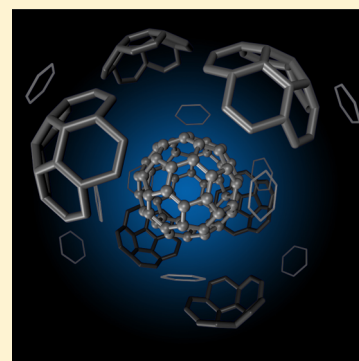


Evaluation of the Heats of Formation of Corannulene and C₆₀ by Means of High-Level Theoretical Procedures

Amir Karton,^{*,†} Bun Chan,^{*,†} Krishnan Raghavachari,^{*,‡} and Leo Radom^{*,†}[†]School of Chemistry and ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, University of Sydney, Sydney, NSW 2006, Australia[‡]Department of Chemistry, Indiana University, Bloomington, Indiana 47408, United States

S Supporting Information

ABSTRACT: In this study, we address the issues associated with predicting usefully accurate heats of formation for moderately-sized molecules such as corannulene and C₆₀. We obtain a high-level theoretical heat of formation for corannulene through the use of reaction schemes that conserve increasingly larger molecular fragments between the reactants and products. The reaction enthalpies are obtained by means of the high-level, ab initio W1h thermochemical protocol, while accurate experimental enthalpies of formation for the other molecules involved in the reactions are obtained from the Active Thermochemical Tables (ATcT) network. Our best theoretical heat of formation for corannulene ($\Delta_f H^\circ_{298}[\text{C}_{20}\text{H}_{10}(\text{g})] = 485.2 \pm 7.9 \text{ kJ mol}^{-1}$) differs significantly from the currently accepted experimental value ($\Delta_f H^\circ_{298}[\text{C}_{20}\text{H}_{10}(\text{g})] = 458.5 \pm 9.2 \text{ kJ mol}^{-1}$), and this suggests that re-examination of the experimental data may be in order. We have used our theoretical heat of formation for corannulene to obtain a predicted heat of formation of C₆₀ through reactions that involve only corannulene and planar polyacenes. Current experimental values span a range of $\sim 200 \text{ kJ mol}^{-1}$. Our reaction enthalpies are obtained by means of double-hybrid density functional theory in conjunction with a large quadruple- ζ basis set, while accurate experimental heats of formation (or our theoretical value in the case of corannulene) are used for the other molecules involved. Our best theoretical heat of formation for C₆₀ ($\Delta_f H^\circ_{298}[\text{C}_{60}(\text{g})] = 2521.6 \text{ kJ mol}^{-1}$) suggests that the experimental value adopted by the NIST thermochemical database ($\Delta_f H^\circ_{298}[\text{C}_{60}(\text{g})] = 2560 \pm 100 \text{ kJ mol}^{-1}$) should be revised downward.



1. INTRODUCTION

Aromatic bowl-shaped hydrocarbons have attracted considerable attention ever since the remarkable synthesis of the smallest geodesic polyarene (corannulene, Figure 1) by Barth and Lawton in 1966.¹ Ten years later, the X-ray crystal

structure of corannulene was determined, unambiguously confirming its bowl-shaped geometry.² Following the development of efficient procedures for synthesizing macroscopic amounts of corannulene by Scott et al.³ and Siegel et al.,⁴ its heat of formation was determined from microbomb combustion calorimetry measurements ($\Delta_f H^\circ_{298}[\text{C}_{20}\text{H}_{10}(\text{g})] = 463.7 \text{ kJ mol}^{-1}$).⁵ Recently, Roux et al.⁶ have critically evaluated the available experimental data for a large number of polycyclic aromatic hydrocarbons (PAHs) and have revised the value for corannulene slightly downward to $\Delta_f H^\circ_{298}[\text{C}_{20}\text{H}_{10}(\text{g})] = 458.5 \pm 9.2 \text{ kJ mol}^{-1}$. The NIST WebBook has adopted their value.⁷ The very recent production of corannulene on the kilogram scale^{4c} is likely to herald the beginning of yet another chapter in the chemistry of this intriguing molecule.

In the present work, we obtain an accurate theoretical heat of formation for corannulene (and other PAHs) through the use of reactions that conserve the chemical environments of the reactants and products to various degrees. Specifically, the following types of reactions are considered:

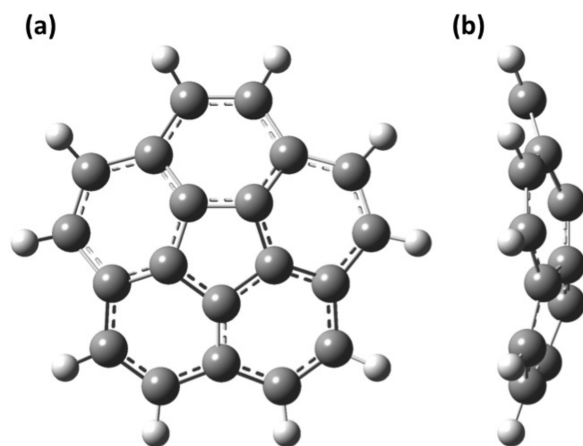
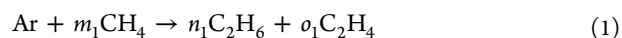
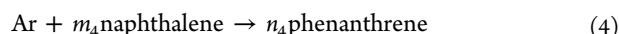
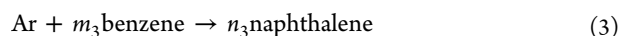
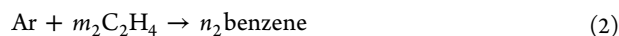


Figure 1. B3-LYP/6-31G(2df,p) optimized structure of corannulene: (a) top view and (b) side view.

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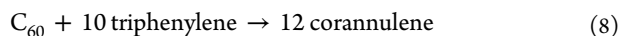
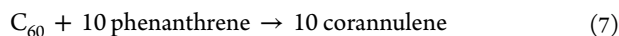
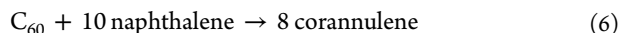
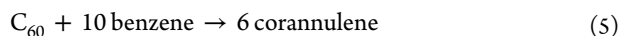




where the aromatic molecules Ar in reactions 1x–4x are naphthalene ($x = a$), phenanthrene ($x = b$), triphenylene ($x = c$), or corannulene ($x = d$).⁸ The reaction enthalpies are obtained by means of the high-level, ab initio W1h thermochemical protocol, while accurate experimental heats of formation for CH₄, C₂H₄, C₂H₆, and benzene are taken from the Active Thermochemical Tables (ATcT) network of Ruscic and co-workers.⁹ Our best theoretical heats of formation for naphthalene, phenanthrene, and triphenylene are in good agreement with the experimental values compiled by Roux et al.⁶ However, a discrepancy of 26.7 kJ mol⁻¹ between our best predicted heat of formation for corannulene and the experimental value indicates that re-examination of the experimental value may be in order.

The fundamental importance of buckminsterfullerene¹⁰ as a molecular allotrope of carbon and as a key building block in nanotechnology and material science is clearly evident to any chemist.¹¹ However, its heat of formation has been a matter of controversy for the past two decades. An accurate heat of formation for C₆₀ is important from an experimental point of view, e.g., for the prediction of formation energies and relative stabilities of fullerenes, and also from a theoretical point of view, e.g., for the validation of computationally cost-effective procedures such as density functional theory (DFT), semi-empirical molecular orbital theory, or molecular mechanics. The latter point is of importance since high-level, ab initio calculations are simply too demanding computationally at the present time to allow detailed investigation of the myriad of interesting fullerene structures and even the determination of the lowest energy isomer of a single-sized fullerene.

In the present work, we make use of our theoretical heat of formation for corannulene to obtain the heat of formation of C₆₀ via reactions that involve only corannulene and planar polyacenes, specifically:



Thus, we use reactions that, in addition to conserving the numbers of each formal bond type and the number of carbon atoms in each hybridization state and hapticity (secondary and tertiary), conserve some of the unique chemical features present in C₆₀ (such as curvature in the π system resulting in a significant strain energy associated with pentagons completely surrounded by hexagons). A number of studies have previously shown that it is important to conserve such features when calculating the heats of formation of fullerenes and PAHs.^{12,13} The reaction energies involving C₆₀ are calculated by means of double-hybrid DFT procedures in conjunction with a quadruple- ζ basis set, while accurate experimental (or theoretical) heats of formation are used for the other molecules involved. Our best theoretical heat of formation for C₆₀ ($\Delta_f H^\circ_{298}[\text{C}_{60}(\text{g})] = 2521.6 \text{ kJ mol}^{-1}$) is within the limits of the error bars of the experimental value adopted by the NIST

thermochemical database ($2560 \pm 100 \text{ kJ mol}^{-1}$). However, it suggests that the NIST value should be revised downward.

2. COMPUTATIONAL DETAILS

The geometries and harmonic vibrational frequencies of all structures have been obtained at the B3-LYP/6-31G(2df,p) level of theory. Zero-point vibrational energies (ZPVEs) and enthalpic temperature corrections ($H_{298} - H_0$) have been obtained from such calculations, within the rigid-rotor harmonic oscillator (RRHO) approximation, and have been scaled using literature scaling factors (namely, 0.9861 for the ZPVE and 0.9909 for the $H_{298} - H_0$ correction).¹⁴ All geometry optimizations and frequency calculations were performed using the Gaussian 09 program suite.¹⁵

2.1. Benchmark CCSD(T) Reaction Energies from the W1h Thermochemical Protocol for Reactions 1–4. In order to obtain reliable reaction energies for reactions 1–4, calculations have been carried out using the high-level, ab initio W1h procedure with the Molpro 2010.1 program suite.¹⁶ In the W1h variant of W1, the diffuse functions are omitted from carbon. This is of little (or no) thermochemical consequence for neutral alkanes, but it does substantially reduce computer resource requirements.^{17,18} W1h represents a layered extrapolation to the relativistic, all-electron CCSD(T) (coupled cluster with singles, doubles, and quasiperturbative triple excitations) basis-set-limit energy, and can achieve subchemical accuracy (i.e., it is associated with a mean absolute deviation from accurate atomization energies of 2.0 kJ mol⁻¹) for molecules whose wave functions are dominated by dynamical correlation.^{18,19}

In the following discussion, the notation cc-pV{L–1,L}Z indicates extrapolation from the standard correlation-consistent cc-pV(L–1)Z and cc-pVLZ basis sets,²⁰ using the two-point extrapolation formula $E(L) = E_\infty + A/L^\alpha$ (where L is the highest angular momentum represented in the basis set). The computational protocol of the W1h method has been specified and rationalized in detail previously.^{17,18,21} In brief, the Hartree–Fock (HF) component is extrapolated from the cc-pV{T,Q}Z basis-set pair with $\alpha = 5$. We note that the present work uses more accurate HF/cc-pV{Q,5}Z energies, but the differences between the HF/cc-pV{T,Q}Z and HF/cc-pV{Q,5}Z components amount to less than $\sim 1 \text{ kJ mol}^{-1}$ for the reactions considered (Table S1 of the Supporting Information). The CCSD valence correlation energy is extrapolated from the cc-pV{T,Q}Z basis-set pair with $\alpha = 3.22$. The (T) valence correlation energy, which converges faster to the basis-set limit, is extrapolated from the cc-pV{D,T}Z basis-set pair with $\alpha = 3.22$. The inner-shell, scalar-relativistic, and diagonal-Born–Oppenheimer corrections are calculated as recommended in ref 22. Specifically, the CCSD inner-shell contribution is calculated with the core–valence weighted correlation-consistent cc-pwCVTZ basis set of Peterson and Dunning,²³ and the (T) inner-shell contribution is obtained using the same basis set without the f functions on C and d functions on H. This basis set is denoted cc-pwCVTZ(no f). The scalar-relativistic correction is obtained as the difference between nonrelativistic CCSD(T)/cc-pVDZ and relativistic CCSD(T)/cc-pVDZ-DK calculations.²² The diagonal-Born–Oppenheimer correction (DBOC) is calculated at the HF/cc-pVTZ level of theory.

For the largest systems involved in reactions 1x–4x, namely, triphenylene ($x = c$) and corannulene ($x = d$), the valence CCSD/cc-pVQZ calculations proved to be too taxing even for our most powerful machines (8 core, 96 GB of RAM, and 1 TB

hard drive). Therefore, in these calculations, the *f* functions were omitted from the hydrogen basis set, the resulting truncated basis set being denoted cc-pVQZ(no *f* on H). In section 3.2, we show that, for the reactions involving naphthalene and phenanthrene that conserve sufficiently large molecular fragments on the two sides, this approximation does not lead to a significant deterioration of performance. Specifically, the CCSD component is affected by 0.3 kJ mol⁻¹ (for reaction 2a) and by 0.1 kJ mol⁻¹ (for reaction 3b).

It is of interest to estimate whether post-CCSD(T) contributions are likely to be significant for the theoretical heats of formation obtained from reactions 1–4. The percentage of the atomization energy accounted for by parenthetical connected triple excitations, %TAE_e[(T)], has been shown to be a reliable energy-based diagnostic indicating the importance of post-CCSD(T) contributions.²⁴ The %TAE_e[(T)] values for the species involved in reactions 1–4 are given in Table S2 of the Supporting Information. The %TAE_e[(T)] values for the aromatic hydrocarbons (2.0–2.6%) indicate mild post-CCSD(T) contributions.²⁴ For example, for aromatic systems that are associated with similar %TAE_e[(T)] values (such as benzene, pyridine, and furan), post-CCSD(T) contributions to the atomization energy range from ~1 to 4 kJ mol⁻¹.²⁵ Nevertheless, it should be pointed out that post-CCSD(T) contributions to reaction energies (e.g., reactions 1–4) should be smaller than for atomization reactions (see also discussion in ref 21). Thus, the predicted theoretical values obtained in the present work for naphthalene, phenanthrene, triphenylene, and corannulene via reactions 1–4 are expected to be little affected by post-CCSD(T) contributions.

2.2. Double-Hybrid Density Functional Theory Reaction Energies for Reactions 5–8. The reaction energies for the reactions that involve C₆₀ (reactions 5–8) are calculated using double-hybrid density functional theory (DHDFT),^{26,27} second-order Møller–Plesset perturbation theory (MP2), and spin-component-scaled MP2 (SCS-MP2)²⁸ procedures. The DHDFT procedures involve both HF-like exchange and MP2-like correlation and have been found to produce gas-phase thermochemical properties (such as reaction energies and enthalpies of formation) with a mean absolute deviation of <10 kJ mol⁻¹ from a wide range of accurate thermochemical determinations.^{19,26,27,29} Two DHDFT procedures are employed, the recently developed spin-component-scaled double-hybrid DSD-PBEP86²⁶ and B2GP-PLYP.²⁷ The DHDFT calculations, which inherit the slow basis-set convergence of MP2 to some degree, are carried out with the cc-pVQZ basis set. Empirical D3 dispersion corrections³⁰ are included using the Becke–Johnson³¹ potential as recommended in ref 32 (denoted by the suffix D3). The DHDFT, MP2, and SCS-MP2 calculations were performed using the Gaussian 09 program suite.¹⁵

3. RESULTS AND DISCUSSION

3.1. General Considerations When Obtaining Theoretical Heats of Formation. In order to obtain a theoretical heat of formation for a molecule (*M*) via a thermochemical cycle (such as in reactions 1–4), one has to (a) calculate the reaction enthalpy at an appropriate level of theory and (b) insert reliable experimental or theoretical heats of formation for all the species in the reaction apart from molecule *M*. Thus, when choosing an appropriate reaction, the following aspects need to be considered: (i) the extent to which molecular fragments are conserved between the reactants and products,

(ii) the level of theory at which the reaction enthalpy is calculated, and (iii) the accuracy of the available experimental or theoretical heats of formation used for the other species in the reaction. These principal considerations are now briefly discussed.

3.1.1. Conservation of Molecular Fragments on the Two Sides of the Reaction. It is well established that, for a given level of theory, the reaction energy becomes more accurate as larger molecular fragments are conserved on the two sides of the reaction due to an increasing degree of error cancellation between reactants and products.^{33,34} A systematic hierarchical scheme of reaction types that conserve the chemical environments of the reactants and products to increasing extents has been recently developed for simple hydrocarbons.³⁵ This scheme is based on increasingly conserving the number of formal bond types and the number of carbons in each hybridization state and hapticity. However, the existing scheme does not take into account chemical concepts (such as aromaticity and ring strain) that ideally should be considered when treating systems like corannulene or C₆₀.³⁵ More recently, a generalized connectivity-based hierarchical (CBH-*n*) approach has been developed.¹² The CBH-*n* scheme preserves the chemical environments of the reactants and products via connectivity-based segmentations. In principle, for a given level of theory, ascending up the reaction hierarchy results in increasingly more accurate reaction energies as larger chemical environments are balanced on the two sides of the reaction. Again, the aromatic molecules considered in this article do not easily fit under the CBH hierarchy. However, we can derive the heat of formation of corannulene using the following sequence of reactions: 1d, 2d, 3d, and 4d. The increasing balance in the bonding environments of the reactants and products in such reactions is expected to yield better error cancellation along this sequence.

3.1.2. Choosing an Appropriate Level of Theory for Calculating the Reaction Enthalpy. As mentioned, there is an inverse relationship between the level of theory at which the reaction enthalpy needs to be calculated and the degree to which the chemical environments are conserved between the reactants and products. In other words, lower levels of theory require greater cancellation of error to be useful. In the context of composite procedures, it has been demonstrated in a systematic manner that higher-level correlation effects (as well as other secondary contributions such as inner-shell-correlation, relativistic, and ZPVE contributions) cancel out to a greater extent between the reactants and products as the reaction hierarchy is traversed.^{12,21,35} In principle, an indication that the reaction enthalpy is calculated using sufficiently high levels of theory (for both the electronic and secondary energy contributions) is provided by the resultant heat of formation for molecule *M* showing relatively little variation with respect to the choice of the reaction. Clearly, this can only be true, if, in addition, sufficiently accurate experimental heats of formation are used for the other species in all cases. In the present work, the energies of the reactions (1–4) used to obtain the heat of formation of corannulene are obtained at the relativistic, all-electron, CCSD(T) basis-set limit (using the W1h procedure). We show that, when sufficiently accurate experimental heats of formation are used for the other species (i.e., reactions 1–3), the resulting heats of formation for corannulene span a narrow range of just a few kJ mol⁻¹. This suggests that the W1h level of theory is reasonable even when only a low level (CBH-1, isodesmic) reaction scheme is employed.

Table 1. Component Breakdown of the W1h Reaction Enthalpies and Predicted Theoretical Enthalpies of Formation for Naphthalene (C₁₀H₈), Phenanthrene (C₁₄H₁₀), Triphenylene (C₁₈H₁₂), and Corannulene (C₂₀H₁₀) (kJ mol⁻¹)

reaction	Δ_{HF}^a	$\Delta_{\text{CCSD}}^{b,c}$	$\Delta(\text{T})^d$	Δ_{CV}^e	Δ_{Rel}^f	Δ_{DBOC}^g	Δ_{ZPVE}^h	$\Delta(\text{H}_{298}-\text{H}_0)^h$	$\Delta_r H_{298}^{\circ i}$	$\frac{\Delta_r H_{298}^{\circ}}{[\text{Ar}(\text{g})]^{j,k}}$	exptl ^l
1a C ₁₀ H ₈ + 12CH ₄ → 6C ₂ H ₆ + 5C ₂ H ₄	409.7	33.6 (31.5)	26.6	3.6	0.1	0.5	47.1	-18.4	500.7	153.1 ± 7.9	
2a C ₁₀ H ₈ + C ₂ H ₄ → 2C ₆ H ₆	-51.8	9.7 (9.5)	3.1	-0.1	0.0	0.0	6.3	-2.8	-35.8	149.8 ± 7.7	150.6 ± 1.5
1b C ₁₄ H ₁₀ + 18CH ₄ → 9C ₂ H ₆ + 7C ₂ H ₄	596.2	57.4 (54.1)	41.5	5.4	0.1	0.8	73.9	-29.5	745.7	208.9 ± 8.0	
2b C ₁₄ H ₁₀ + 2C ₂ H ₄ → 3C ₆ H ₆	-96.1	21.6 (21.1)	6.2	-0.2	0.0	0.1	12.8	-6.2	-61.9	206.6 ± 7.8	
3b C ₁₄ H ₁₀ + C ₆ H ₆ → 2C ₁₀ H ₈	7.5	2.1 (2.2)	0.0	0.0	0.0	0.0	0.1	-0.6	9.1	208.9 ± 8.3	202.2 ± 2.3
1c C ₁₈ H ₁₂ + 24CH ₄ → 12C ₂ H ₆ + 9C ₂ H ₄	771.5	87.2	57.5	7.1	0.0	1.0	101.1	-41.4	984.1	271.2 ± 8.3	
2c C ₁₈ H ₁₂ + 3C ₂ H ₄ → 4C ₆ H ₆	-151.6	39.5	10.5	-0.3	0.0	0.1	19.6	-10.3	-92.7	268.2 ± 7.8	
3c C ₁₈ H ₁₂ + 2C ₆ H ₆ → 3C ₁₀ H ₈	3.8	10.3	1.2	0.0	-0.1	0.0	0.6	-1.9	13.9	271.5 ± 8.9	
4c C ₁₈ H ₁₂ + C ₁₀ H ₈ → 2C ₁₄ H ₁₀	-11.2	6.1	1.2	-0.1	0.0	0.0	0.4	-0.7	-4.4	258.2 ± 9.1	270.1 ± 4.4
1d C ₂₀ H ₁₀ + 30CH ₄ → 15C ₂ H ₆ + 10C ₂ H ₄	718.6	122.7	76.7	8.3	0.1	1.3	140.5	-53.7	1014.6	488.9 ± 8.5	
2d C ₂₀ H ₁₀ + 5C ₂ H ₄ → 5C ₆ H ₆	-435.3	63.1	17.9	-1.0	0.0	0.1	38.6	-14.8	-331.3	485.2 ± 7.9	
3d C ₂₀ H ₁₀ + 5C ₆ H ₆ → 5C ₁₀ H ₈	-176.3	14.4	2.4	-0.5	0.0	0.0	7.0	-0.7	-153.7	490.7 ± 10.9	
4d C ₂₀ H ₁₀ + 5C ₁₀ H ₈ → 5C ₁₄ H ₁₀	-213.9	3.8	2.5	-0.5	0.1	0.0	6.4	2.2	-199.4	457.4 ± 15.7	458.5 ± 9.2

^aExtrapolated from the cc-pVQZ and cc-pVSZ basis sets. ^bExtrapolated from the cc-pVTZ and cc-pVQZ(no f on H) basis sets. ^cThe values in parentheses are extrapolated from the cc-pVTZ and cc-pVQZ basis sets. This component is used in the final reaction energy whenever available. ^dExtrapolated from the cc-pVDZ and cc-pVTZ basis sets. ^eCCSD(T) core-valence correction obtained as CCSD/cc-pwCVTZ + (T)/cc-pwCVTZ(no f). ^fCCSD(T)/cc-pVDZ-DK scalar relativistic correction. ^gHF/cc-pVTZ DBOC correction. ^hScaled B3-LYP/6-31G(2df,p) values. ⁱOverall reaction enthalpy at 298 K. ^jTheoretical heats of formation at 298 K for Ar obtained from the reaction listed in the second column (where Ar is the first reactant listed) using the W1h reaction enthalpies and experimental heats of formation (taken from the ATcT network for CH₄, C₂H₄, C₂H₆, and C₆H₆ and from ref 6 for C₁₀H₈ and C₁₄H₁₀). ^kThe associated uncertainties are obtained using the reported experimental uncertainties and an estimated uncertainty of ±7.7 kJ mol⁻¹ for the W1h reaction enthalpies taken from ref 19. Note, however, that, in principle, the uncertainty associated with the W1h reaction enthalpies should go down in the sequence 1 → 2 → 3 → 4. ^lFrom ref 6.

3.1.3. Accuracy and Reliability of the Experimental Data Used. In order to obtain a reliable predicted heat of formation for molecule M, the experimental data used for the other molecules in the reaction need to be associated with small uncertainties. This point becomes increasingly more important as the number of these other molecules grows. Consider, for example, reaction 1c involving triphenylene, CH₄, C₂H₄, and C₂H₆, i.e., C₁₈H₁₂ + 24CH₄ → 12C₂H₆ + 9C₂H₄. An uncertainty of just ±1 kJ mol⁻¹ for each of the molecules other than triphenylene could result in an error of up to ~28 kJ mol⁻¹ (!) in the estimated heat of formation of triphenylene. However, in reaction 4c involving triphenylene, naphthalene, and phenanthrene, i.e., C₁₈H₁₂ + C₁₀H₈ → 2C₁₄H₁₀, an uncertainty of ±1 kJ mol⁻¹ for each molecule other than triphenylene would lead to a contributed uncertainty in the estimated heat of formation of triphenylene of just 2.2 kJ mol⁻¹.

It is no less imperative, however, that the uncertainties in the experimental data be reliable. The danger of relying on quoted experimental uncertainties (without theoretical confirmation) is best illustrated by the following recent example. The experimental heat of formation of tetracene was re-evaluated

in the compilation by Roux et al.,⁶ who recommended a value of $\Delta_r H_{298}^{\circ}[\text{C}_{18}\text{H}_{12}(\text{g})] = 342.6 \pm 5.9$ kJ mol⁻¹. This value was adopted by the NIST thermochemical database.⁷ However, despite the relatively modest uncertainty associated with this value, it was found in a recent theoretical investigation (using the high-level, ab initio W1-F12 procedure) that this experimental value should be revised downward by approximately ~30 kJ mol⁻¹ (!).²²

For a comparatively small set of molecules, very accurate experimental heats of formation, that are associated with *well-defined* error bars, are available from the Active Thermochemical Tables (ATcT) of Ruscic and co-workers.⁹ ATcT is a novel paradigm in thermochemistry that overcomes limitations of the traditional sequential approach by utilizing available knowledge in a very large thermochemical network. Thus, ATcT provides *accurate, reliable, and internally consistent* thermochemical values. In the present work, we use the following ATcT heats of formation: $\Delta_r H_{298}^{\circ}[\text{CH}_4(\text{g})] = -74.53 \pm 0.06$,³⁶ $\Delta_r H_{298}^{\circ}[\text{C}_2\text{H}_4(\text{g})] = 52.4 \pm 0.2$,^{37,38} $\Delta_r H_{298}^{\circ}[\text{C}_2\text{H}_6(\text{g})] = -83.76 \pm 0.17$,³⁹ and $\Delta_r H_{298}^{\circ}[\text{C}_6\text{H}_6(\text{g})] = 83.2 \pm 0.3$ kJ mol⁻¹.³⁶

For naphthalene and phenanthrene, for which ATcT values are currently not available, the values compiled by Roux et al. are used,⁶ namely, $\Delta_f H^\circ_{298}[C_{10}H_8(g)] = 150.6 \pm 1.5$ and $\Delta_f H^\circ_{298}[C_{14}H_{10}(g)] = 202.2 \pm 2.3$ kJ mol⁻¹, respectively. To increase our confidence in these values, we obtain predicted heats of formation for naphthalene and phenanthrene using reactions 2a and 2b (i.e., reactions that involve only species for which ATcT heats of formation are available). Our predicted theoretical heats of formation are in reasonably good agreement with the experimental values within overlapping uncertainties (see section 3.3). We also note that the recently reported W1-F12 heat of formation, derived from atomization energies, for naphthalene ($\Delta_f H^\circ_{298}[C_{10}H_8(g)] = 146.2$ kJ mol⁻¹) is in reasonable agreement with the experimental data.²²

3.2. Overview of the W1h Reaction Enthalpies. The component breakdown of the W1h reaction enthalpies and our resultant predicted heats of formation are gathered in Table 1. The following observations are noted when considering the sequence of reactions 1 \rightarrow 2 \rightarrow 3 \rightarrow 4: (i) The magnitude of the HF component (Δ_{HF}) can be very large (particularly for the isodesmic reaction 1) but decreases in the order 1 > 2 > 3. (ii) The magnitude of the valence CCSD correlation contribution (Δ_{CCSD}) is generally smaller than Δ_{HF} , but again decreases in the order 1 > 2 > 3 > 4. For example, for triphenylene, it is 87.2 (reaction 1c), 39.5 (reaction 2c), 10.3 (reaction 3c), and 6.1 (reaction 4c) kJ mol⁻¹. Also note that, for reactions that conserve the largest molecular fragments on the two sides of the reaction, Δ_{CCSD} is 9.5 (2a, naphthalene), 2.2 (3b, phenanthrene), 6.1 (4c, triphenylene), and 3.8 (4d, corannulene) kJ mol⁻¹. (iii) The difference between the CCSD/cc-pV{T,Q}Z component and the CCSD component extrapolated from the cc-pVTZ and cc-pVQZ (no f on H) basis sets shrinks in the same order. For example, for naphthalene, it goes down from 2.1 (reaction 1a) to 0.3 (reaction 2a) kJ mol⁻¹, while for phenanthrene it is 3.3 (reaction 1b), 0.5 (reaction 2b), and 0.0 (reaction 3b) kJ mol⁻¹. (iv) The magnitude of the valence (T) correlation contribution decreases in the order 1 > 2 > 3. Specifically, it is just 3.1 (2a, naphthalene), 0.0 (3b, phenanthrene), 1.2 (3c, triphenylene), and 2.4 (3d, corannulene) kJ mol⁻¹. (v) The magnitude of the core–valence (Δ_{CV}) correlation contribution is chemically significant for the isodesmic reaction 1 reaching up to 8.3 kJ mol⁻¹ (for corannulene). However, it is ≤ 1.0 kJ mol⁻¹ for reactions 2 and higher. (vi) The scalar relativistic (Δ_{Rel}) contributions are essentially nil for all the reactions, including the isodesmic reaction 1. (vii) DBOC contributions (Δ_{DBOC}) are basically nil for all the reactions apart from the isodesmic reaction 1, for which they reach up to 1.3 kJ mol⁻¹ (reaction 1d, corannulene). (viii) Appreciable ZPVE contributions (Δ_{ZPVE}) are obtained for the isodesmic reaction 1, ranging from 47.1 (reaction 1a, naphthalene) up to 140.5 (reaction 1d, corannulene) kJ mol⁻¹. However, they drop significantly as the reaction hierarchy is traversed. For example, for corannulene, the following ZPVE contributions are obtained: 38.6 (reaction 2d), 7.0 (reaction 3d), and 6.4 (reaction 4d) kJ mol⁻¹. (ix) Finally, we note that, for a given reaction type (1, 2, 3, or 4), the HF, correlation CCSD and (T), and CV components tend to increase in the order Ar = naphthalene, phenanthrene, triphenylene, and corannulene.

3.3. Predicted Heat of Formation for Corannulene. The differences between the theoretical heats of formation obtained from the various reactions (1–4) span relatively narrow ranges (Table 1). Specifically, the ranges are 3.3

(naphthalene), 2.3 (phenanthrene), 3.3 (triphenylene), and 5.5 (corannulene) kJ mol⁻¹ (excluding reaction 4, the main outlier for triphenylene and corannulene, due to the uncertainty in the experimental heat of formation of phenanthrene, vide infra). As discussed in section 3.1, this suggests that the W1h level used for calculating the reaction energies is sufficiently high for obtaining reliable theoretical heats of formation. In light of the very narrow error bars associated with the experimental enthalpies of formation obtained from the ATcT network (≤ 0.3 kJ mol⁻¹), we will use reaction 2 for obtaining the most reliable theoretical estimates. Our results for naphthalene, phenanthrene, and triphenylene obtained using reaction 2 are in good to excellent agreement with the experimental values of Roux et al.⁶ Specifically, the deviations (theory–experiment) are -0.8 (naphthalene), 4.4 (phenanthrene), and -1.9 (triphenylene) kJ mol⁻¹. However, for corannulene, our best predicted heat of formation (485.2 ± 7.9 kJ mol⁻¹) is higher than the experimental value⁶ (458.5 ± 9.2 kJ mol⁻¹) by 26.7 kJ mol⁻¹. This discrepancy between theory and experiment exceeds the sum of the respective uncertainties and suggests that a re-examination of the experimental value would be desirable.

The heats of formation obtained from reaction 4 (for triphenylene and corannulene) differ significantly from the heats of formation obtained from reactions 1–3 (Table 1). In particular, reactions 4c and 4d result in heats of formation that are lower by 10.0 (triphenylene) and 27.8 (corannulene) kJ mol⁻¹ than our preferred values (obtained from reaction 2, Table 1). These deviations are consistent with the discrepancy of 4.4 kJ mol⁻¹ between our best theoretical value (obtained from reaction 2b) and the experimental value for phenanthrene, and with the number of phenanthrenes involved in reactions 4c and 4d (i.e., two and five phenanthrenes, respectively).

Finally, we note that the uncertainties associated with the theoretical heats of formation are obtained using an estimated uncertainty for the W1h reaction energies of 7.7 kJ mol⁻¹ (taken from ref 19), which is assumed to be the same for all the reactions (1–4). The fact that the uncertainty in the W1h reaction energies is expected to decrease as the reaction hierarchy is traversed, i.e., along the sequence 1 \rightarrow 2 \rightarrow 3, is thus not reflected in the uncertainties attached to the theoretical heats of formation.

3.4. Heat of Formation of C₆₀. Having assessed the reliability of the experimental heats of formation for naphthalene, phenanthrene, and triphenylene and having obtained a reliable theoretical heat of formation for corannulene paves the way for calculating the heat of formation for C₆₀ via reactions 5–8. That is, we can use reactions that, in addition to conserving the numbers of each formal bond type and number of carbon atoms in each hybridization state and hapticity (secondary and tertiary), also conserve some of the unique chemical features present in C₆₀ (such as curvature in the π system and the strain energy associated with pentagons surrounded by hexagons).

3.4.1. Review of Existing Experimental Data for C₆₀. Following the development of an efficient procedure for synthesizing macroscopic amounts of buckminsterfullerene by arc vaporization of graphite in 1990,⁴⁰ a number of experimental determinations of the heat of formation of C₆₀ using microcombustion calorimetry techniques were reported. The first measurement was carried out by Beckhaus et al. in 1992,⁴¹ who reported a standard heat of formation in the gas-phase ($\Delta_f H^\circ_{298}[C_{60}(g)]$) of 2464 ± 7 kJ mol⁻¹.^{42,43} The same

Table 2. DSD-PBEP86-D3/cc-pVQZ Reaction Energies for Reactions 5–8 and Predicted Theoretical Enthalpies of Formation for C₆₀ (kJ mol⁻¹)

	reaction	ΔE_e^a	$\Delta D3^b$	$\Delta ZPVE^c$	$\Delta(H_{298}-H_0)^c$	$\Delta_f H_{298}^\circ[C_{60}(g)]^d$
5	$C_{60} + 10C_6H_6 \rightarrow 6C_{20}H_{10}$	-489.6	6.5	28.1	-1.0	2535.2
6	$C_{60} + 10C_{10}H_8 \rightarrow 8C_{20}H_{10}$	-162.1	15.2	14.1	0.4	2508.0
7	$C_{60} + 10C_{14}H_{10} \rightarrow 10C_{20}H_{10}$	252.9	31.1	1.3	-4.0	2548.8
8	$C_{60} + 10C_{18}H_{12} \rightarrow 12C_{20}H_{10}$	615.5	55.6	-7.9	-15.4	2473.7

^aElectronic reaction energy calculated at the DSD-PBEP86/cc-pVQZ level of theory. ^bEmpirical D3 dispersion correction. ^cScaled B3-LYP/6-31G(2df,p) values. ^dTheoretical heat of formation for C₆₀ obtained from the reaction listed in the second column using the DSD-PBEP86-D3/cc-pVQZ reaction enthalpies and experimental heats of formation for the other species involved (see text).

Table 3. B2GP-PLYP-D3, MP2, and SCS-MP2 Reaction Energies for Reactions 5–8 and Predicted Theoretical Enthalpies of Formation for C₆₀ (kJ mol⁻¹)

reaction	B2GP-PLYP-D3			MP2		SCS-MP2	
	ΔE_e^a	$\Delta D3^b$	$\Delta_f H_{298}^\circ[C_{60}(g)]^{c,d}$	ΔE_e^a	$\Delta_f H_{298}^\circ[C_{60}(g)]^{c,d}$	ΔE_e^a	$\Delta_f H_{298}^\circ[C_{60}(g)]^{c,d}$
5 $C_{60} + 10C_6H_6 \rightarrow 6C_{20}H_{10}$	-500.7	9.8	2543.1	-375.8	2428.0	-439.1	2491.2
6 $C_{60} + 10C_{10}H_8 \rightarrow 8C_{20}H_{10}$	-167.0	18.5	2509.6	-72.2	2433.3	-129.1	2490.2
7 $C_{60} + 10C_{14}H_{10} \rightarrow 10C_{20}H_{10}$	253.0	36.7	2543.2	351.7	2481.1	278.7	2554.1
8 $C_{60} + 10C_{18}H_{12} \rightarrow 12C_{20}H_{10}$	617.1	65.6	2462.1	758.8	2385.9	642.2	2502.6

^aElectronic reaction energy calculated in conjunction with the cc-pVQZ basis set. ^bEmpirical D3 dispersion correction. ^cThe $\Delta ZPVE$ and $\Delta(H_{298}-H_0)$ components are given in Table 2. ^dTheoretical heats of formation for C₆₀ obtained from the reaction listed in the second column using B2GP-PLYP-D3, MP2, or SCS-MP2 reaction energies calculated in conjunction with the cc-pVQZ basis set and experimental heats of formation for the other species involved (see text).

year, Steele et al.⁴⁴ revised this value substantially upward to 2656 ± 25 kJ mol⁻¹.⁴⁵ The large discrepancy between these two experimental determinations has stimulated a series of subsequent macro- and microcombustion calorimetric studies^{43,46–53} (for a compilation of the experimental $\Delta_f H_{298}^\circ[C_{60}(cr)]$ and $\Delta_f H_{298}^\circ[C_{60}(g)]$ values, see Table S3 of the Supporting Information). Thus, the reported experimental values extend over a wide energy range of 199 kJ mol⁻¹, from $2457 \pm 16^{42,46}$ to 2656 ± 25^{44} kJ mol⁻¹. The reasons for these large discrepancies include the difficulties associated with the production of samples of C₆₀ of sufficiently high purity and the limited accuracy of calorimetric measurements on relatively small samples.⁵⁴ An additional contributor to the discrepancies between the $\Delta_f H_{298}^\circ[C_{60}(g)]$ values comes about because, in some cases, separate estimates of the enthalpies of sublimation (used for converting the crystalline heat of formation into the gaseous heat of formation) show a variation of as much as ~ 50 kJ mol⁻¹ (Table S3, Supporting Information). However, even the reported solid-phase heats of formation span a wide energy range of 149 kJ mol⁻¹. In the light of this state of affairs, the NIST Webbook has adopted a standard heat of formation for C₆₀ of 2560 ± 100 kJ mol⁻¹, which was obtained as the average of six $\Delta_f H_{298}^\circ[C_{60}(g)]$ values (Table S3, Supporting Information).⁷

3.4.2. Predicted Heat of Formation for C₆₀. On the theoretical front, there has been one previous attempt to obtain an ab initio heat of formation for C₆₀. In 2005, Grimme⁵⁵ carried out MP2 and modified MP2 (SCS-MP2²⁸ and SOS-MP2⁵⁶) calculations with basis sets of up to quadruple- ζ quality. Using extrapolation techniques and an empirical higher-level-correction scheme (similar to that used in the *Gn* protocols⁵⁷), he obtained $\Delta_f H_{298}^\circ[C_{60}(g)]$ values of 1865.7 (MP2), 2331.3 (SCS-MP2), and 2511.7 (SOS-MP2) kJ mol⁻¹ from calculated atomization energies. The large differences between these three values reflect the difficulties in obtaining a reliable heat of formation for C₆₀ via brute force atomization energy calculations with MP2-type procedures.

A computationally more effective approach is the use of reactions that conserve larger molecular fragments on the two sides of the reaction. In this section, we will obtain a theoretical heat of formation for C₆₀ using reactions 5–8. They represent four different reactions that use a relatively small number of well-defined species while maintaining the hybridization state and hapticity of the carbon atoms. They all use corannulene as one of the molecules along with different acenes. While reaction 8 provides the ideal match in the number of pentagons on both sides of the reaction, it is also associated with the largest uncertainties in the heats of formation of the reference molecules (and involves the largest number of reactants). The reaction energies are calculated by means of the recently developed spin-component-scaled DHDFT DSD-PBEP86-D3 procedure in conjunction with the cc-pVQZ basis set. We note that, for the set of nine reactions (reactions 2–4) in which naphthalene, phenanthrene, triphenylene, and corannulene are separated into smaller acenes, the DSD-PBEP86-D3/cc-pVQZ level of theory attains a mean absolute deviation of 2.8 kJ mol⁻¹ relative to the W1h reaction energies. For the other molecules involved, we use experimental heats of formation for benzene (83.2 ± 0.3 kJ mol⁻¹, ATcT⁹), naphthalene (150.6 ± 1.5 kJ mol⁻¹, Roux et al.⁶), phenanthrene (202.2 ± 2.3 kJ mol⁻¹, Roux et al.⁶), and triphenylene (270.1 ± 4.4 kJ mol⁻¹, Roux et al.⁶), while for corannulene, we use our best theoretical heat of formation (485.2 ± 7.9 kJ mol⁻¹, see section 3.3).

Table 2 lists the DSD-PBEP86/cc-pVQZ, dispersion, ZPVE, and $H_{298}-H_0$ components of the reaction enthalpies for reactions 5–8, as well as the resulting predicted heats of formation for C₆₀. The differences between the heats of formation for C₆₀ obtained from reactions 5–8 span a relatively wide range of 75.1 kJ mol⁻¹. Specifically, $\Delta_f H_{298}^\circ[C_{60}(g)] = 2535.2$ (reaction 5), 2508.0 (reaction 6), 2548.8 (reaction 7), and 2473.7 (reaction 8) kJ mol⁻¹. Even after removal of the main outlier, obtained from reaction 8, the heats of formation for C₆₀ still span a range of 40.8 kJ mol⁻¹. Furthermore, it should be emphasized that, due to (i) the magnitude of the

uncertainties associated with the experimental/theoretical heats of formation used for the other molecules involved in the reactions and (ii) the number of reactants involved, the estimated heats of formation of C_{60} are associated with large uncertainties. For example, taking an uncertainty of just ± 10 kJ mol⁻¹ for the DSD-PBEP86-D3 reaction enthalpies would result in error bars in the predicted heats of formation for C_{60} of 48.6 (reaction 5), 65.8 (reaction 6), 82.9 (reaction 7), and 105.1 (reaction 8) kJ mol⁻¹. In light of these error bars, it would seem that reaction 5 would be the best candidate for predicting the most reliable heat of formation for C_{60} , as it involves (i) benzene (for which a highly accurate ATcT heat of formation is available), and (ii) the smallest number of corannulene molecules (with which an appreciable uncertainty of ± 7.9 kJ mol⁻¹ is associated). However, reactions 6–8 conserve larger molecular fragments on both sides of the reaction. Taking the average of the heats of formation obtained from reactions 5 and 6 results in $\Delta_f H^\circ_{298}[C_{60}(g)] = 2521.6$ kJ mol⁻¹, which we adopt as our best predicted value. We have chosen to exclude from the average the heats of formation obtained from reactions 7 and 8, as these values are associated with larger uncertainties (see also section 3.3).

It is of interest to also obtain theoretical heats of formation for C_{60} via reactions 5–8, using other levels of theory. Table 3 lists the reaction energies calculated with the B2GP-PLYP-D3, MP2, and SCS-MP2 procedures in conjunction with the cc-pVQZ basis set. We note that, for the nine reactions 2–4, the mean absolute deviations from W1h reaction energies are 5.1 (B2GP-PLYP-D3), 2.4 (MP2), and 2.3 (SCS-MP2) kJ mol⁻¹. The $\Delta_f H^\circ_{298}[C_{60}(g)]$ values derived from the B2GP-PLYP-D3 reaction energies agree very well with those obtained from the DSD-PBEP86-D3/cc-pVQZ reaction energies (Table 2). In particular, the differences (in absolute value) between the two $\Delta_f H^\circ_{298}[C_{60}(g)]$ values are 7.9 (reaction 5), 1.6, (reaction 6), 5.6 (reaction 7), and 11.6 (reaction 8) kJ mol⁻¹. However, using MP2/cc-pVQZ reaction energies leads to significantly lower $\Delta_f H^\circ_{298}[C_{60}(g)]$ values relative to the DSD-PBEP86-D3/cc-pVQZ results, specifically by amounts ranging from 67.7 (reaction 7) to 107.3 (reaction 5) kJ mol⁻¹ (Table 3). Using SCS-MP2/cc-pVQZ reaction energies leads to $\Delta_f H^\circ_{298}[C_{60}(g)]$ values that cluster around ~ 2500 kJ mol⁻¹ (excluding reaction 7, which gives $\Delta_f H^\circ_{298}[C_{60}(g)] = 2554.1$ kJ mol⁻¹). However, it should be emphasized that heats of formation obtained from the DHDFE reaction energies (in particular, the spin-component-scaled DSD-PBEP86-D3 procedure) should be more reliable than the SCS-MP2 results.²⁹

4. CONCLUDING REMARKS

In this study, we address the issues that are associated with trying to predict heats of formation of useful accuracy for moderately-sized molecules such as corannulene and C_{60} . This requires (a) careful consideration of the defining reaction(s), (b) use of a sufficiently high level of theory, and (c) use of auxiliary experimental data of sufficient accuracy. We initially predict the heats of formation for naphthalene, phenanthrene, triphenylene, and corannulene via reactions that conserve large molecular fragments between the reactants and products (reactions 1–4). The reaction enthalpies are obtained by means of the high-level, ab initio W1h thermochemical protocol, while accurate experimental enthalpies of formation (from the ATcT network⁹ or from Roux et al.⁶) are used for the other species involved in the reactions. In the light of the very narrow error bars associated with the experimental ATcT

enthalpies of formation (≤ 0.3 kJ mol⁻¹), we obtain our recommended theoretical estimates from reactions that conserve the largest molecular fragments on the two sides of the reaction while still exclusively using ATcT enthalpies of formation for the other species involved (i.e., reaction 2). Our best predicted heats of formation are 149.8 ± 7.7 (naphthalene), 206.6 ± 7.8 (phenanthrene), 268.2 ± 7.8 (triphenylene), and 485.2 ± 7.9 (corannulene) kJ mol⁻¹. The fact that similar theoretical heats of formation are obtained from reactions 1 and 3 increases our confidence in our best values. More specifically, reactions 1 and 3 result in heats of formation that are within 3.3 (naphthalene), 2.3 (phenanthrene), 3.3 (triphenylene), and 5.5 (corannulene) kJ mol⁻¹ from those obtained using reaction 2. Our best values for naphthalene, phenanthrene, and triphenylene are in reasonably good to excellent agreement with the accepted experimental values, specifically the deviations (theory–experiment) being -0.8 (naphthalene), $+4.4$ (phenanthrene), and -1.9 (triphenylene) kJ mol⁻¹. However, our predicted $\Delta_f H^\circ_{298}$ value for corannulene is higher than the experimental value adopted by the NIST thermochemical database by 26.7 kJ mol⁻¹, and this suggests that re-examination of the experimental data may be in order.

We use our predicted heat of formation for corannulene to estimate the heat of formation of C_{60} through reactions that involve only corannulene and planar polyacenes (reactions 5–8). For this purpose, we also use the experimental heats of formation for benzene, naphthalene, phenanthrene, and triphenylene. The reaction enthalpies are obtained by means of double-hybrid density functional theory (DSD-PBEP86-D3 and B2GP-PLYP-D3) and standard ab initio (MP2 and SCS-MP2) procedures in conjunction with the cc-pVQZ basis set. Despite the fact that reactions 5–8 involve only corannulene and polyacenes, i.e., conserve increasingly larger molecular fragments on both sides of the reaction, obtaining a reliable predicted heat of formation for C_{60} is associated with the following difficulties: (i) the number of corannulene molecules involved in reactions 5–8 (namely, 6–12) in conjunction with the uncertainty associated with our predicted heat of formation for corannulene (± 7.9 kJ mol⁻¹) results in error bars in the predicted heat of formation for C_{60} ranging between ~ 50 and 100 kJ mol⁻¹; (ii) using our best level of theory for calculating the reaction energies (DSD-PBEP86-D3/cc-pVQZ) still results in a wide spread in the resultant heats of formation for C_{60} of 40.8 kJ mol⁻¹ (excluding the main outlier, reaction 8), indicating a significant residual uncertainty.

This exemplifies the difficulties associated more generally with predicting the heats of formation of moderately-sized molecules. Overall, our best predicted heat of formation for C_{60} obtained using DSD-PBEP86-D3/cc-pVQZ reaction energies ($\Delta_f H^\circ_{298}[C_{60}(g)] = 2521.6$ kJ mol⁻¹) suggests that the experimental value adopted by NIST ($\Delta_f H^\circ_{298}[C_{60}(g)] = 2560 \pm 100$ kJ mol⁻¹) should be revised downward.

■ ASSOCIATED CONTENT

Supporting Information

Comparison between HF/cc-pV{T,Q}Z and HF/cc-pV{Q,5}Z components for reactions 1–4 (Table S1); diagnostics indicating the importance of post-CCSD(T) correlation effects for the species involved in reactions 1–4 (Table S2); summary of reported experimental heats of formation for C_{60} (Table S3); B3-LYP/6-31G(2df,p) optimized geometries for all the species in reactions 1–8 (Table S4); and full references for ref 15

(Gaussian 09) and ref 16 (Molpro 2010) (Table S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: amir.karton@chem.usyd.edu.au (A.K.); chan_b@chem.usyd.edu.au (B.C.); kraghava@indiana.edu (K.R.); radom@chem.usyd.edu.au (L.R.).

Notes

The authors declare no competing financial interest.

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