

Heats of Formation of Platonic Hydrocarbon Cages by Means of High-Level Thermochemical Procedures

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Hydrocarbon cages are key reference materials for the validation and parameterization of computationally cost-effective procedures such as density functional theory (DFT), semiempirical molecular orbital theory, and molecular mechanics. We obtain accurate total atomization energies (TAEs) and heats of formation ($\Delta_f H^\circ_{298}$) for platonic and prismatic hydrocarbon cages by means of the *Wn*-F12 explicitly correlated thermochemical protocols. We consider the following kinetically stable (CH)_n polycyclic hydrocarbon cages: (i) platonic hydrocarbons (tetrahedrane, cubane, and dodecahedrane), (ii) prismatic hydrocarbons (triprismane, cubane, and pentaprismane), and (iii) one truncated tetrahedrane (octahedrane). Our best theoretical heat of formation for cubane (144.8 kcal mol⁻¹) suggests that the experimental value adopted by the NIST thermochemical database (142.7 ± 1.2 kcal mol⁻¹) should be revised upwards by ~2 kcal mol⁻¹. Our best heat of formation for dodecahedrane (20.2 kcal mol⁻¹) suggests that the semiex-

perimental value (22.4 ± 1 kcal mol⁻¹) should be revised downward by ~2 kcal mol⁻¹. We use our benchmark *Wn*-F12 TAEs to evaluate the performance of a variety of computationally less demanding composite thermochemical procedures. These include the Gaussian-*n* (*Gn*) and the complete basis set (CBS) methods. The CBS-QB3 and CBS-APNO procedures show relatively poor performance with root-mean-squared deviations (RMSDs) of 4.2 and 2.5 kcal mol⁻¹, respectively. The best performers of the *Gn* procedures are G4 and G3(MP2)B3 (RMSD = 0.5 and 0.6 kcal mol⁻¹, respectively), while the worst performers are G3 and G4(MP2)-6X (RMSD = 2.1 and 2.9 kcal mol⁻¹, respectively). Isodesmic and even homodesmotic reactions involving these species are surprisingly challenging targets for DFT computations. © 2015 Wiley Periodicals, Inc.

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Introduction

Platonic hydrocarbons—the hydrocarbon analogs of the platonic solids—attracted considerable attention due to the aesthetically pleasing symmetry of their hydrocarbon framework (**1–3**, Fig. 1).^[1,2] In fact, for a long time, it was believed that these highly symmetric (CH)_n hydrocarbon cages were purely hypothetical. For example, long before the platonic hydrocarbon dodecahedrane was synthesized, the Nobel laureate Gerhard Herzberg conjectured that “it is not likely that molecules of *I_h* symmetry will ever be found.”^[3] Nevertheless, dodecahedrane—an array of twelve *cis*-fused cyclopentane rings with *I_h* symmetry—was synthesized by Paquette and coworkers in 1982.^[4,5] Tetrahedrane and cubane—tetrahedral and cubic configurations of CH (methine) groups—are platonic hydrocarbons in which the bond angles around the carbon atoms deviate significantly from a tetrahedral geometry (namely, with ∠C—C—C angles of 60° and 90°, respectively). These platonic hydrocarbons were believed to be impossible to synthesize due to their high angular strain energies. Nevertheless, cubane was first synthesized in 1964 by Eaton and Cole.^[6] Parent tetrahedrane has not been synthesized to date, however, its tetra-*tert*-butyl derivative was prepared by Maier et al. in 1978.^[7]

Prismanes are another class of (CH)_n hydrocarbon cages, which are formed by two parallel regular *n*-gons connected by rectangular faces (**2**, Fig. 1; **4** and **5**, Fig. 2). Prismanes are highly strained cage systems in which the bond angles around

the carbon atoms deviate significantly from tetrahedral geometry. The prismanes that have been synthesized thus far (**2**,^[6] **4**,^[8] and **5**)^[9] are characterized by ∠C—C—C angles of 60/90° (triprismane, Ladenburg prismatic, **4**), 90° (**2**), and 90/108° (pentaprismane, **5**). These compounds (and many of their derivatives) are kinetically stable as their rearrangement and decomposition reactions are symmetry-forbidden.^[1] Despite its strain, octahedrane (**6**, Fig. 2) also is the most thermodynamically stable (CH)₁₂ hydrocarbon.^[10,11]

In this work, we obtain accurate theoretical heats of formation for the following (CH)_n polycyclic hydrocarbon cages by means of the high-level W1-F12 and W2-F12 theories:^[12]

- Platonic hydrocarbons **1–3** (Fig. 1)

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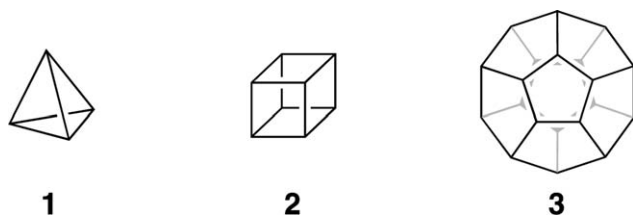


Figure 1. Platonic hydrocarbons: Tetrahedrane (**1**, C_4H_4), cubane (**2**, C_8H_8), and dodecahedrane (**3**, $C_{20}H_{20}$).

- Prismatic hydrocarbons **4** and **5** (Fig. 2)
- Truncated tetrahedrane: octahedrane (**6**) (Fig. 2)

The theoretical heats of formation for cubane and dodecahedrane deviate substantially (by 2–4 kcal mol⁻¹) from the reported experimental heats of formation. These discrepancies between theory and experiment suggest that re-examination of some of the experimental data may be in order. Interestingly, we also find an almost perfect linear correlation between the total atomization energies (TAEs) of the (CH)_n hydrocarbon cages and the number of CH groups in these systems.

Computational Methods

To obtain reliable TAEs, computations have been performed using the high-level, *ab initio* *Wn*-F12 procedures ($n = 1$ and 2) with the MOLPRO 2012.1 program suite.^[13,14] W1-F12 and W2-F12 theories^[12] (and their predecessors W1 and W2.2)^[15,16] represent layered extrapolations to the relativistic, all-electron CCSD(T)/CBS (coupled cluster with single, double, and quasiperturbative triple excitations complete-basis-set limit energy). These composite theories can achieve “subchemical accuracy” for atomization reactions.^[12,15–17] For example, W1-F12 and W2-F12 theories are associated with root-mean-squared deviations (RMSDs) of 0.74 and 0.42 kcal mol⁻¹ for a set of 137 very accurate atomization energies obtained at the full configuration interaction (FCI) infinite basis-set limit.^[12,17] The performance of these theories for systems containing only first-row elements (and H) is of greater relevance to this study. For the subset of 97 first-row atomization energies in the W4-11 database, W1-F12 shows significantly better performance with an RMSD of 0.45 kcal mol⁻¹.^[12,17] In this work, we obtain TAEs at the W2-F12 level for the smaller (CH)_n hydrocarbons ($n = 4, 6$, and 8) and at the W1-F12 level for the larger hydrocarbons ($n = 10, 12$, and 20). We note that the W1-F12 calculations for the largest system (CH)₂₀ strained our computational resources to the limit. In total, all the W1-F12 single-point energy calculations for (CH)₂₀ took 155 CPU days on Intel Xeon E5-4650L cores (at 3.1 GHz) with 512 GB of RAM and 4 TB of solid-state disk.

W1-F12 and W2-F12 theories combine explicitly correlated F12 techniques^[18] with basis-set extrapolations to approximate the CCSD(T) infinite basis-set-limit energy. For the sake of making the article self-contained, we will briefly outline the various steps in these theories (for further details see Refs. 12,19). In W2-F12, the Hartree–Fock (HF) component is calculated with the VQZ-F12 basis set (where *Vn*Z-F12 denotes the

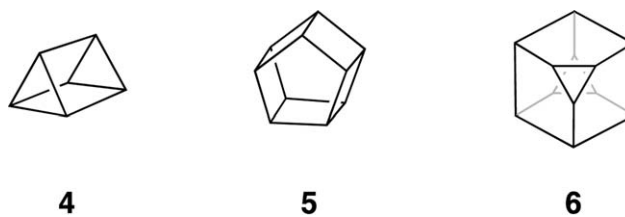


Figure 2. Additional (CH)_n polycyclic hydrocarbon cages: Triprismane (**4**, C_6H_6), pentaprismane (**5**, $C_{10}H_{10}$), and octahedrane (**6**, $C_{12}H_{12}$).

cc-pVnZ-F12 basis set of Peterson et al.,^[20] which was specifically developed for explicitly correlated calculations). Note that the complementary auxiliary basis set singles correction is included in the self-consistent field (SCF) energy.^[21,22] The valence CCSD-F12 correlation energy is extrapolated from the VTZ-F12 and VQZ-F12 basis sets, using the $E(L) = E_\infty + A/L^\alpha$ two-point extrapolation formula, with $\alpha = 5.94$. Optimal values for the geminal Slater exponents (β) used in conjunction with the *Vn*Z-F12 basis sets were taken from Ref. 23. The quasiperturbative triples, (T), corrections are obtained from standard CCSD(T)/VTZ-F12 calculations (i.e., without inclusion of F12 terms) and scaled by the factor $f = 0.987 \times E^{MP2-F12}/E^{MP2}$. This approach has been shown to accelerate the basis set convergence.^[12,24] In all of the explicitly correlated coupled cluster calculations the diagonal, fixed-amplitude 3C(FIX) ansatz^[25–28] and the CCSD-F12b approximation are used.^[24,29] The CCSD inner-shell contribution is calculated with the core–valence weighted correlation-consistent aug'-cc-pwCVTZ basis set of Peterson and Dunning,^[30] while the (T) inner-shell contribution is calculated with the cc-pwCVTZ(no *f*) basis set (where cc-pwCVTZ(no *f*) indicates the cc-pwCVTZ basis set without the *f* functions). The scalar relativistic contribution (in the second-order Douglas–Kroll–Hess approximation)^[31,32] is obtained as the difference between nonrelativistic CCSD(T)/A'VDZ and relativistic CCSD(T)/A'VDZ-DK calculations.^[33] The notation A'*Vn*Z indicates the combination of the standard correlation-consistent cc-pVnZ basis sets on hydrogen,^[34] and the aug-cc-pVnZ basis sets on carbon.^[35] The atomic spin-orbit coupling terms are taken from the experimental fine structure,^[36] and the diagonal Born–Oppenheimer corrections (DBOCs) are calculated at the HF/cc-pVTZ level of theory using the CFOUR program suite.^[37,38] In this work, we additionally include a correlation correction to the DBOCs calculated at the CCSD/cc-pVDZ level.

The geometries and harmonic frequencies of all structures have been obtained at the B3LYP-D3BJ level of theory^[39–41] with the Weigend–Ahlich def2-TZVPP basis set.^[42] Throughout the manuscript, the suffix D3BJ refers to the inclusion of the D3 empirical dispersion corrections^[43,44] but with a Becke–Johnson^[45] damping function as recommended in Ref. 46. Harmonic vibrational analyses were performed at the same level as the optimizations to confirm that all structures are local minima. Zero-point vibrational energy (ZPVE), thermal enthalpy ($H_{298} - H_0$), and entropy (S) corrections were obtained from these frequencies within the RRHO (rigid rotor-harmonic oscillator) approximation. The ZPVE corrections have been scaled by 0.99 in accordance with a recent compilation of vibrational scale factors.^[19,47]

Table 1. Component breakdown of the W1-F12 and W2-F12 TAEs for tetrahedrane (**1**, C₄H₄), triprismane (**4**, C₆H₆), cubane (**2**, C₈H₈), pentaprismane (**5**, C₁₀H₁₀), octahedrane (**6**, C₁₂H₁₂), and dodecahedrane (**3**, C₂₀H₂₀) (kcal mol⁻¹).

	1		4		2		5	6	3
	W1-F12	W2-F12	W1-F12	W2-F12	W1-F12	W2-F12	W1-F12	W1-F12	W1-F12
ΔHF	571.02	571.03	917.35	917.39	1253.88	1253.98	1627.84	2036.94	3476.91
ΔCCSD	201.16	201.03	304.65	304.32	409.80	409.28	513.89	615.22	1034.02
Δ(T)	16.85	16.68	25.67	25.52	34.45	34.24	43.51	52.03	87.50
ΔCV ^[a]	5.09	5.16	6.96	7.10	8.86	9.10	11.21	14.10	23.03
ΔRel ^[b]	-0.78	-0.77	-1.11	-1.11	-1.45	-1.45	-1.81	-2.21	-3.67
ΔS-O ^[c]	-0.34	∅	-0.51	∅	-0.68	∅	-0.85	-1.02	-1.69
ΔDBOC ^[d]	0.15	∅	0.17	∅	0.18	∅	0.23	0.32	0.42
ΔZPVE ^[e]	36.96	∅	60.18	∅	82.82	∅	105.64	129.37	222.97
TAE _e ^[f]	794.11	793.90	1254.62	1254.32	1706.99	1706.59	2196.46	2718.29	4621.46
TAE ₀ ^[g]	756.20	755.99	1192.99	1192.69	1622.22	1621.82	2088.38	2586.01	4393.55
Δ _f H ₀ ^[h]	130.43	130.64	136.95	137.26	151.03	151.44	128.19	73.88	39.59
Δ _f H ₂₉₈ ^[h]	128.36	128.57	132.53	132.84	144.38	144.78	119.42	63.08	20.18
Δ _f H ₂₉₈ ^[i]		128.62		132.92		144.89	120.41	64.27	22.18
Expt.						142.7 ± 1.2 ^[k]			22.4 ± 1 ^[l]

[a] Core–valence correction. [b] Scalar relativistic correction. [c] First-order spin-orbit coupling. [d] Diagonal Born–Oppenheimer correction. [e] Zero-point vibrational energy correction. [f] Nonrelativistic, all-electron, vibrationless CCSD(T) basis set limit TAEs (these values can be used for evaluation of DFT and *ab initio* procedures). [g] Relativistic, all-electron, ZPVE-inclusive CCSD(T) basis set limit TAEs at 0 K (for comparison with experiment and for the evaluation of composite *ab initio* procedures). [h] Theoretical heats of formation at 0 and 298 K. [i] Heats of formation at 298 K obtained from isodesmic reaction (1) using AtCT $\Delta_f H_{298}^\circ$ values for methane (-17.814 ± 0.014) and isobutene (-32.352 ± 0.096) and reaction energies from W2-F12 theory for the reactions involving C₄H₄, C₆H₆, and C₈H₈, and reaction energies from W1-F12 theory for the reactions involving C₁₀H₁₀, C₁₂H₁₂, and C₂₀H₂₀. [j] From W1-F12 theory. [k] Taken from the NIST WebBook (see text). [l] Derived from the experimental $\Delta_f H_{298}^\circ$ values for dodecahedrane and pagodane derivatives (see Ref. 92 for further details).

The main difference between W1-F12 and W2-F12 theories is that W1-F12 uses smaller basis sets for extrapolating the HF, CCSD-F12, and (T) contributions. Specifically, the HF and CCSD-F12 contributions are extrapolated from the VDZ-F12 and VTZ-F12 basis-sets using the two-point extrapolation formula with $\alpha = 5.00$ and 3.67, respectively.^[12,19] The (T) valence correlation energy is obtained in the same way as in the original W1 theory,^[12,15] that is, extrapolated from the A'VDZ and A'VTZ basis sets with $\alpha = 3.22$.

As W1-F12 and W2-F12 theories represent layered extrapolations to the all-electron CCSD(T) basis-set-limit energy, it is of interest to estimate whether the contributions from post-CCSD(T) excitations are likely to be significant for the (CH)_n hydrocarbon cages. The percentage of the TAE accounted for by parenthetical connected triple excitations, %TAE_e[(T)], has been found to be a reliable energy-based diagnostic for the importance of post-CCSD(T) contributions. It has been suggested that %TAE_e[(T)] < 2% indicates systems that are dominated by dynamical correlation, while 2% < %TAE_e[(T)] < 5% indicates systems that are characterized by mild nondynamical correlation.^[16,17,48] Supporting Information Table S1 gathers the %TAE_e[(T)] values for the hydrocarbon cages. The %TAE_e[(T)] values for these species span a narrow range between 1.9 (dodecahedrane) and 2.1 (tetrahedrane). These values suggest that these systems are dominated by dynamical correlation effects and that our bottom-of-the-well CCSD(T)/CBS TAEs should be well below ~ 1 kcal mol⁻¹ from the corresponding TAEs at the FCI basis-set limit.^[16,17]

We use our W1-F12 and W2-F12 benchmark TAEs to evaluate the performance of a range of more approximate composite procedures. Namely, the Gn-type methods: G4,^[49,50]

G4(MP2),^[51] G4(MP2)-6X,^[52] G3,^[53] G3(MP2),^[54] G3B3,^[55] and G3(MP2)B3,^[55] and the complete basis set (CBS) methods: CBS-APNO^[56] and CBS-QB3.^[57] All geometry optimizations, frequency calculations, and the calculations for the Gn and CBS procedures were performed using the Gaussian 09 program suite.^[58]

A number of density functional theory (DFT) methods were evaluated for their performance on bond separation reactions involving the platonic/prismatic hydrocarbon cages. The basis sets used were the Weigend–Ahlich^[42] def2-TZVPP and def2-QZVP basis sets; the functionals include the hybrid GGAs B3LYP and PBE0,^[59,60] the hybrid meta-GGA TPSS0,^[61–63] the highly empirical meta-GGAs M06 and M06-2X,^[64,65] the range-separated hybrids ω B97X-D,^[66,67] M11,^[68] and ω B97X-V,^[69] the double hybrids^[70] B2PLYP^[71] and B2GP-PLYP^[72] and the spin-component-scaled double hybrids DSD-PBEP86-D3BJ,^[73,74] DSD-PBEPBE-D3BJ,^[74] and DSD-PBEB95-D3BJ.^[74] Some of these DFT calculations, particularly the double hybrid and ω B97X-V, were performed using a locally modified version of the ORCA program suite.^[75,76]

Results and Discussion

Overview of the Wn-F12 total atomization energies

The component breakdown of the Wn-F12 TAEs and our resulting predicted heats of formation are gathered in Table 1. The magnitude of the HF component (Δ HF) can be very large. For example, at the W1-F12 level this component ranges from 571.02 (**1**) up to 3476.91 (**3**) kcal mol⁻¹. Nevertheless, for the three hydrocarbons for which we were able to obtain results at the W2-F12 level (**1**, **2**, and **4**), the differences between the

Table 2. Overview of the valence CCSD-F12 correlation contribution to the TAEs for tetrahedrane (**1**, C₄H₄), triprismane (**4**, C₆H₆), cubane (**2**, C₈H₈), pentaprismane (**5**, C₁₀H₁₀), octahedrane (**6**, C₁₂H₁₂), and dodecahedrane (**3**, C₂₀H₂₀) (kcal mol⁻¹).

Basis sets	$\alpha^{[a]}$	1	4	2	5	6	3
V{D,T}Z-F12	3.14 ^[b]	201.54	305.23	410.59	514.90	616.43	1036.08
V{D,T}Z-F12	3.38 ^[c]	201.35	304.94	410.20	514.40	615.83	1035.06
V{D,T}Z-F12	3.67 ^[d]	201.16	304.65	409.80	513.89	615.22	1034.02
V{T,Q}Z-F12	4.60 ^[b]	201.15	304.48	409.50	N/A	N/A	N/A
V{T,Q}Z-F12	5.94 ^[d]	201.03	304.32	409.28	N/A	N/A	N/A

[a] Extrapolation exponent used in the two-point extrapolations. [b] From Ref. 23, optimized over a set of 14 absolute CCSD correlation energies. [c] Optimized to minimize the RMSD over 97 first-row atomization energies in the W4-11 dataset (see Refs. 12,17). [d] Optimized to minimize the RMSD over 137 first- and second-row atomization energies in the W4-11 dataset (see Refs. 12,17,19).

HF/V{D,T}Z-F12 (W1-F12) and HF/VQZ-F12 (W2-F12) components amount to less than 0.1 kcal mol⁻¹ (Table 1).

The magnitude of the valence CCSD correlation contribution (Δ CCSD) to the TAEs is generally about one-third that of the Δ HF component. For example, the Δ CCSD component from W1-F12 theory extends from 201.16 (**1**) up to 1034.02 (**3**) kcal mol⁻¹. In contrast to the Δ HF component, which is practically converged at the W1-F12 level, the differences between the Δ CCSD contribution calculated at the CCSD-F12/V{D,T}Z-F12 (W1-F12) and CCSD-F12/V{T,Q}Z-F12 (W2-F12) level of theories can get quite significant for the larger hydrocarbon cages. Table 2 gives an overview of basis set convergence of the CCSD-F12 component of the TAE. Extrapolating the CCSD-F12 energy from the V{D,T}Z-F12 basis set pair with an extrapolation exponent ($\alpha = 3.38$), which was optimized to minimize the RMSD over the 97 first-row systems in the W4-11 dataset,^[12,17] overshoots the W2-F12 value by 0.32 (**1**), 0.63 (**4**), and 0.92 (**2**) kcal mol⁻¹. Using a larger extrapolation exponent of 3.67 (optimized over the entire W4-11 set of 137 first- and second-row systems) improves the situation, namely the deviations between W1-F12 and W2-F12 are reduced to 0.13 (**1**), 0.33 (**4**), and 0.52 (**2**) kcal mol⁻¹. Conversely, using the extrapolation exponent optimized by Hill et al.^[23] over a smaller set of 14 absolute correlation energies ($\alpha = 3.144$), results in larger differences from W2-F12, namely 0.51 (**1**), 0.91 (**4**), and 1.31 (**2**) kcal mol⁻¹.

The valence (T) correlation contributions (Δ (T), Table 1) can be quite hefty, reaching up to 87.50 kcal mol⁻¹ for (CH)₂₀, **3**. For the smaller species, the differences between W1-F12 and W2-F12 amount to 0.17 (**1**), 0.15 (**4**), and 0.21 (**2**) kcal mol⁻¹; in all cases, W1-F12 overestimates the W2-F12 contribution. The core-valence (Δ CV) correlation contributions for the con-

sidered systems are also rather large, reaching up to 23.03 kcal mol⁻¹ for **3**. The differences between W1-F12 and W2-F12 amount to 0.08 (**1**), 0.14 (**4**), and 0.24 (**2**) kcal mol⁻¹. Here, however, the Δ CV component from W1-F12 consistently underestimates the W2-F12 contribution. Overall, taking into account the Δ HF, Δ CCSD, Δ (T), and Δ CV components, the W1-F12 TAEs overestimate the W2-F12 values by 0.22 (**1**), 0.30 (**4**), and 0.39 (**2**) kcal mol⁻¹. This is due to some error cancellation between the Δ HF and Δ CV components (for which W1-F12 underestimates W2-F12) and the Δ CCSD and Δ (T) components (for which W1-F12 overestimates W2-F12).

The scalar relativistic (Δ Rel) and first-order spin-orbit coupling (Δ S-O) contributions both reduce the atomization energies by quite significant amounts. Specifically, Δ Rel ranges from -0.78 (**1**) to -3.67 (**3**) kcal mol⁻¹, and Δ S-O ranges between -0.34 (**1**) and -1.69 (**3**) kcal mol⁻¹. This demonstrates once again that relativistic effects can become thermodynamically significant for medium-sized hydrocarbons (see for example Refs. 12,77,78).

Table 3 gives an overview of the HF and CCSD correlation contributions to the DBOC component of the TAEs. The DBOC contributions at the HF/cc-pVTZ level of theory range between 0.23 (**1**) and 0.78 (**3**) kcal mol⁻¹. We note the sizeable DBOC contribution for **3**: for comparison, the DBOC contributions to the TAE (at the HF level) for other medium-sized organic systems are: 0.63 (corannulene, C₂₀H₁₀),^[79] 0.59 (naphthalene, C₁₈H₁₂),^[80] 0.61 (triphenylene, C₁₈H₁₂),^[79] 0.60 (lysine, C₆H₁₄N₂O₂),^[19] and 0.72 (arginine, C₆H₁₄N₄O₂)^[19] kcal mol⁻¹. It is also worth pointing out that the HF/cc-pVDZ level of theory gives essentially the same results at a much lower computational cost, namely the differences amount to less than 0.03 kcal mol⁻¹ (Table 3). It has been previously found (see for example Refs. 19,77, and Refs. therein) that for systems with many hydrogen atoms correlation contributions to the DBOC will reduce the Δ DBOC contribution to the TAE by up to ~50%. For the hydrocarbon cages, the CCSD correlation correction to the DBOCs reduces the DBOC contribution to the TAEs by 35–46% (Table 3).

Comparison of the Wn-F12 heats of formation with available experimental data

Our best TAEs at 0 K (TAE₀, Table 1) are: 755.99 (**1**), 1192.69 (**4**), 1621.82 (**2**), 2088.38 (**5**), 2586.01 (**6**), and 4393.55 (**3**) kcal

Table 3. Overview of the DBOC contribution to the TAEs for tetrahedrane (**1**, C₄H₄), triprismane (**4**, C₆H₆), cubane (**2**, C₈H₈), pentaprismane (**5**, C₁₀H₁₀), octahedrane (**6**, C₁₂H₁₂), and dodecahedrane (**3**, C₂₀H₂₀) (kcal mol⁻¹).

	1	4	2	5	6	3
HF/cc-pVDZ	0.23	0.29	0.34	0.43	0.55	0.81
HF/cc-pVTZ	0.23	0.28	0.33	0.41	0.54	0.78
Δ CCSD/cc-pVDZ ^[a]	-0.08	-0.11	-0.15	-0.18	-0.22	-0.36
Best ^[b]	0.15	0.17	0.18	0.23	0.32	0.42

[a] Δ CCSD = CCSD - HF correlation contribution to the DBOC. [b] Best = HF/cc-pVTZ + Δ CCSD/cc-pVDZ.

mol^{-1} . Using the ATcT atomic heats of formation at 0 K (H 51.633 ± 0.000 and C 170.024 ± 0.014 kcal mol^{-1}),^[81–83] we convert our best TAE₀ to heats of formation at 0 K ($\Delta_f H_0$, Table 1). Consequently, the $\Delta_f H_0$ values are converted to heats of formation at 298 K ($\Delta_f H_{298}^\circ$) using the CODATA enthalpy functions ($H_{298} - H_0$) for the elemental reference states (H₂(g) = 2.024 ± 0.000 and C(cr, graphite) = 0.251 ± 0.005 kcal mol^{-1})^[84] and the enthalpy functions for the (CH)_n species are obtained (within the rigid-rotor harmonic oscillator approximation) from the B3LYP-D3BJ/Def2-TZVPP geometries and harmonic frequencies. Our best Wn-F12 $\Delta_f H_{298}^\circ$ values are: 128.57 (1), 132.84 (4), 144.78 (2), 119.42 (5), 63.08 (6), and 20.18 (3) kcal mol^{-1} . We note that, while the present manuscript was in the final stages of preparation, Agapito et al. reported a W1-F12 $\Delta_f H_{298}^\circ$ of 144.2 kcal mol^{-1} for (2).^[85] We also note that Ref. 85 provides an excellent review of the previous experimental and theoretical works on the heat of formation of cubane. The W1-F12 value of Agapito et al. is in excellent agreement with our own W1-F12 value of 144.38 kcal mol^{-1} ; the residual difference of about 0.2 kcal mol^{-1} can be partially attributed to the slightly smaller scaling factor used in that work for the ZPVE (0.985 from the original W1 paper^[15] instead of 0.99 from Ref. 47). While a difference of 0.005 in the ZPVE scaling factor would be insignificant compared for small molecules, it was found in Ref. 19 to lead to nontrivial systematic errors for systems the size of arginine.

Soon after, the first synthesis of **2**^[6] the enthalpy of formation of crystalline **2** and the enthalpy of sublimation were measured to be 129.5 ± 0.8 and 19.2 ± 0.4 kcal mol^{-1} , respectively.^[86] These result in a gas-phase heat of formation at 298 K ($\Delta_f H_{298}^\circ$) of 148.7 ± 1 kcal mol^{-1} . This heat of formation is identical to the value estimated from Benson's group additivity method,^[87] and is higher by almost 4 kcal mol^{-1} than our W2-F12 value of 144.78 kcal mol^{-1} . Bashir-Hashemi et al. remeasured the sublimation enthalpy of **2**,^[88,89] and reported a value of 13.2 ± 0.5 kcal mol^{-1} , which is smaller than the above value by as much as 6 kcal mol^{-1} (The smaller sublimation enthalpy is in excellent agreement with the value of 13.1 ± 0.5 kcal mol^{-1} recently reported by Chickos).^[90] Using this corrected enthalpy of sublimation, we obtain an experimental $\Delta_f H_{298}^\circ$ value of 142.7 ± 1.2 kcal mol^{-1} . This value, which was adopted by the NIST thermochemical database,^[91] is 2.08 kcal mol^{-1} lower than our W2-F12 value. Assigning a conservative error bar of 1 kcal mol^{-1} to our W2-F12 value, to account for potential issues with the scaled harmonic ZPVE, the discrepancy between theory and experiment is just below the sum of the respective uncertainties. Nevertheless, it should be pointed out that the error bar of the experimental enthalpy of formation of crystalline **2** may be larger than the assigned value of 0.8 kcal mol^{-1} due to the use of an unspecified correction in the conversion of the combustion measurements to a crystalline enthalpy of formation.^[86,88] Finally, as a "sanity check" on the theoretical and experimental gas-phase $\Delta_f H_{298}^\circ$ values for **2** we consider the following isodesmic reaction:

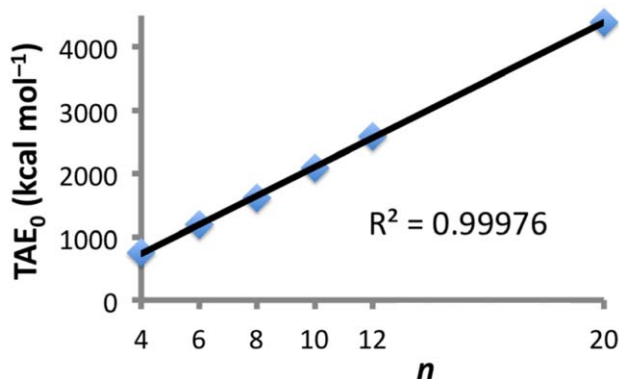
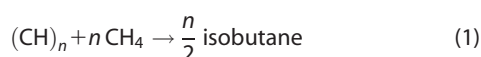


Figure 3. Linear correlation between the TAEs at 0 K (TAE₀) and the number of CH groups in the (CH)_n polycyclic hydrocarbon cages 1–6.

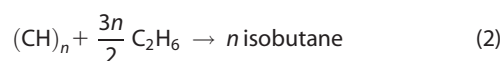
for which ATcT $\Delta_f H_{298}^\circ$ values are available for all the species apart from **2**. Using the W2-F12 reaction enthalpy at 298 K (-131.78 kcal mol^{-1}) and the ATcT $\Delta_f H_{298}^\circ$ values (-17.814 ± 0.014 for methane, and -32.352 ± 0.096 kcal mol^{-1} for isobutene) we obtain a $\Delta_f H_{298}^\circ$ value for **2** of 144.89 kcal mol^{-1} in close agreement with our theoretical W2-F12 value.

A "semiexperimental" heat of formation of $\Delta_f H_{298}^\circ = 22.4 \pm 1$ kcal mol^{-1} for **3** was derived by Beckhaus et al.^[92] from the experimental heats of formation for derivatives of **3** and pagodane. This value is higher by 2.22 kcal mol^{-1} than our best W1-F12 value. Again, this discrepancy between theory and experiment is only slightly above the sum of the respective uncertainties. However, our theoretical heat of formation suggests that the experimental value should be revised downwards.

Linear correlation between the number of CH groups and the components of the total atomization energies

Interestingly, we find an almost perfect linear correlation between all the components of the TAEs in Table 1 (Δ_{HF} , Δ_{CCSD} , $\Delta(\text{T})$, Δ_{CV} , Δ_{Rel} , Δ_{DBOC} , $\Delta_{\text{S-O}}$, Δ_{ZPVE} , TAE_e, and TAE₀) and the number of CH groups in the (CH)_n hydrocarbon cages. Supporting Information Table S2 gives the squared correlation coefficients (R^2) for all the components of the TAE. Suffice to say that, with the exception of the Δ_{DBOC} component for which $R^2 = 0.9437$, all the components of the TAE are associated with $R^2 \geq 0.9996$. The final atomization energies (TAE_e and TAE₀) are both associated with $R^2 = 0.9998$. Figure 3 illustrates the linear correlation between the TAE₀ and the number of CH groups in the considered (CH)_n polycyclic hydrocarbon cages.

This linear relationship indicates that the platonic and prismatic hydrocarbons form a homologous series even though they involve different angular strain energies. For example, the strain energies involved in the considered polycyclic hydrocarbon cages could be estimated from the energy of the following homodesmotic reaction (see also below):^[11]



Using our best heats of formation ($\Delta_f H_{298}^\circ$, Table 1), we obtain the following reaction enthalpies at 298 K: -136.18 (1),

Table 4. Deviations for computationally economical composite procedures for the TAE₀ of tetrahedrane (**1**, C₄H₄), triprismane (**4**, C₆H₆), cubane (**2**, C₈H₈), pentaprismane (**5**, C₁₀H₁₀), octahedrane (**6**, C₁₂H₁₂), and dodecahedrane (**3**, C₂₀H₂₀) (kcal mol⁻¹).^[a,b]

	1	4	2	5	6	3	RMSD ^[c]
G3	-1.80	-2.61	-2.71	-2.73	-1.17	-0.82	2.12
G3B3	-1.23	-1.94	-1.72	-1.76	-0.43	0.17	1.39
G3(MP2)	-0.57	-1.46	-1.63	-1.90	-0.67	-1.06	1.31
G3(MP2)B3	0.18	-0.48	-0.18	-0.34	0.77	1.21	0.64
G4	0.15	-0.20	-0.34	-0.67	0.79	0.23	0.47
G4(MP2)	1.12	0.77	0.78	0.31	1.35	0.66	0.90
G4(MP2)-6X	0.85	1.06	1.50	1.69	3.64	5.43	2.88
CBS-QB3	-2.20	-3.09	-3.95	-4.56	-3.82	-6.24	4.17
CBS-APNO	0.06	0.77	0.13	0.91	4.46	4.13	2.53

[a] Reference values are the best TAE₀ values from Table 1 (i.e., from W2-F12 theory for **1**, **4**, and **2**; and from W1-F12 theory for **5**, **6**, and **3**). [b] The tabulated values are TAE₀(given method)–TAE₀(Wn-F12). [c] RMSD over the six systems.

–144.24 (**4**), –159.99 (**2**), –139.55 (**5**), –87.24 (**6**), and –60.45 (**3**) kcal mol⁻¹. Cubane (**2**) is characterized by the highest strain energy ($E_{st} = 160.0$ kcal mol⁻¹). The platonic/prismatic hydrocarbons **1**, **4**, and **5** are characterized by lower strain energies ($E_{st} = 136.2$ – 144.2 kcal mol⁻¹). Octahedrane (**6**) displays a significantly lower strain energy ($E_{st} = 87.2$ kcal mol⁻¹), and dodecahedrane (**3**) is associated with the lowest strain energy ($E_{st} = 60.5$ kcal mol⁻¹). It is also instructive to compare the strain energies per CH group, these values are: –34.0 (**1**), –24.0 (**4**), –20.0 (**2**), –14.0 (**5**), –7.3 (**6**), and –3.0 (**3**) kcal mol⁻¹. We note that for the hydrocarbon cages (CH)_n ($n = 4$ – 12), there is a reasonably high statistical correlation between the strain energy per CH group and the number of CH groups (with $R^2 = 0.9827$). However, inclusion of the anomalous (CH)₂₀ system results in $R^2 = 0.8426$.

Performance of computationally economical composite procedures

Table 4 reports the deviations from our best Wn-F12 benchmark TAE₀ for the (CH)_n polycyclic hydrocarbon cages for a range of more approximate composite procedures (e.g., G4, G4(MP2), G4(MP2)-6X, CBS-QB3, and CBS-APNO). We can see that the G3 method performs poorly with almost all deviations exceeding the “chemical accuracy” threshold of 1 kcal mol⁻¹. For three out of the six systems (**2**, **4**, and **5**), the deviations from Wn-F12 theory exceed 2 kcal mol⁻¹, and the overall RMSD is 2.1 kcal mol⁻¹. The G3B3 variant of G3 in which the geometries and ZPVEs are calculated at the B3LYP/6-31G(d) level of theory (rather than MP2/6-31G(d) geometries and HF/6-31G(d) ZPVEs in G3) cuts the deviations by 0.6–1.0 kcal mol⁻¹ and the overall RMSD to 1.4 kcal mol⁻¹. However, deviations of above 1 kcal mol⁻¹ are still obtained for **1**, **4**, **2**, and **5**. Interestingly, the computationally more economical G3(MP2) procedure shows similar performance to G3B3 with an overall RMSD of 1.3 kcal mol⁻¹. An even more striking result, however, is the performance of the G3(MP2)B3 variant of G3(MP2). Apart from **3**, for which a deviation of 1.2 kcal mol⁻¹ is obtained, all the deviations are below the “chemical accuracy” threshold, and the overall RMSD is only 0.6 kcal mol⁻¹.

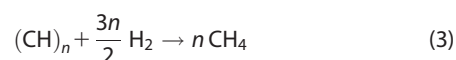
Moving on to the performance of the Gaussian-4 family, the G4 method shows excellent performance with all deviations

below 0.8 kcal mol⁻¹, and an overall RMSD of merely 0.5 kcal mol⁻¹. We note that the G4 method puts in the best performance out of all the composite procedures. The G4(MP2) procedure, which is computationally more economical than G4, performs fairly well relative to its computational cost, with an overall RMSD of 0.9 kcal mol⁻¹ and a largest deviation of 1.4 kcal mol⁻¹ (for **6**). Finally, the G4(MP2)-6X procedure, which usually shows similar performance to G4(MP2) for difficult reactions in which multiple bonds are being broken and formed,^[17,93] gives poor performance for the hydrocarbon cages. The overall RMSD is 2.9 kcal mol⁻¹ and particularly large deviations of 3.6 and 5.4 kcal mol⁻¹ are obtained for **3** and **6**, respectively.

We now turn our attention to the CBS procedures. The computationally economical CBS-QB3 shows very poor performance with an overall RMSD of 4.2 kcal mol⁻¹. We note that in contrast to the general tendency of this procedure to overestimate TAEs,^[17,93,94] here it tends to strongly underestimate the atomization energies. The CBS-APNO procedure shows good performance with deviations below the “chemical accuracy” threshold for all the systems apart from octahedrane and dodecahedrane. However, for these two systems unacceptably large deviations of 4.5 and 4.1 kcal mol⁻¹ are obtained.

Isodesmic and homodesmotic reactions at lower levels of theory

Wheeler et al. introduced the RC-*n* hierarchy of isodesmic and homodesmotic reactions for hydrocarbons;^[95,96] the connectivity-based hierarchy (CBH) of Ramabhadran and Raghavachari represents a generalization of the same concept.^[97,98] RC-1 and CBH-0 both correspond to Pople-style isogyric bond separation reactions. For the problem at hand, they work out to:

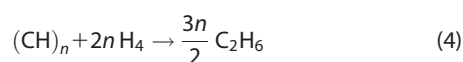


RC-2 and CBH-1 correspond to isodesmic bond separation reactions (i.e., that preserve the number of bonds of each formal type). In the present case, they correspond to:

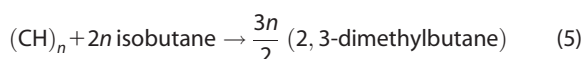
Table 5. W1-F12 component breakdown of bond separation reaction energies (kcal mol⁻¹).^[a]

	W1-F12	HF	CCSD	(T)	CV	W1-F12	HF	CCSD	(T)	CV
		RC-1, CBH-0 ^[b]					RC-2, CBH-1 ^[c]			
Ethane	18.18	21.24	-2.56	-0.58	0.08					
Propane	34.20	41.58	-6.12	-1.38	0.14	-2.16	-0.90	-1.00	-0.23	-0.02
Isobutane	48.67	61.69	-10.76	-2.44	0.19	-5.88	-2.03	-3.08	-0.71	-0.05
Diisopropyl	80.90	106.18	-20.89	-4.69	0.31	-10.02	-0.02	-8.09	-1.82	-0.09
(CH) ₄ , 1	230.55	252.05	-16.16	-5.15	-0.19	121.45	124.61	-0.80	-1.70	-0.67
(CH) ₆ , 4	282.36	317.26	-27.16	-8.12	0.40	118.72	126.10	-4.12	-2.95	-0.32
(CH) ₈ , 2	342.33	392.26	-39.81	-11.05	0.95	124.14	137.38	-9.09	-4.15	-0.01
(CH) ₁₀ , 5	365.20	429.84	-51.40	-14.26	1.05	92.46	111.24	-13.00	-5.63	-0.15
(CH) ₁₂ , 6	355.70	432.28	-60.23	-16.93	0.61	28.40	49.96	-14.15	-6.58	-0.83
(CH) ₂₀ , 3	501.85	638.45	-109.04	-29.00	1.49	-43.64	1.25	-32.24	-11.75	-0.91
		RC-4, CBH-2 ^[d]					RC-5, CBH-3 ^[e]			
Diisopropyl	1.74	4.04	-1.93	-0.39	0.01					
(CH) ₄ , 1	144.96	132.72	11.53	1.16	-0.46	134.55	108.49	23.09	3.49	-0.53
(CH) ₆ , 4	153.98	138.26	14.39	1.34	-0.02	138.35	101.92	31.72	4.84	-0.13
(CH) ₈ , 2	171.15	153.60	15.58	1.56	0.40	150.32	105.14	38.70	6.23	0.25
(CH) ₁₀ , 5	151.23	131.51	17.84	1.51	0.36	125.19	70.94	46.73	7.34	0.18
(CH) ₁₂ , 6	98.93	74.28	22.86	1.99	-0.22	67.68	1.60	57.52	8.99	-0.43
(CH) ₂₀ , 3	73.90	41.79	29.44	2.53	0.11	21.82	-79.35	87.22	14.20	-0.25

[a] Nonrelativistic, clamped-nuclei reaction energy. [b] Isogyric bond separation reactions, eq. (3). [c] Isodesmic bond separation reactions, eq. (4). [d] (Quasi)homodesmotic bond separation reactions, eq. (2). [e] (Quasi)hyperhomodesmotic bond separation reactions, eq. (5).



The distinction between RC-3 (hypohomodesmotic) and RC-4 (homodesmotic) reactions is not applicable for the present problem owing to the absence of multiple bonds. RC-4 and CBH-2 are equivalent here, both corresponding to eq. (2) above. Note that this reaction preserves the number of carbons of each branching degree. Barić and Maksić,^[99] however, apply the label “quasihomodesmotic” to reactions like (2) for severely strained cases like **2**, as the strain engenders additional p-character in the C–C bonds, leading to an effective imbalance in the number of sp³ carbons. For similar reasons, it appears (Table 5) that the hyperhomodesmotic reaction (RC-5 or CBH-3)



is probably better described as “quasihyperhomodesmotic”: despite formally preserving the numbers of CH₃–CH₂, CH₃–CH<, –CH₂–CH₂–, ... the p-character of these bonds in fact undergoes considerable change.

Under normal circumstances, reaction energies along this hierarchy would exhibit ever faster convergence in the basis set and the electron correlation method. In the present case, however, the p-strain imbalance leads to a considerable slowdown in convergence. Still, as can be seen for the W1-F12 component breakdown in Table 5, the (T) contribution to the reaction energies for RC-4, eq. (2), is much smaller than for RC-2, eq. (4), which in turn is smaller still than that for RC-1, eq. (3), which finally is still a huge improvement over raw TAEs (which one might term RC-0). RC-5 appears to be of very limited value in the present scenario. The SCF and CCSD valence correlation components drop precipitously from TAE/RC-0 to RC-1 (isogyric) to RC-2 (isodesmic), but do not appear to be

significantly reduced beyond this point. The CCSD(T)–MP2 difference still drops from RC-2 to RC-4 though. Core–valence correlation contributions are reduced dramatically from raw TAEs to RC-1, with more modest further reductions for RC-2 and RC-4.

Let us now consider some more approximate methods. The RMSDs relative to the W1-F12 values are summarized in Table 6. As can be seen, basis set sensitivity for MP2 drops precipitously from isogyric to isodesmic reactions, yet even for the isodesmic reaction the Weigend–Ahlich def2-TZVPP still is almost 1.5 kcal mol⁻¹ RMSD away from the basis set limit, compared with 0.9 kcal mol⁻¹ for the homodesmotic reactions. For B3LYP, conversely, def2-TZVPP is adequately converged even for the isogyric reactions, and definitely for the isodesmic and homodesmotic ones. The same applies, to a somewhat lesser extent, to the DSD-PBEP86 double hybrid functional. We have thus chosen def2-TZVPP as the basis set for the DFT evaluations.

Clearly, the present problem is “a tough nut to crack” for conventional DFT functionals: while B3LYP and PBE0 can get RMSDs in the 3 kcal mol⁻¹ range for the homodesmotic reactions, they go up to the 9 kcal mol⁻¹ range for the isodesmic reactions and still higher for the isogyric ones. Highly empirical functionals like M06, M06-2X, and even the range-separated hybrids M11 and ωB97X-D3 yield RMSDs of 9–13 kcal mol⁻¹ even for the homodesmotic reactions, and similar or poorer errors for the isodesmic ones.

Comparison of the B3LYP values with and without D3BJ reveals the great importance of dispersion corrections. In fact, replacing the molecular mechanics-like D3BJ correction with the Vydrov–Van Voorhis nonlocal dispersion functional^[100,101] (i.e., B3LYP-NL) leads to a significant reduction in the isogyric and isodesmic (the surprisingly good result for the TAEs being presumably fortuitous). The recent “survival of the most

Table 6. RMSD (in kcal mol⁻¹) for bond separation reactions from the W1-F12 nonrelativistic, clamped-nuclei reference values.

Method ^[a]	RC-0 TAE	RC-1, CBH-0 isogyric	RC-2, CBH-1 isodesmic	RC-4, CBH-2 homodesmotic
ω B97X-D3	3.8	25.3	10.9	6.6
ω B97X-V	8.7	7.3	5.2	4.9
B3LYP-D3BJ	16.3	23.1	9.4	3.3
B3LYP-D3BJ ^[b]	16.8	22.9	9.1	3.3
B3LYP-NL ^[b]	4.5	12.7	6.8	2.9
B3LYP ^[b]	58.7	45.0	14.4	23.1
B2PLYP-D3BJ	23.2	16.8	3.9	3.5
B2GPPLYP-D3BJ	23.3	16.3	3.6	2.3
PBE0-D3BJ	49.0	13.9	8.8	3.7
TPSS0-D3BJ	3.5	7.1	6.5	11.5
M06-2X	9.9	8.6	15.3	8.9
M06	17.9	29.4	11.7	11.5
M11	19.9	32.1	9.7	13.1
DSD-PBEPBE-D3BJ	1.5	0.7	1.0	3.6
DSD-PBEB95-D3BJ	8.3	3.3	4.4	9.4
DSD-PBEP86-D3BJ	15.0	4.7	3.4	0.9
DSD-PBEP86-D3BJ ^[b]	2.0	4.1	3.6	1.3
MP2	3.4	13.4	11.1	2.9
MP2 ^[b]	35.3	14.6	10.3	2.2
MP2-F12/VTZ-F12	59.2	19.4	9.8	2.1
MP2-F12/VQZ-F12	59.6	19.5	9.7	2.1
CBS-QB3	4.2	16.2	5.8	2.8
CBS-APNO	2.5	1.8	2.2	1.6

[a] Unless otherwise noted, the def2-TZVPP basis set is used. [b] Performed in conjunction with the def2-QZVP basis set.

transferable" ω B97X-V empirical range-separated hybrid,^[69] which has only a modest number of adjustable parameters but does use the Vydrov–Van Voorhis dispersion treatment, appears to outperform both hybrids and fellow range-separated hybrids for the present problem.

The DSD-PBEP86-D3BJ double hybrid, conversely, holds its own well for the isodesmic reactions and yields excellent performance for the homodesmotic ones; for the isogyric reactions, it has a clear advantage over the older B2PLYP and B2GP-PLYP double hybrids. DSD-PBEPBE and DSD-PBEB95 likewise perform well. (Exploratory calculation with the very recently proposed DSD-PBEP86-NL^[102] functional yielded no further improvement, as a large portion of the dispersion is already captured by the double hybrid itself.)

Second-order Møller–Plesset perturbation theory near the basis set limit (in this case, MP2-F12/cc-pVQZ-F12) yields good performance for the (quasi)homodesmotic reactions, but clearly does not capture all the correlation effects for the isodesmic reactions.

Finally, it is useful to look at the performance of the composite methods that perform poorly for the atomization reactions. Table 6 gives these results for the CBS-QB3 and CBS-APNO methods. For both methods, the (quasi)homodesmotic bond separation reactions represent improvements relative to the atomization reactions. Namely, for CBS-QB3 the RMSD drops from 4.2 to 2.8 kcal mol⁻¹, while for CBS-APNO the RMSD drops from 2.5 to 1.6 kcal mol⁻¹. The isogyric and isodesmic bond separation reactions result in similar improvements for the CBS-APNO method, however, for CBS-QB3 they result in poor performance.

Conclusions

We have obtained benchmark TAEs and heats of formation at the relativistic, all-electron CCSD(T)/CBS limit for the platonic and prismatic (CH)_n hydrocarbon cages by means of the W1-F12 and W2-F12 thermochemical protocols. Our best TAEs at 0 K (TAE₀, Table 1) are: 755.99 (tetrahedrane), 1192.69 (triprismane), 1621.82 (cubane), 2088.38 (pentaprismane), 2586.01 (octahedrane), and 4393.55 (dodecahedrane) kcal mol⁻¹. An interesting observation is that these TAEs (and their components) vary almost linearly with the number of CH groups in the hydrocarbon cages. Our best $\Delta_f H_{298}^\circ$ values are: 128.57 (tetrahedrane), 132.84 (triprismane), 144.78 (cubane), 119.42 (pentaprismane), 63.08 (octahedrane), and 20.18 (dodecahedrane) kcal mol⁻¹. Our W2-F12 heat of formation for cubane ($\Delta_f H_{298}^\circ = 144.8$ kcal mol⁻¹) suggests that the experimental gas-phase heat of formation from the NIST WebBook ($\Delta_f H_{298}^\circ = 142.7 \pm 1.2$ kcal mol⁻¹) should be revised upwards by ~ 2 kcal mol⁻¹. These results are consistent with the recently published W1-F12 results of Agapito et al.^[85] Our heat of formation for dodecahedrane suggests that the reported "semixperimental" heat of formation of 22.4 ± 1 kcal mol⁻¹ should be revised downwards by ~ 2 kcal mol⁻¹.

Using our W1-F12 and W2-F12 benchmark TAEs, we evaluate the performance of a variety of composite *Gn* and CBS procedures. We obtain the following RMSDs: 0.47 (G4), 0.64 (G3(MP2)B3), 0.90 (G4(MP2)), 1.31 (G3(MP2)), 1.39 (G3B3), 2.53 (CBS-APNO), 2.12 (G3), 2.88 (G4(MP2)-6X), and 4.17 (CBS-QB3) kcal mol⁻¹. Thus, G4 gives excellent performance, and the G3(MP2)B3 and G4(MP2) procedures appear to offer the best performance-to-computational cost ratio.


Isodesmic and even homodesmotic reactions involving these species are surprisingly challenging targets for DFT calculations, due especially to large dispersion contributions (cf. also Ref. 103).

Acknowledgments

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Keywords: computational thermochemistry · CCSD(T) · explicitly correlated coupled cluster · platonic hydrocarbon cages · prismatic hydrocarbon cages

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 Additional Supporting Information may be found in the online version of this article

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