\circ$)

**Table 1** Constants $h_i$/a.u. in equation for different computational schemes

| Computational scheme | $h_C$ | $h_H$ |
|---|---|---|
| CCSD(T)/cc-pVTZ | 38.0492 | 0.5805 |
| B3LYP/6-31G* | 38.1168 | 0.5809 |
| CBS-QB3 | 38.0559 | 0.5805 |
| W1 | 38.1234 | 0.5807 |
| G2 | 38.0548 | 0.5807 |
| G4 | 38.1047 | 0.5821 |
| DLPNO-CCSD(T)/def2-TZVP [a] | 38.0423 | 0.5775 |
| DLPNO-CCSD(T)/def2-QZVP [a] | 38.0516 | 0.5811 |
| This work from discrete least squares method | 38.0598 | 0.5816 |

a) From reference [26].

for a group of molecules relative to values derived from experiment ($\Delta_f H^\circ_{exp}$) can be defined as:

$$D = \sqrt{\sum_j^M (\Delta_f H^\circ_{cal} - \Delta_f H^\circ_{exp})^2}, \qquad (3)$$

where $M$ is total number of molecules, and the subscript $j$ means the $j$th molecule. Substituting Eq. (1) into Eq. (3), we have

$$D = \sqrt{\sum_j^M \left( E_j + ZPVE_j + \Delta_0^T H_j - \left( \sum_i^N n_i h_i \right)_j - \Delta_f H^\circ_{exp\,j} \right)^2}. \qquad (4)$$

If we let

$$C_j = E_j + ZPVE_j + \Delta_0^T H_j - \Delta_f H^\circ_{exp\,j}, \qquad (5)$$

then the discrete value of Eq. (4) can be written as

$$D = \sqrt{\sum_j^M \left( C_j - \sum_i^N n_i h_i \right)^2}. \qquad (6)$$

For the $j$th molecule, $C_j$ can be estimated uniquely from a comparison of values found by high-precision theoretical calculation and experimental results in the literature. Thus, the discrete value depends on $h_i$. It can be seen from Table 1 that the value ranges for $h_C$ and $h_H$ are from 38.00 to 39.00 a.u. and from 0.50 to 0.60 a.u., respectively. The best values for $h_C$ and $h_H$ can be obtained by a discrete least squares method, and the flow chart is shown in Fig. 1. A group of 30 hydrocarbon molecules for which the experimental values of $\Delta_f H^\circ_{exp}$ are known (Table S1, cf. Electronic Supplementary Material, ESM), was chosen to fit the values of $h_C$ and $h_H$. In this way, the values of 38.0598 a.u. and 0.5816 a.u. were determined for $h_C$ and $h_H$, respectively.

## 2.2 Accurate single-point energy from CBH

The detailed introduction and applications for the CBH approach developed by Ramabhadran and Raghavachari can be found in the literature [24]. Here we just present a short summary of this method and develop it further to accurately calculate the single-point energy of PAH molecules at the CCSD(T)/CBS level.
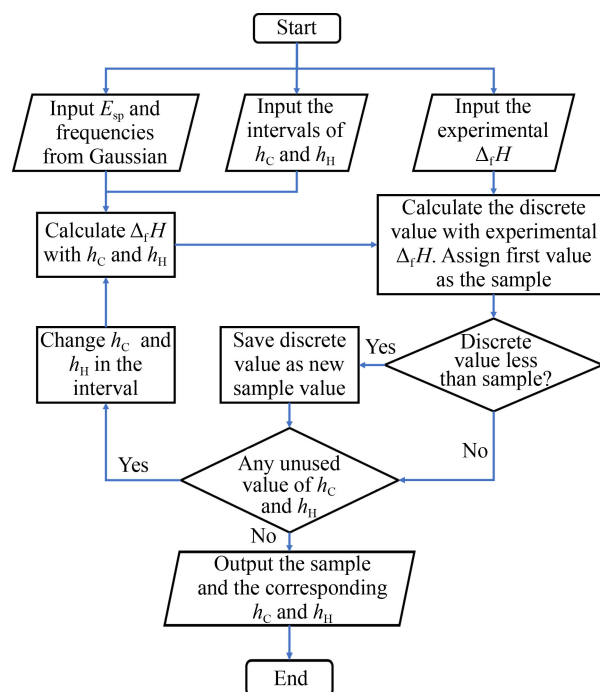


**Fig. 1** Flow chart for calculating the values of $h_C$ and $h_H$ by the discrete least squares method.

CBH is a structure-based approach in which the connectivity is used to construct hierarchies with several rungs. The molecules in the CBH rung alternate between being atom-centered and bond-centered and are saturated by adding hydrogen molecules. The number of hydrogen molecules is equal to the number of covalent bonds between heavy atoms. The simplest rung is CBH-0, an atom-centered rung. This is followed by CBH-1, a bond-centered rung, then CBH-2, the atom-centered rung with one directly-connected bond, CBH-3, the bond-centered rung with one directly-connected bond, and CBH-4, the atom-centered rung with two directly-connected bonds [24]. The higher rungs are reserved for the more complete chemical environments.

For the CBH approach, the reaction energy of $\Delta E$ for a given reaction

$$M + aX \rightarrow bY + cZ \qquad (7)$$
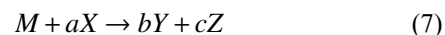
at any CBH-$n$ can be represented by

$$\Delta E_{CBH-n} = cE_Z + bE_Y - aE_X - E_M = \sum_i^F K_i E_i - E_M, \qquad (8)$$

where $E_M$ is the energy of the parent molecule, $E_i$ is the energy of each fragment, $K_i$ is the coefficient of each fragment, and $F$ is the number of species for fragments. CBH schemes have the features of isodesmic reactions that preserve the chemical environments of bond and hybridization types between reactants and products. Energy differences between high- and low-precision theoretical methods mainly arise from the calculations of electron correlations. Due to the characteristic of

additivity, these electron correlations can be cancelled for a specified isodesmic reactions, making the reaction enthalpies from high- and low-precision methods approximately equal [24], i.e.,

$$\Delta E_{\text{CBH}-n}^{\text{Low}} \approx \Delta E_{\text{CBH}-n}^{\text{High}}. \tag{9}$$

From Eqs. (8) and (9), the highly accurate energy of a larger parent molecule can be written as

$$E_M^{\text{High}} \approx E_M^{\text{Low}} + \sum_i^F K_i(E_i^{\text{High}} - E_i^{\text{Low}}). \tag{10}$$

Thus, the accurate energies of larger molecules using a high-precision method can be derived by low-precision calculations of larger molecules together with system error of small fragments between high- and low-precision methods. Thus, it is straightforward to use CBH schemes to arrive at an extrapolated energy calculation using a high-precision method for larger molecules. As summarized in Ref. [24], the protocol of any given CBH-$n$ rung ($n > 1$) is based on the following processes: (i) generate the CBH reaction scheme for $M$ and obtain the corresponding fragments, (ii) optimize geometries of the parent molecule $M$ and the fragments at a reasonable level of theory, (iii) calculate the energies at high- and low-precision on the fragments to get $E_i^{\text{High}}$ and $E_i^{\text{Low}}$, respectively, (iv) perform a low-precision calculation for $M$ to obtain $E_M^{\text{Low}}$, and (v) obtain the extrapolated high-precision energy of $M$ according to Eq. (10). It has been stated that the CBH-3 rung is not appropriate for PAHs molecules [24], because the fragments of the CBH-3 rung cannot reserve the complete chemical environments of PAHs due to the lack of consideration of the delocalization energies, leading to unbalanced reaction energies. To overcome this problem, we put forward a scheme for a CBH-4 rung that can better preserve the chemical environment of PAHs in this work. In addition, the small fragments used in the CBH protocol are limited for a given rung, allowing the energetic properties to be accurately calculated and integrated into a database. It is anticipated that this approach will increase computational efficiency.

## 3    Computational details

The geometries of 50 PAHs (Fig. S1, cf. ESM) and their 19 fragments used in the proposed CBH-4 rung were optimized by density functional theory using B3LYP hybrid functional [27] with 6-31G(2df,p) basis set. It has been proved B3LYP/6-31G(2df,p) level can give reliable geometries for CBH schemes [24]. Vibrational analyses were performed to identify the characteristics of the stationary points and provide zero-point energy corrections. The frequency scaling factor of 0.9854 was applied for *ZPVE* and thermal correction. No imaginary frequencies were detectable. Seven different functionals

were tested by Ramabhadran and Raghavachari [24]. They found the M06-2X functional can achieve the target accuracy for CBH scheme. Thus, M06-2X/6-311++G** [28] and CCSD(T)/CBS [29] methods were chosen to calculate single point energies at low- and high-precision level of theory, respectively. All electronic structures were calculated using Gaussian 09 software package [30].

Figure 1 illustrates the flow chart for calculating the values of $h_C$ and $h_H$ by the discrete least squares method described in Section 2. The inputs are the intervals of $h_C$ and $h_H$, single-point energies and frequencies, as well as experimental values of standard enthalpies of formationfor each molecule. Nested loops are then used to solve the least-squares problem. The minimum discrete value can be obtained by constantly adjusting $h_C$ and $h_H$ within the given intervals. The final output is the minimum discrete values of $h_C$ and $h_H$.

## 4    Results and discussion

In this work, the standard enthalpy of formation for 50 PAHs at the CCSD(T)/CBS level was investigated. According to the CBH strategy, the reactant fragments for the CBH-4 rung are in turn the same as the product fragments for the CBH-3 rung. The products of fragments for CBH-4 rung are then obtained by preserving the atom-centered rung with its two directly connected bonds [24]. For these PAHs, a total of 19 fragments (Fig. 2) are identified. It should be noted (Table S2, cf. ESM) that there are *cis* and *trans* isomers in these fragments during the geometric optimization.

Figure 3 shows the optimized possible structures of the *cis* and *trans* isomers with their single point energies. It is found the use of different *cis* and *trans* isomers will lead to energy differences, which affects the accuracy of the standard enthalpy of formation for the parent molecule. To preserve the most complete chemical environment, the appropriate structures from the PAHs must be selected as the fragments for the CBH-4 rung.
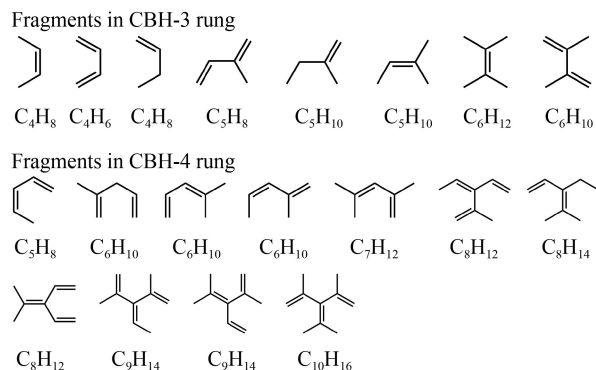


**Fig. 2**  The geometric structures of 19 fragments used in the CBH-4 rung scheme.
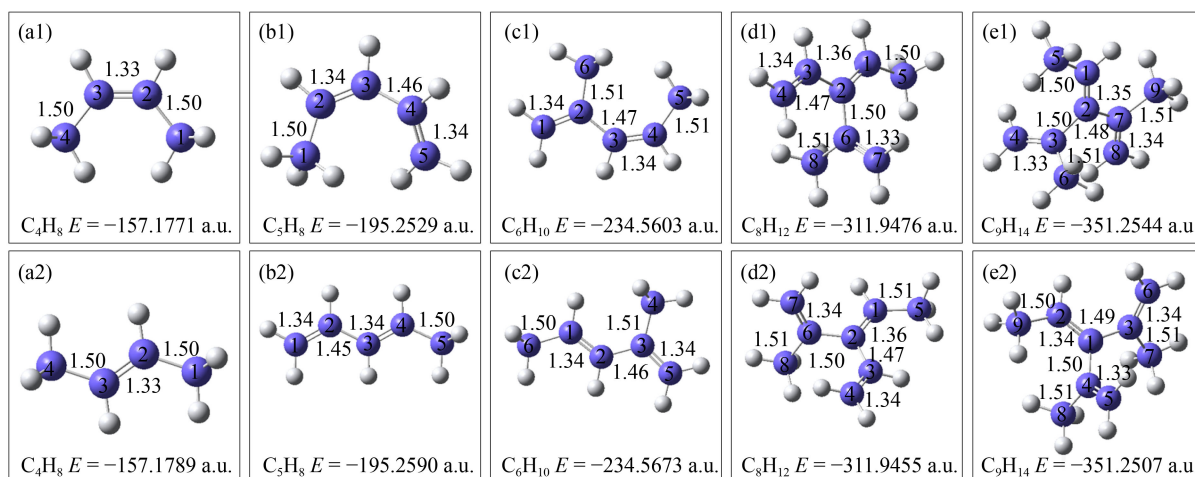
**Fig. 3** The optimized *cis* and *trans* isomers in the CBH-4 reaction scheme with their energies (unit in a.u.). (a1 and a2), (b1 and b2), (c1 and c2), (d1 and d2), and (e1 and e2) are the *cis* and *trans* isomers of $C_4H_8$, $C_5H_8$, $C_6H_{10}$, $C_8H_{12}$, and $C_9H_{14}$, respectively. The bond lengths are in Å. The isomers on the top row are used as the CBH fragments.

To ensure the accuracy of the extrapolated energies of the CBH-4 rung of the parent molecule, three PAHs (benzene, naphthalene, and 1,3-cyclopentadiene) were chosen for high-precision CCSD(T)/CBS calculation. Table 2 gives the obtained energies using both the CBH-4 and the CCSD(T)/CBS methods. As can be seen, the extrapolation energies of the CBH-4 rung are in good agreement with those of the CCSD(T)/CBS calculation, with energy deviations of less than 1 kcal·mol$^{-1}$.

Then, the values of the standard enthalpy of formation for 50 PAHs were calculated based on Eq. (1) with the single-point energies from the CBH-4 rung and the fitting values of $h_C$ and $h_H$. Table 3 lists the calculated standard enthalpies of formation, together with experimental results from the literature [31,32] and theoretical predictions derived from the *ab initio* thermochemistry calculations using optimal-balance models with isodesmic corrections (ATOMIC) protocol [33] and GA method [34]. Here, ATOMIC is a fixed-recipe composite protocol for larger molecules that can achieve high-precision calculations through consistent *ab initio* of Pople's BS isodesmic reaction scheme [35]. Figure 4 shows our calculated values of the standard enthalpy of formation for 13 PAHs (benzene, naphthalene, azulene, acenaphthylene, anthracene, phenanthrene, pyrene, fluoranthene, chrysene, triphenylene, perylene, benzo[c]phenanthrene and coronene) are in line with the calculated results from ATOMIC and in good agreement with experimental findings, with the errors of less than 1 kcal·mol$^{-1}$, whereas the GA method

failed to accurately reproduce standard enthalpies of formation for PAHs containing more than three aromatic rings. But there are discrepancies with the values for pyracyclene, naphthacene, benz[a]anthracene, corannulene and fluorine. The differences of the standard enthalpies of formation between experimental findings [31,32] and high-precision calculations were analyzed in reference [36], which reveals that the experimentally derived the standard enthalpies of formation are questionable for those PAHs.

It was also found that the isomers of PAHs have a noticeable effect on the standard enthalpy of formation. For $C_{26}H_{16}$ isomers, the deviation between the standard enthalpies of formation between naphtha[1,2-b]triphenylene and hexacene is up to 30 kcal·mol$^{-1}$. The GA method is again unable to provide a good description for the isomer. For example, for naphtho[1,2-b]chrysene and benzo[h]pentaphene, there are 21 kcal·mol$^{-1}$ differences between the standard enthalpies of formation, while the GA method gives identical values. This arises because the additional groups and compensatory ring structures used in the GA method are the same for these two PAHs.

The energetic properties of the 19 fragments listed in Table S2 can be integrated into a database for future use, which will increase computational efficiency. Overall, the proposed extension to the CBH scheme with a discrete correction of atomization energy is a high-precision and efficient calculation method for the standard enthalpies of formation of PAHs.

## 5  Conclusions

A high-precision and efficient method based on the CBH strategy with a discrete correction of atomization energy was developed and used to obtain the accurate values of the standard enthalpy of formation for PAHs. The CBH

**Table 2** Single-point energies at CBH-4 and CCSD(T)/CBS methods and their corresponding deviations

| Chemical name | Single-point energies/a.u. | | Energy deviations/ (kcal·mol$^{-1}$) |
| --- | --- | --- | --- |
|  | CBH-4 | CCSD(T)/CBS |  |
| Benzene | −231.9207 | −231.9212 | −0.31 |
| Naphthalene | −385.3468 | −385.3481 | −0.82 |
| 1,3-Cyclopentadiene | −193.8327 | −193.8336 | −0.56 |

**Table 3** Enthalpies of formation (298 K) from different methods and available experimental values

| No. | Molecule | Chemical name | Enthalpy of formation/(kcal·mol⁻¹) | | | |
|---|---|---|---|---|---|---|
| | | | Expt. | GA [a] | ATOMIC [b] | This work [c] |
| 1 | $C_6H_6$ | Benzene | 19.81 [d] | 19.8 | 20.10 ± 0.9 | 19.83 |
| 2 | $C_{10}H_8$ | Naphthalene | 35.85 [e] | 35.02 | 35.70 ± 1.6 | 35.38 |
| 3 | $C_{10}H_8$ | Azulene | 73.61 [e] | 85.03 | 71.80 ± 1.4 | 72.96 |
| 4 | $C_{12}H_8$ | Acenaphthylene | 62.91 [e] | 51.73 | 62.80 ± 2.1 | 63.55 |
| 5 | $C_{13}H_{10}$ | Fluorene | 42.23 [e] | | 45.00 ± 2.7 | 45.01 |
| 6 | $C_{13}H_{10}$ | 1H-Phenalene | | | | 50.13 |
| 7 | $C_{14}H_8$ | Pyracyclene | 97.66 [e] | 68.43 | 103.40 ± 2.5 | 106.9 |
| 8 | $C_{14}H_{10}$ | Anthracene | 54.83 [e] | 50.24 | 54.70 ± 2.5 | 54.74 |
| 9 | $C_{14}H_{10}$ | Phenanthrene | 48.28 [e] | 48.04 | 49.00 ± 3.1 | 47.28 |
| 10 | $C_{16}H_{10}$ | Pyrene | 53.90 [e] | 50.31 | 53.80 ± 2.9 | 54.04 |
| 11 | $C_{16}H_{10}$ | Fluoranthene | 69.65 [e] | 57.02 | 68.20 ± 3.4 | 69.43 |
| 12 | $C_{17}H_{12}$ | 1H-Benz[de]anthracene | | | | 42.99 |
| 13 | $C_{18}H_{12}$ | Naphthacene | 81.88 [e] | 65.46 | 75.70 ± 4.0 | 78.16 |
| 14 | $C_{18}H_{12}$ | Benz[a]anthracene | 69.38 [e] | 63.26 | | 65.98 |
| 15 | $C_{18}H_{12}$ | Chrysene | 64.22 [e] | 61.06 | 64.00 ± 4.1 | 64.07 |
| 16 | $C_{18}H_{12}$ | Benzo[c]phenanthrene | 69.60 [e] | 63.26 | 69.80 ± 3.8 | 70 |
| 17 | $C_{18}H_{12}$ | Triphenylene | 64.56 [e] | 58.86 | 63.60 ± 4.2 | 64.03 |
| 18 | $C_{20}H_{10}$ | Corannulene | 110.33 [e] | 118.57 | 115.40 ± 4.1 | 117.6 |
| 19 | $C_{20}H_{12}$ | Perylene | 76.08 [e] | 67.73 | 75.20 ± 4.5 | 76.75 |
| 20 | $C_{22}H_{14}$ | Pentacene | | 80.69 | | 101.46 |
| 21 | $C_{22}H_{14}$ | Benzo[a]naphthacene | | 78.49 | | 87.48 |
| 22 | $C_{22}H_{14}$ | Pentaphene | | 78.49 | | 83.91 |
| 23 | $C_{22}H_{14}$ | Picene | | 74.09 | | 78.41 |
| 24 | $C_{22}H_{14}$ | Benzo(c)chrysene | | 76.29 | | 83.3 |
| 25 | $C_{22}H_{14}$ | Naphtho[1,2-a]anthracene | | 78.49 | | 89.09 |
| 26 | $C_{22}H_{14}$ | Dibenzo[c,g]phenanthrene | | 78.49 | | 88.27 |
| 27 | $C_{22}H_{14}$ | Benzo[ghi]perylene | | 63.39 | | 71.35 |
| 28 | $C_{22}H_{14}$ | Benzo[b]chrysene | | 76.29 | | 83.36 |
| 29 | $C_{22}H_{14}$ | Benzo(g)chrysene | | 74.09 | | 83.3 |
| 30 | $C_{22}H_{14}$ | Dibenz[a,j]anthracene | | 76.29 | | 79.9 |
| 31 | $C_{22}H_{14}$ | Dibenz[a,h]anthracene | | 76.29 | | 79.68 |
| 32 | $C_{24}H_{12}$ | Coronene | 70.51 [e] | 65.66 | 69.70 ± 5.1 | 70.07 |
| 33 | $C_{26}H_{16}$ | Dibenzo[g,p]chrysene | | 87.11 | | 105.4 |
| 34 | $C_{26}H_{16}$ | Hexahelicene | | 93.71 | | 103.45 |
| 35 | $C_{26}H_{16}$ | Dibenzo[a,c]naphthacene | | 89.31 | | 104.03 |
| 36 | $C_{26}H_{16}$ | Benzo[a]pentacene | | 93.71 | | 112.18 |
| 37 | $C_{26}H_{16}$ | Naphtho[1,2-b]triphenylene | | 87.11 | | 95.1 |
| 38 | $C_{26}H_{16}$ | Hexaphene | | 93.71 | | 106.91 |
| 39 | $C_{26}H_{16}$ | Benzo[c]pentaphene | | 91.51 | | 97.6 |
| 40 | $C_{26}H_{16}$ | Dibenzo[b,k]chrysene | | 91.51 | | 102.87 |
| 41 | $C_{26}H_{16}$ | Naphtho[2,3-g]chrysene | | 89.31 | | 103.89 |
| 42 | $C_{26}H_{16}$ | Benzo[b]picene | | 89.31 | | 97.46 |
| 43 | $C_{26}H_{16}$ | Naphtho[2,1-a]naphthacene | | 91.51 | | 105.15 |
| 44 | $C_{26}H_{16}$ | Benzo[h]pentaphene | | 89.31 | | 100.49 |
| 45 | $C_{26}H_{16}$ | Naphtho[1,2-b]chrysene | | 89.31 | | 121.59 |
| 46 | $C_{26}H_{16}$ | Naphtho[1,2-a]naphthacene | | 93.71 | | 109.69 |
| 47 | $C_{26}H_{16}$ | Dibenzo[a,j]naphthacene | | 91.51 | | 100.05 |
| 48 | $C_{26}H_{16}$ | Hexacene | | 95.91 | | 124.12 |
| 49 | $C_{26}H_{16}$ | Naphtho[2,1-b]chrysene | | 89.31 | | 93.15 |
| 50 | $C_{28}H_{14}$ | Phenanthro[1,10,9,8-opqra]perylene | | 76.48 | | 115.82 |

The chemical structures for each species are listed in Fig. S1. a) From GA method of reaction mechanism generator [37]; b) from ATOMIC method [33]; c) this work using CBH-4 with the discrete correction; d) from experimental findings [31]; e) from Ref. [32].
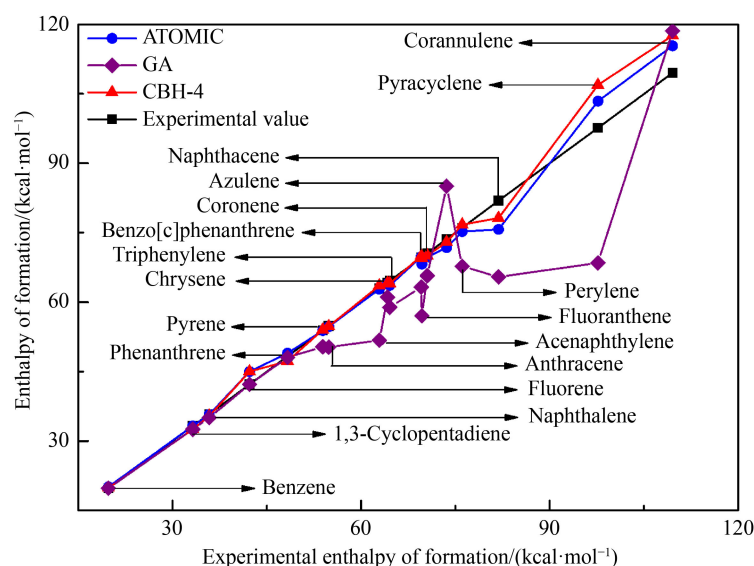
**Fig. 4** X-axis using the value of experimental standard enthalpy of formation to represent the species. The experimental value is shown in Table 3. Y-axis are the values of standard enthalpies of formation from different methods.

scheme can broaden the scope of application for larger molecules to achieve a high-precision calculation of the energetic properties of larger molecules at the CCSD(T)/CBS level. The CBH-4 rung was chosen to ensure the preservation of the conjugate environment of PAHs. Values for $h_C$ and $h_H$ of 38.0598 a.u. and 0.5816 a.u., respectively, were determined using a discrete least-squares method. Based on the CBH strategy, the energy properties of 19 fragments were determined by considering *cis* and *trans* isomers to create a CBH database. The obtained values of the standard enthalpies of formation for 50 aromatic molecules were in good agreement with the available experimental results and high-precision theoretical values derived using the ATOMIC protocol. In addition, the choice of isomer was found to have a noticeable effect on the calculated standard enthalpies of formation.

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