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Fullerenes Pose a Strain on Hybrid Density Functional Theory

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ABSTRACT: The computational modeling of fullerenes plays a fundamental role in designing low-dimension carbon nanostructures. Nevertheless, the relative energies of fullerenes larger than C_{20} and C_{24} have not been comprehensively examined by means of highly accurate ab initio methods, for example, the CCSD(T) method. Here we report such an investigation for a diverse set of 29 C_{40} isomers. We calculate the energies of the C_{40} fullerenes using the G4(MP2) composite ab initio method, which approximates the CCSD(T) energy in conjunction with a triple- ζ -quality basis set (CCSD(T)/TZ). The CCSD(T)/TZ isomerization energies span 43.1–763.3 kJ mol⁻¹. We find a linear correlation ($R^2 = 0.96$) between the CCSD(T)/TZ isomerization energies and the



fullerene pentagon signatures (P_1 index), which reflect the strain associated with fused pentagon-pentagon rings. Using the reference CCSD(T)/TZ isomerization energies, we examine the relationship between the percentage of exact Hartree–Fock (HF) exchange in hybrid density functional theory (DFT) methods and the pentagon–pentagon strain energies. We find that the performance of hybrid DFT methods deteriorates with the pentagon–pentagon strain energy. This deterioration in performance becomes more pronounced with the inclusion of high amounts of HF exchange. For example, for B3LYP (20% HF exchange), the root-mean-square deviation (RMSD) relative to G4(MP2) increases from 8.9 kJ mol⁻¹ for the low-strain isomers ($P_1 = 11$) to 18.0 kJ mol⁻¹ for the high-strain isomers ($P_1 > 13$). However, for BH&HLYP (50% HF exchange) the RMSD increases from 23.0 ($P_1 = 11$) to 113.2 ($P_1 > 13$) kJ mol⁻¹. A similar trend is observed for the M06/M06-2X pair of functionals. Namely, for M06 (27% HF exchange) the RMSD increases from 0.8 ($P_1 = 11$) to 21.0 ($P_1 > _13$) kJ mol⁻¹, whereas for M06-2X (54% HF exchange) the RMSD increases from 16.7 ($P_1 = 11$) to 77.7 ($P_1 > 13$) kJ mol⁻¹. Overall, we find that the strain associated with pentagon adjacency is an inherently challenging problem for hybrid DFT methods involving high amounts of HF exchange and that there is an inverse relationship between the optimal percentage of HF exchange and the pentagon–pentagon strain energy. For example, for BLYP the optimal percentages of HF exchange are 13% ($P_1 = 11$), 10% ($P_1 = 12$), 7.5% ($P_1 = 13$), and 6% ($P_1 > 13$).

1. INTRODUCTION

Carbon fullerenes are pseudospherical carbon cages comprising of (idealized) sp²-hybridized carbons.¹⁻⁴ Classical fullerenes consist of pentagon and hexagon rings, which results in a positive Gaussian curvature.⁵ Fullerenes have many structural isomers with different three-dimensional shapes, depending on the distribution and connectivities of the pentagon rings. For example, the different distribution of the 12 pentagons in C₆₀ results in 1812 structural isomers.² Fullerenes (in particular, the smaller ones) are characterized by a curved π -electron system delocalized over the whole molecule as well as strain energy, which increases with the number of fused pentagon—pentagon rings.^{6–12} These two features make fullerenes a challenging target for quantum-chemical theoretical procedures. However, because of their prohibitive computational cost, high-level ab initio investigations of fullerenes are scarce.^{1,13–16}

Manna and Martin examined the relative stability of two C_{20} fullerenes of D_{3d} and D_{2h} symmetry at the CCSD(T)/CBS level of theory (i.e., coupled-cluster energy with single, double, and

quasiperturbative triple excitations near the complete basis-set limit). At the MP2-F12/V{D,T}Z-F12 + CCSD(T)/VTZ – MP2/VTZ level (denoted by CCSD(T)/CBS(MP2)), they found that the highly symmetric D_{3d} structure is more stable by 1.9 kJ mol⁻¹ than the D_{2h} structure. Remarkably, they were also able to obtain the energies of two C₂₄ fullerenes (of O_h and D_{3d} symmetries) using the valence part of the high-level composite W1h theory.¹⁷ Briefly, in W1h theory the Hartree–Fock (HF) and valence CCSD and (T) correlation energies are calculated using the following basis set extrapolations HF/V{T,Q}Z + CCSD^{corr}/V{T,Q}Z + (T)^{corr}/V{D,T}Z. At the W1h level, the

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Figure 1. Optimized structures of the C_{40} isomers in the iso- C_{40} database. The CCSD(T)/TZ isomerization energies from G4(MP2) theory are listed in Table 1.

 C_{24} fullerene in O_h symmetry is higher in energy than the D_{3d} isomer by as much as 152.0 kJ mol⁻¹.

By necessity, high-level investigations of the much larger C_{60} fullerenes used more approximate CCSD(T)-based methods and only a handful of selected isomers of the entire set of 1812 C_{60} isomers. Sure et al.¹ obtained domain-based local pair natural orbital (DLPNO)¹⁸ CCSD(T) isomerization energies for a subset of 10 C_{60} isomers. In particular, they estimated DLPNO-CCSD(T)/CBS* energies from DLPNO-CCSD-(T)/Def2-TZVP energies and MP2/V{D,T}Z energies.^{1,19} This study considered the five energetically most stable C_{60} isomers and five higher-energy isomers with energies of up to 690 kJ mol⁻¹. A later study¹⁶ calculated the relative energies of eight highly symmetric C_{60} isomers using the high-level G4(MP2) composite method.²⁰ The G4(MP2) composite procedure approximates the CCSD(T)/TZ) via an MP2based basis-set additivity scheme.²¹ G4(MP2) theory has been found to consistently obtain structural isomerization energies with chemical (or better) accuracy, arbitrarily defined as 1 kcal $mol^{-1} = 4.2 \text{ kJ } mol^{-1}$).^{22–27} Of particular relevance to the present work is the excellent performance of G4(MP2) for isomerization energies in polycyclic aromatic hydrocarbons,²² conjugated \rightarrow nonconjugated isomerizations in dienes,²³ C₈H₈ structural isomerizations,²⁴ and isomerization energies in carborane cages.²⁶ In addition, here we evaluate the performance of G4(MP2) theory for the above C_{20} and C_{24} CCSD(T)/ CBS isomerization energies of Manna and Martin. For the C₂₀ fullerenes, G4(MP2) deviates from the CCSD(T)/CBS(MP2)reference isomerization energy by merely 0.2 kJ mol⁻¹. For the C_{24} fullerenes, the G4(MP2) isomerization energy is higher by 3.3 kJ mol⁻¹ than the W1h reference value; we note that this represents a deviation of merely 2.1%.

What is missing from the literature is a study that considers a larger set of fullerene isomers at the CCSD(T) level of theory. Here we calculate the isomerization energies of a diverse set of 29 C_{40} fullerenes at the CCSD(T)/TZ level (to be known as the iso- C_{40} database). The isomers in the iso- C_{40} database are shown in Figure 1. The database covers a broad spectrum of structures with relative energies ranging between 43.1 and 763.3 kJ mol⁻¹ relative to the most stable C_{40} isomer (1, Figure 1). Reference isomerization energies at the CCSD(T)/TZ level are approximated by means of the G4(MP2) composite procedure. These benchmark values allow us to assess the performance of a variety of contemporary density functional theory (DFT) procedures for the isomerization energies. An important finding is that the inclusion of even moderate amounts of HF exchange in the functional form results in improved performance for the low-strain isomers but significantly deteriorates performance for the high-strain isomers.

2. COMPUTATIONAL METHODS

CCSD(T)-based composite ab initio methods are theoretical procedures specifically designed for approximating the CCSD-(T) energy close to the complete basis set limit (CCSD(T)/CBS).²⁸ In the present work, we use the well-established G4(MP2) method^{20,21} to calculate the relative energies of the C₄₀ isomers. In G4(MP2) theory, the CCSD(T) energy is approximated using the following formula.

$$E[CCSD(T)/TZ]$$

$$\approx E[CCSD(T)/6 - 31G(d)] + E[MP2/G3MP2$$

$$LargeXP] - E[MP2/6 - 31G(d)] + E[HF/{T, Q}]$$

$$- E[HF/G3LargeXP]$$
(1)

Here, HF/{T,Q} indicates extrapolation of the HF energy from truncated versions of the aug-cc-pVTZ and aug-cc-pVQZ basis sets.²⁰ All ab initio calculations involved in the G4(MP2) procedure were calculated using Molpro 2016.^{29,30} G4(MP2) theory has been found to reproduce isomerization energies in conjugated, aromatic, and cage systems within chemical accuracy.^{22–27} All the C₄₀ isomers were confirmed to have singlet ground states at the MN15/Def2-TZVPP level of theory. The adiabatic singlet—triplet separation energies are presented in Table S1 of the Supporting Information.

The DFT exchange-correlation (XC) functionals considered in the present study (ordered by their rung on Jacob's Ladder)³¹ are the local spin density approximation (LSDA) SVWN3,^{32,33} the generalized gradient approximation (GGA) methods BLYP,^{34,35} PBE,³⁶ BP86,^{34,37} BPW91;^{35,38} the meta-GGA (MGGA) methods M06-L,³⁹ TPSS,⁴⁰ B97M-V;⁴¹ the nonseparable gradient approximation (NGA) MN15-L;⁴² the global hybrid-GGA (HGGA) methods BH&HLYP,⁴³ B3LYP,^{34,44,45} PBE0;⁴⁶ the hybrid-meta-GGA (HMGGA) methods M06,⁴⁷ M06-2X,⁴⁷ TPSSh,⁴⁸ TPSS0,⁴⁸ PW6B95;⁴⁹ the hybrid-meta NGA MN15;⁵⁰ the range-separated methods CAM-B3LYP,⁵¹ HSE06,⁵² LC- *ω*PBE,⁵³ *ω*B97X-D,⁵⁴ M11,⁵⁵ N12-SX,⁵⁶ MN12-SX;⁵⁶ and the double hybrid (DH) methods B2-PLYP,⁵⁷ mPW2-PLYP,⁵⁸ B2GP-PLYP,⁵⁹ B2K-PLYP,⁶⁰ B2T-PLYP,⁶⁰ DSD-PBEP86,^{61,62} and PWPB95.⁶³ Empirical dispersion corrections are included where possible using the atomic-charge dependent D4 dispersion correction.^{64,65} All the DFT and DHDFT single-point energy calculations were performed in conjunction with the Def2-QZVPP basis set,⁶⁶ using the ORCA 5.0 and Gaussian 16 program suites.⁶⁷⁻⁶⁹ Following the work of Sure et al.,¹ the geometries of all structures were optimized at the PBE-D3/Def2-TZVPP level of theory and confirmed to have all real harmonic vibrational frequencies. Zero-point vibrational energies (ZPVEs) and enthalpic corrections are calculated within the rigid rotor-harmonic oscillator (RRHO) approximation at the same level of theory. All geometry optimizations and frequency calculations were performed using the Gaussian 16 program suite.⁶⁹

3. RESULTS AND DISCUSSION

3.1. CCSD(T)/TZ Isomerization Energies for the C_{40} Isomers from G4(MP2) Theory. Table 1 depicts the

Table 1. CCSD(T)/TZ Relative Energies from G4(MP2) Theory: Electronic Energy ($\Delta E_{e,iso}$), Zero-Point Vibrational Inclusive Energy ($\Delta E_{0,iso}$), Enthalpy at 298 K ($\Delta H_{298,iso}$), and Gibbs Free Energy at 298 K($\Delta G_{298,iso}$) (in kJ mol⁻¹)^{*a*}

isomer No.	P_1	$(\Delta E_{e, \rm iso})$	$(\Delta E_{0,\rm iso})$	$(\Delta H_{298,\mathrm{iso}})$	$(\Delta G_{298, \mathrm{iso}})$
1	10	0.0	0.0	0.0	0.0
2	10	43.1	44.0	43.9	44.0
3	11	65.4	63.0	63.4	62.7
4	11	94.3	92.0	92.4	91.7
5	11	117.4	115.6	115.9	115.4
6	12	142.7	136.5	137.8	135.7
7	12	159.9	157.1	157.5	156.8
8	12	164.2	160.9	161.4	160.5
9	12	167.2	164.0	164.4	163.5
10	12	173.4	168.6	169.6	167.8
11	12	194.2	190.5	191.1	189.9
12	12	198.5	193.1	193.9	192.4
13	12	206.3	202.6	203.1	202.2
14	13	210.8	205.2	206.1	204.5
15	13	216.2	213.0	213.4	212.5
16	13	219.5	213.3	214.5	212.3
17	13	237.3	232.4	233.1	231.8
18	13	241.8	236.4	237.2	235.7
19	13	286.2	281.4	282.0	280.8
20	13.5	294.3	288.6	289.4	287.9
21	14	332.5	326.6	327.4	326.0
22	14	342.6	334.1	335.6	333.0
23	14	377.0	367.7	369.1	366.4
24	14	388.5	379.7	381.2	378.4
25	15	400.4	392.7	393.8	391.8
26	15	412.3	403.4	404.8	402.3
27	15	448.0	438.8	440.2	437.8
28	16	472.6	461.8	463.4	460.5
29	20	763.3	736.8	742.8	729.7
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^{*a*}The single pentagon signature (P_1) indices are also listed.

G4(MP2) isomerization energies (ΔE_{iso}) along with the single pentagon signature (P_1) indices for the isomers in the iso-C₄₀ database (Figure 1), where P_1 is defined as the weighted sum of the Fowler–Manolopoulos pentagon indices (p_n), that is, the number of pentagons attached to *n* neighboring pentagons.

$$P_1 = \frac{1}{2} \sum_{n=1}^{5} np_n$$

The two energetically most stable C_{40} isomers are associated with $P_1 = 10$ and are separated by 43.1 kJ mol⁻¹. 60% of the isomers are associated with P_1 values of 11–13 with relative energies ranging between 65.4 and 286.2 kJ mol⁻¹. The rest of



Figure 2. CCSD(T)/TZ relative energies from G4(MP2) theory $(\Delta E_{e,iso}, in kJ mol^{-1})$ as a function of the single pentagon signature P_1 indices.

shows the CCSD(T)/TZ isomerization energies ($\Delta E_{e,iso}$) as a function of the single pentagon signature P_1 indices. With few exceptions, there is a linear correlation between the $\Delta E_{e,iso}$ and P_1 values. For example, the squared correlation coefficient between the $\Delta E_{e,iso}$ and P_1 values is $R^2 = 0.96$. Thus, our high-level G4(MP2) isomerization energies confirm that the P_1 values are a good qualitative measure of the fullerene energetic stability.

Figure 3 shows the relative energy distribution of the C_{40} isomers on the electronic potential energy surface. With the exception of the highly energetic tube-like isomer (29), the isomerization energies vary more or less continuously in the energy range between 43.1 and 472.6 kJ mol⁻¹, where the majority of isomers (62%) lie in a range of 100–400 kJ mol⁻¹. The energy difference between consecutive isomers varies between 2.9 kJ mol⁻¹ (isomers 8 and 9) and 44.4 kJ mol⁻¹ (isomers 18 and 19). Thus, unlike the case for the C_{60} isomers, where many consecutive isomers are separated by less than 1.0 kJ mol⁻¹ from each other, ¹ it is reasonable to expect that a good DFT method should be able to predict the energetic ordering of the C_{40} isomers.

The G4(MP2) electronic isomerization energies ($\Delta E_{e,iso}$) are converted to isomerization energies at 0 K ($\Delta E_{0,iso}$) by including PBE-D3/Def2-TZVPP harmonic ZPVE corrections scaled as recommended in ref 70. The ZPVE corrections are listed in Table S2 of the Supporting Information. The scaled harmonic ZPVE corrections tend to reduce the isomerization energies by amounts ranging from 1.8 (isomer 5) to 26.5 (isomer 29) kJ mol⁻¹. As might be expected, a particularly large ZPVE correction is obtained for the highly energetic, tube-like isomer 29. We note that the corrections for the ellipsoid-like isomers (e.g., isomers 22–28) are still on the order of ~10 kJ mol⁻¹ (Table S2).

The isomerization energies at 0 K can be converted to isomerization Gibbs free energies at 298 K ($\Delta G_{298,iso}$) by including PBE-D3/Def2-TZVPP enthalpic temperature and entropic corrections. The two corrections tend to have opposite signs, and their sum amounts to less than ~1 kJ mol⁻¹ (with the exception of isomer **29**, for which their sum amounts to -7.1 kJ mol⁻¹, Table S2). Overall, the Gibbs free isomerization energies at 298 K range between 44.0 and 729.7 kJ mol⁻¹ (Table 1).

3.2. Performance of DFT Procedures as a Function of the P₁ Strain Indices. In the previous section, we showed that there is a correlation between the single pentagon signature P_1 indices and relative CCSD(T)/TZ isomerization energies $(\Delta E_{e,iso})$. Here we will examine the performance of DFT methods across the rungs of Jacob's Ladder for the isomerization energies as a function of the P_1 values. Table 2 gives an overview of the root-mean-square deviations (RMSDs) for the DFT methods that were considered in this work. The RMSDs over the entire set of isomers span for the conventional DFT methods over a wide range between 11.4 (TPSSh) and 103.0 (LC- ω PBE) kJ mol⁻¹. Inspection of the RMSDs for the different P_1 values in Table 2 reveals that, for most functionals, there is a clear correlation between the deterioration in performance and the P_1 value. Figure 4 depicts the RMSDs for a representative set of functionals as a function of the pentagon P_1 indices. For the subset of isomers associated with a low strain index of $P_1 = 11$, the HGGA and HMGGA methods that include moderate amounts of HF exchange outperform the GGA and MGGA functionals. However, as the strain energy increases, the performance of the HGGA and HMGGA methods deteriorates significantly, whereas the deterioration in the performance of the GGA and MGGA functionals is much less sensitive to the strain energy. As a result, the pure functionals significantly outperform the HGGA and HMGGA functionals for the isomerization energies involving the highly strained C_{40} isomers with $P_1 > 13$.

It is instructive to consider the performance of the rangeseparated hybrid and hybrid-meta GGA methods to gain insights into the role of short-range (SR) and long-range (LR) HF exchange in the above errors. Let us begin with the screened exchange hybrid functional HSE06, which is based on PBE0 in



Figure 3. (a) CCSD(T)/TZ relative energies from G4(MP2) theory ($\Delta E_{e,iso}$, in kJ mol⁻¹) for the C₄₀ isomers (the isomer structures are shown in Figure 1). (b) Normal distribution of isomerization energies between 0 and 473 kJ mol⁻¹. The Gaussian is centered around a mean of 236.0 kJ mol⁻¹ and has a standard deviation of 124.5 kJ mol⁻¹; the *x*- and *y*-axes represent the probability and the isomerization energy, respectively.

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Table 2. Root-Mean-Square Deviations (RMSDs) for the Isomerization Energies in the iso- C_{40} Database as a Function of the P_1 Strain Indices (in kJ mol⁻¹)^{*a*}

type ^b	method	11 ^c	12 ^c	13 ^c	>13 ^c	everything ^d
LSDA	SVWN3	14.0	23.8	22.3	30.6	25.1
GGA	BLYP	8.9	13.6	12.3	18.0	14.5
	BP86	11.5	18.8	17.4	24.5	19.9
	BPW91	11.4	18.4	16.8	23.4	19.2
	PBE	12.4	20.4	19.0	26.3	21.5
MGGA	TPSS	10.0	15.4	13.1	18.2	15.3
	M06-L	7.6	11.7	8.8	16.4	12.6
	MN15-L	11.9	20.5	17.5	22.9	19.8
	B97M-V	6.0	6.1	6.1	21.6	13.7
HGGA	B3LYP	4.2	12.4	19.5	38.5	25.6
	PBE0	4.7	12.5	20.0	42.5	27.9
	BH&HLYP	23.0	50.5	64.8	113.2	79.1
HMGGA	TPSSh	4.1	3.7	5.1	18.2	11.4
	TPSS0	6.3	16.3	24.8	50.4	33.5
	PW6B95	5.7	15.1	21.6	41.3	27.9
	M06	0.8	4.4	7.2	21.0	13.3
	M06-2X	16.7	36.7	44.6	77.7	54.8
	MN15 ^c	9.2	21.5	26.0	44.0	31.3
RS	HSE06	3.7	9.3	16.3	36.3	23.6
	N12-SX	3.7	9.2	16.3	36.5	23.6
	MN12-SX	3.2	8.2	14.7	34.5	22.2
	CAM-B3LYP	22.3	48.4	58.6	99.1	70.5
	ωB97X-D	22.0	47.9	56.7	97.5	69.3
	M11	29.6	62.2	71.4	116.8	84.7
	LC-@PBE	34.8	73.6	86.6	143.2	103.0
DHDFT	B2-PLYP	8.6	14.7	13.5	17.8	14.9
	mPW2-PLYP	5.2	6.7	7.0	9.1	7.5
	B2GP-PLYP	8.2	13.4	12.7	13.7	12.7
	B2K-PLYP	8.2	13.3	12.8	12.2	12.1
	B2T-PLYP	7.2	11.5	10.6	11.3	10.7
	DSD-PBEP86	8.6	15.6	15.2	21.4	17.1
	PWPB95	2.2	3.5	8.7	15.3	10.2

^{*a*}The CCSD(T)/TZ reference values from G4(MP2) theory are listed in Table 1. ^{*b*}LSDA = local spin density approximation, GGA = generalized gradient approximation, HGGA = hybrid-GGA, MGGA = meta-GGA, HMGGA = hybrid-meta-GGA, RS = range separated, DH = double hybrid. ^{*c*}P₁ value. ^{*d*}RMSD over the entire set of isomers.

the SR and includes no LR exact exchange. HSE06 shows better performance than the global hybrid PBE0 across all isomer subsets. In particular, the RMSD for HSE06 is lower than that for PBE0 by 1.0 ($P_1 = 11$), 3.2 ($P_1 = 12$), 3.7 ($P_1 = 13$), and 6.2 $(P_1 > 13)$ kJ mol⁻¹ (Table 2). Thus, on the one hand, the improvement in performance increases with the level of pentagon-pentagon strain energy. On the other hand, the long-range-corrected (LC) LC-wPBE functional, which includes 100% of HF exchange in the long range, leads to a sharp deterioration in performance with an overall RMSD of 103.0 kJ mol^{-1} (Table 2). Again, deterioration in performance is more pronounced for the highly strained isomers. The other considered screened exchange hybrid and hybrid-meta functionals N12-SX and MN12-SX show very similar performance to that of HSE06 across all the isomer subsets. We note that HSE06, N12-SX, and MN12-SX all involve 25% of short-range HF exchange and all have a range-separation parameter of ω = $0.11a_0^{-1}$. The considered LC functionals ω B97X-D, M11, and CAM-B3LYP with 65–100% exact exchange at long-range show very poor performance, albeit better than that of LC- ω PBE. The improved performance of these LC functionals relative to LC- ω PBE may be partly attributed to smaller range-separation

parameters, namely, $\omega = 0.4a_0^{-1}$ for LC- ω PBE compared to $(0.20-0.33)a_0^{-1}$ for ω B97X-D, M11, and CAM-B3LYP.

The inclusion of MP2-type correlation energy in the functional form mitigates the deterioration in performance with respect to the strain energy. As a result, most of the DHDFT methods exhibit relatively uniform performance across the isomers with $P_1 \ge 12$ (Table 2). The main exception to this is the PWPB95 functional, for which there is a linear correlation between the RMSD and strain energy, namely, we obtain the following RMSDs: 2.2 ($P_1 = 10$), 3.5 ($P_1 = 11$), 8.7 ($P_1 = 12$), and 15.3 ($P_1 > 13$) kJ mol⁻¹. Nevertheless, the exceptional performance of PWPB95 for the low strain isomers is remarkable. Overall, the RMSDs over the entire set of C₄₀ isomers exceed 10 kJ mol⁻¹ for the DHDFT methods. The exception to this is mPW2-PLYP, which shows excellent performance with an overall RMSD of merely 7.5 kJ mol⁻¹.

3.3. Exact HF Exchange and Strain Energy. In the previous section, we found that inclusion of even moderate amounts of HF exchange in the functional results in significant deterioration in performance for the highly strained isomers. Remarkably, for isomers with $P_1 > 13$ the GGA and MGGA methods (and even the LSDA method SVWN3) outperform most of the HGGA and HMGGA methods (Figure 4 and Table



Figure 4. RMSDs over the isomerization energies in the iso- C_{40} database relative to CCSD(T)/TZ reference values from G4(MP2) theory for selected DFT procedures as a function of the P_1 indices (in kJ mol⁻¹).

2). To further examine the relationship between the inclusion of HF exchange in the functional and the performance for strained isomers, Figure 5 compares the performance of two popular GGA methods (BLYP and PBE) with that of their hybrid GGA counterparts (B3LYP and PBE0). It is evident that the inclusion of a moderate amount of exact exchange (20-25%) makes these XC functionals highly sensitive to strain in the C₄₀ fullerenes. However, the variation in performance is not systematic. Namely, performance is significantly improved for the low-strain systems but significantly deteriorates for the high-strain isomers. First, let us consider the BLYP/B3LYP pair of functionals, both of which use Becke's 1988 GGA functional³⁵ with Lee, Yang, and Parr's correlation functional.³⁴ The RMSD over the systems involving low strain ($P_1 = 11$) drops from 8.9 (BLYP) to 4.2 (B3LYP) kJ mol⁻¹, while the RMSD over the

highly strained systems ($P_1 > 13$) increases from 18.0 (BLYP) to 38.5 (B3LYP) kJ mol⁻¹. For the systems involving moderate strain ($P_1 = 13$), the difference between the two functionals is still significant, namely, BLYP outperforms B3LYP by 7.2 kJ mol⁻¹ (Table 2 and Figure 5). For the isomers associated with P_1 = 12, BLYP and B3LYP result in similar performance with RMSDs of 13.6 and 12.4 kJ mol⁻¹, respectively.

Similar trends are observed for the PBE and PBE0 functional pair. For the low-strain isomers, PBE0 outperforms PBE by 7.7 ($P_1 = 11$) and 7.9 ($P_1 = 12$) kJ mol⁻¹. For the isomers with $P_1 = 13$, both functionals give a similar performance with RMSDs of 19.0 (PBE) and 20.0 (PBE0) kJ mol⁻¹, whereas for the highly strained systems ($P_1 > 13$) PBE outperforms PBE0 by as much as 16.2 kJ mol⁻¹ (Table 2 and Figure 5).

The above results indicate that the inclusion of a moderate percentage of HF exchange in the functional form (20-25%) results in a significant improvement in performance for the lowstrain systems and a significant deterioration in performance for the high-strain systems. It is instructive to examine in more detail the relationship between the amount of HF exchange included in the functional and the strain energy. For this purpose, we scanned the percentage of HF exchange between 0 and 100% for BLYP and PBE. Figure 6 shows the relationship between the amount of HF exchange and the RMSD over the subsets with increasing strain energy. For all the subsets ($P_1 = 11, 12, 13, and$ 13.5-20) the RMSD exhibits a clear parabolic dependence on the amount of HF exchange. However, the minimum is shifted to smaller amounts of HF exchange as the pentagon-pentagon strain in the fullerene increases. For the BLYP functional we obtain the minima at optimal percentages of HF exchange of $13\% (P_1 = 11), 10\% (P_1 = 12), 7.5\% (P_1 = 13), and 6\% (P_1 > 13)$ (Figure 6a). In addition, the RMSD at the minimum increases in the same order, namely, the RMSDs at the minima are 1.3 (P_1 = 11), 1.8 ($P_1 = 12$), 4.4 ($P_1 = 13$), and 10.9 ($P_1 > 13$) kJ mol⁻¹. Similar trends are obtained for the PBE functional (Figure 6b). However, the optimal percentage of HF exchange is shifted to higher values compared to BLYP. Namely, the optimal percentages of HF exchange of 18% ($P_1 = 11$), 15% ($P_1 = 12$), 12% ($P_1 = 13$), and 9% ($P_1 > 13$). The minimum RMSDs are also slightly higher compared to BLYP, namely, they are 2.6 (P_1



Figure 5. RMSDs (in kJ mol⁻¹) for two popular GGA and HGGA functional pairs (a) BLYP and B3LYP and (b) PBE and PBE0. The red arrows indicate the effect including a moderate amount of HF exchange in the functional form.



Figure 6. Dependence of the RMSDs on the HF exchange mixing coefficient for two GGA functionals (a) BLYP and (b) PBE for the subsets involving varying degrees of pentagon–pentagon strain ($P_1 = 11, 12, 13, \text{ and } P_1 > 13$).

= 11), 2.9 (P_1 = 12), 4.0 (P_1 = 13), and 12.6 (P_1 > 13) kJ mol⁻¹ (Figure 6b).

It has been found that, for systems with an appreciable degree of multireference character, the inclusion of high percentages of exact exchange leads to a deterioration in the performance of the XC functional.^{25,50,71,72} This deterioration in performance may be attributed to the replacement of DFT exchange, which includes some static correlation effects, 73-77 with HF exchange, which introduces a static correlation error for highly multireference systems.⁷⁸ This static correlation error may become more pronounced for DFT methods with high percentages of HF exchange. It is therefore of interest to examine the multireference character of the C_{40} isomers. Here, we will consider two coupled-cluster-based diagnostics for multireference character. The first is an energy-based diagnostic of the form $\text{%TAE}[(T)] = 100 \times (TAE[CCSD(T)] - TAE$ [CCSD])/TAE[CCSD(T)] (where TAE[CCSD] and TAE-[CCSD(T)] are the total atomization energies calculated at the CCSD and CCSD(T) levels, respectively).^{25,28,79,80} It has been found that %TAE[(T)] values below 2% indicate systems dominated by dynamical correlation and that values between 2 and 5% indicate mild nondynamical correlation effects.^{25,28,79} The %TAE[(T)] values for the C₄₀ isomers are given in Table S3 of the Supporting Information. For the C_{40} isomers, we obtain % TAE[(T)] values between 1.25 and 1.5% at the CCSD(T)/6-31G(d) level of theory. For reasons of computational cost, we are unable to calculate the %TAE[(T)] diagnostic with a larger basis set. However, it has been found that the %TAE[(T)]diagnostic exhibits a relatively weak basis set dependence, and values obtained with a double- ζ basis set are normally within ~1% of the basis-set-limit values.²⁵ Despite the relatively low % TAE[(T)] values, we note that there seems to be a weak linear correlation ($R^2 = 0.85$) between the %TAE[(T)] values and the pentagon signature P_1 values (see Figure S1 of the Supporting Information).

The above %TAE[(T)] values are in good agreement with the T_1 diagnostics for multireference character, which are obtained from CCSD T_1 amplitudes. It has been suggested that T_1 values below 0.02 indicate systems that are not dominated by a multireference character. With one exception, the T_1 values range between 0.01 and 0.02. For isomer **23** ($P_1 = 14$) we obtain

a T_1 value of 0.03. We note that, in contrast to the %TAE[(T)] values, there seems to be no correlation between the T_1 and P_1 values. For example, the least strained isomer ($P_1 = 10$) and the most strained isomer ($P_1 = 20$) are associated with similar T_1 values of 0.14–0.16 (see Table S3 and Figure S1 of the Supporting Information). Overall, these results suggest that nondynamical correlation effects play a relatively minor role in the deterioration in performance of functionals with high percentages of exact exchange for the highly strained isomers.

In the context of the performance of functionals with high percentages of HF exchange, it is also worth performing a restricted/unrestricted stability analysis (Stable = Opt keyword in Gaussian). For reasons of computational cost, we performed these calculations in conjunction with the Def2-TZVPP basis set for one popular functional with a moderate amount of HF exchange (B3LYP) and two popular functionals with high percentages of HF exchange (BH&HLYP and M06-2X). For B3LYP (20% HF exchange), employing the UB3LYP formalism leads to relatively small energy lowering relative to RB3LYP by 1-10 kJ mol⁻¹ for seven of the isomers. However, these symmetry-broken solutions lead to a negligible reduction in the overall RMSD by 0.8 kJ mol⁻¹. For M06-2X (54% HF exchange), the UM06-2X formalism leads to energy lowering by 3-18 kJ mol⁻¹ for six of the isomers. Again, this only leads to a small reduction in the overall RMSD by 1.8 kJ mol⁻¹. For BH&HLYP, the UBH&HLYP formalism leads to a significant lowering of the energies relative to RBH&HLYP and to a more significant reduction in the overall RMSD by 22.2 kJ mol⁻¹. Having said that, the overall RMSD for UBH&HLYP/Def2-TZVPP still remains very high at 56.7 kJ mol⁻¹. We note that it has been found that fullerenes that are not strongly correlated may exhibit artificial symmetry breaking with heavily spincontaminated unrestricted HF (UHF) solutions.⁸¹

The above results indicate that the energetic destabilization associated with pentagon adjacency in fullerenes is a challenging problem for DFT methods and that functionals with high percentages of exact exchange show poor performance for fullerenes with larger pentagon signature P_1 indices. Pentagon fusion in fullerenes involves both angular and π -electronic strain effects.^{82–84} It is already well-established that isomerization energies involving strained hydrocarbon rings and cages pose a

significant challenge for many DFT functionals.^{23,24,27,85–87} Although it is difficult to separate between different types of strain energies, ^{23,24,88} it seems there is little correlation between deterioration in performance and the inclusion of moderate-to-high percentages of exact exchange for the benchmark sets involving high angular strain. Thus, the observed deterioration in performance in the present study may be attributed to π -electronic effects or the combination of both π -electronic and angular strain effects. To further examine this issue, we constructed a small benchmark set comprising polycyclic hydrocarbons with two, three, and four fused pentagon rings, shown in Scheme 1. For these small model systems containing

Scheme 1. Schematic Representation of the Isomerization Reactions in Which a Fused-Polypentagon Is Converted to Ethynyl-Substituted Benzene



up to 12 carbon atoms, we were able to obtain CCSD(T)/CBS isomerization energies for the fused-polypentagon \rightarrow ethynylsubstituted benzene isomerization reaction. The CCSD(T)/CBS reference values are obtained from W1–F12 theory.⁸⁹ For the purpose of this benchmark, it is sufficient to use the valence part of the W1–F12 energy (denoted by W1–F12_{val}).

Table 3 gives the W1–F12_{val} isomerization energies as well as the deviations from the W1–F12_{val} isomerization energies for selected DFT methods. We start by noting that G4(MP2) attains a mean-absolute deviation of 3.6 kJ mol^{-1} (and an RMSD

Table 3. Deviations from W1-F12_{val} CCSD(T)/CBS Reaction Energies for Selected DFT Methods for the Isomerization Reactions 1-3 (Scheme 1)^{*a*}

method	(1)	(2)	(3)	RMSD ^b
TPSS	3.9	6.6	-15.4	9.9
TPSSh	3.5	6.2	-11.4	7.8
PBE	-2.2	-10.3	-46.7	27.6
PBE0	-2.3	-8.3	-31.0	18.6
BLYP	29.3	56.7	59.8	50.5
B3LYP	26.3	51.3	60.2	48.1
BH&HLYP	26.2	55.8	83.1	59.7
M06-L	20.1	34.0	21.2	25.9
M06	20.2	37.0	40.8	33.9
M06-2X	24.2	41.8	57.2	43.2
M06-HF	22.8	41.3	76.2	51.7
W1-F12 _{val}	52.7	101.9	112.9	N/A

^{*a*}Deviations in the isomerization energies relative to the W1–F12val reference values listed in the bottom line. ^{*b*}RMSD over the three reactions.

of 4.2 kJ mol⁻¹) relative to the CCSD(T)/CBS reference energies from $W1-F12_{val}$ theory. The selected functionals in Table 3 comprise several GGA methods and their HGGA/ HMGGA counterparts. For all hybrid functionals, the deviations from W1-F12_{val} theory (in absolute value) increase with the pentagon adjacency count, that is, in the order (1) < (2) < (3)(Table 3). However, the deterioration in performance becomes significantly more pronounced for the methods with high amounts of HF exchange (BH&HLYP, M06-2X, and M06-HF). It is instructive to consider the Minnesota family of functionals M06-L, M06, M06-2X, and M06-HF. For reaction (1) all functionals attain similar deviations ranging between 20.1 (M06-L) and 24.2 (M06-2X) kJ mol⁻¹, which do not correlate with the amount of HF exchange in the functional form (Table 3). For reaction (2), which involves a higher degree of pentagon-pentagon strain, there seems to be some correlation between the performance of the functionals and the amount of HF exchange. Namely, M06-L/M06 attain deviations of 34.0/ 37.0 kJ mol⁻¹, while M06-2X/M06-HF attain deviations of 41.8/41.3 kJ mol⁻¹. However, for reaction (3), which involves the highest degree of pentagon-pentagon strain, there is a clear correlation between performance and the amount of HF exchange. Namely, we obtain deviations of 21.2 (M06-L, 0% HF exchange), 40.8 (M06, 27% HF exchange), 57.2 (M06-2X, 54% HF exchange), and 76.2 (M06-HF, 100% HF exchange) kJ mol^{-1} .

3.4. Dispersion Corrections. Table 4 gathers the differences in RMSD between the dispersion-corrected and uncorrected DFT functionals using the recently developed D4 correction ($\Delta D4 = RMSD(DFT) - RMSD(DFT-D4)$). A positive $\Delta D4$ value indicates that the D4 correction improves the performance of the functional, whereas a negative value indicates deterioration in performance. Upon inspection of Table 4 two general trends emerge, namely, (i) dispersion corrections tend to systematically deteriorate the performance of the GGA, MGGA, and DHDFT methods and systematically improve the performance of the HGGA and HMGGA methods and (ii) the effect of the dispersion correction tends to increase with the strain in the system. The inclusion of the D4 correction affects the isomers involving low strain energies $(P_1 = 11)$ by less than 2 kJ mol⁻¹. For the subsets of isomers with $P_1 = 12$ and 13, the effects of the D4 correction increase up to ~ 5 kJ mol⁻¹. However, for the highly strained isomers ($P_1 > 13$), the $\Delta D4$ values are more pronounced and exceed 5 kJ mol⁻¹ for nearly all GGA, MGGA, HGGA, and HMGGA methods. Notably large $\Delta D4$ values of up to ~10 kJ mol⁻¹ in absolute value are obtained for the BLYP, BPW91, and B3LYP methods (Table 4).

4. CONCLUSIONS

We obtain high-level CCSD(T) isomerization energies for a large and diverse set of 29 C_{40} fullerenes. The isomerization energies are calculated using the high-level G4(MP2) composite ab initio method. This is the first time that CCSD(T)/TZ reference isomerization energies are obtained for a comprehensive set of fullerene isomers. We show that there is a linear correlation between the isomerization energies and the single pentagon signature P_1 indices, which reflect the strain associated with fused pentagon–pentagon rings. Overall, the G4(MP2) isomerization energies span 43.1–763.3 kJ mol⁻¹, where the energy distribution has the shape of a Poisson function but with a small number of highly stable or highly energetic isomers and a large number of isomers (60%) with intermediate energetic stability. These benchmark isomerization energies enable a

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Table 4. Overview of the Performance of Various DFT Functionals with and without Empirical D4 Dispersion Corrections^{*a,b*}

type ^c	method	11 ^c	12 ^c	13 ^c	>13 ^c	everything ^c
GGA	BLYP	-1.7	-4.8	-6.2	-10.5	-7.3
	BP86	-0.9	-2.6	-3.4	-5.6	-3.9
	BPW91	-1.9	-4.9	-6.3	-10.3	-7.3
	PBE	-0.8	-2.2	-2.9	-4.8	-3.4
MGGA	TPSS	-1.1	-3.0	-3.8	-5.2	-3.9
	B97M-V	-1.1	-3.3	0.1	5.3	2.2
HGGA	B3LYP	1.0	3.0	5.0	9.4	6.3
	PBE0	0.3	1.4	2.4	4.4	2.9
	BH&HLYP	0.9	2.4	3.6	6.8	4.6
HMGGA	TPSSh	-1.0	-2.6	1.0	4.7	2.3
	TPSS0	0.6	2.1	3.5	6.6	4.4
	PW6B95	0.6	1.9	3.0	5.9	3.9
DHDFT	B2-PLYP	-0.6	-1.7	-1.8	-3.6	-2.4
	mPW2-PLYP	-0.3	-0.9	-0.1	0.5	-0.1
	B2GP-PLYP	-0.4	-0.9	-0.8	-1.8	-1.2
	DSD-PBEP86	-0.1	-0.3	-0.3	-0.5	-0.4
	PWPB95	0.1	0.9	2.4	4.5	2.9

^{*a*}The tabulated values are $\Delta D4 = RMSD(DFT) - RMSD(DFT-D4)$ (in kJ mol⁻¹). ^{*b*}A positive value indicates the dispersion correction improves the performance of the functional, whereas a negative value indicates deterioration in performance. ^{*c*}Footnotes *a* and *b* to Table 2 apply here.

comprehensive examination of hybrid DFT methods. We find that (i) there is a general correlation between the performance of hybrid DFT methods and the single pentagon signature P_1 indices and (ii) hybrid methods with high percentages of HF exchange perform poorly for the highly strained isomers. In particular, the inclusion of moderate amounts of exact Hartree-Fock exchange improves performance for the low-strain isomers but significantly deteriorates performance for the high-strain isomers. For example, for the GGA method BLYP we obtain RMSDs of 8.9 $(P_1 = 11)$, 13.6 $(P_1 = 12)$, 12.3 $(P_1 = 13)$, and 18.0 $(P_1 > 13.5)$ kJ mol⁻¹, whereas for the hybrid GGA method B3LYP we obtain RMSDs of 4.2 ($P_1 = 11$), 12.4 ($P_1 = 12$), 19.5 $(P_1 = 13)$, and 38.5 $(P_1 > 13.5)$ kJ mol⁻¹. Examination of the optimal percentages of Hartree-Fock exchange reveals that there is an inverse relationship between the optimal percentage of HF exchange and the strain energy reflected by the P_1 indices. For example, for the BLYP functional the optimal percentages of HF exchange are 13% ($P_1 = 11$), 10% ($P_1 = 12$), 7.5% ($P_1 = 13$), and 6% ($P_1 > 13$), and the corresponding RMSDs are 1.3 ($P_1 =$ 11), 1.8 ($P_1 = 12$), 4.4 ($P_1 = 13$), and 10.9 ($P_1 > 13$) kJ mol⁻¹. These results indicate that functionals with low percentages of HF exchange should be used for investigating moderately or highly strained fullerenes. Overall, the strain associated with pentagon adjacency is an inherently challenging problem for hybrid DFT methods involving high percentages of exact exchange. The best-performing DFT functionals from each rung of Jacob's Ladder are as follows.

- LSDA: SVWN3 (RMSD = 25.1 kJ mol^{-1})
- GGA: BLYP (RMSD = 14.5 kJ mol^{-1})
- Meta-GGA: M06-L (RMSD = 12.6 kJ mol^{-1})
- Hybrid-GGA: B3LYP (RMSD = 25.6 kJ mol^{-1})
- Hybrid-meta-GGA: TPSSh (RMSD = 11.4 kJ mol⁻¹)
- Range-separated: MN12-SX (RMSD = 22.2 kJ mol^{-1})
- Double-hybrid DFT: mPW2-PLYP (RMSD = 7.5 kJ mol⁻¹)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c02246.

Adiabatic singlet-triplet separation energies for the iso-C₄₀ database, ZPVE, enthalpic, and entropic corrections to the C₄₀ isomerization energies, %TAE[(T)] and T_1 multireference diagnostics for the iso-C₄₀ database, optimized geometries for the species considered in the present study, and full references for the Gaussian and Molpro program suites (PDF)

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Notes

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REFERENCES

(1) Sure, R.; Hansen, A.; Schwerdtfeger, P.; Grimme, S. Comprehensive theoretical study of all 1812 C_{60} isomers. *Phys. Chem. Chem. Phys.* **2017**, *19*, 14296–14305.

(2) Schwerdtfeger, P.; Wirz, L. N.; Avery, J. The topology of fullerenes. WIREs Comput. Mol. Sci. **2015**, *5*, 96–145.

(3) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes;* Dover: New York, 2006.

(4) Cioslowski, J. Electronic Structure Calculations on Fullerenes and Their Derivatives; Wooden Books: New York, 1995.

(5) Rickhaus, M.; Mayor, M.; Juricek, M. Chirality in curved polyaromatic systems. *Chem. Soc. Rev.* **2017**, *46*, 1643–1660.

(6) Chan, B. Fullerene Thermochemical Stability: Accurate Heats of Formation for Small Fullerenes, the Importance of Structural Deformation on Reactivity, and the Special Stability of C_{60} . J. Phys. Chem. A **2020**, 124, 6688–6698.

(7) Chan, B.; Kawashima, Y.; Dawson, W.; Katouda, M.; Nakajima, T.; Hirao, K. A Simple Model for Relative Energies of All Fullerenes Reveals the Interplay between Intrinsic Resonance and Structural Deformation Effects in Medium-Sized Fullerenes. *J. Chem. Theory Comput.* **2019**, *15*, 1255–1264.

(8) Guan, J.; Jin, Z.; Zhu, Z.; Chuang, C.; Jin, B.-Y.; Tománek, D. Local Curvature and Stability of Two-Dimensional Systems. *Phys. Rev.* B 2014, *90*, 245403.

(9) Sun, C. H.; Yao, D.; Lu, G. Q.; Cheng, H. M. Effects of resonance energy and nonplanar strain energy on the reliability of hyper-homodesmotic reactions for corannulene. *Chem. Phys. Lett.* **2007**, *434*, 160–164.

(10) Sun, C. H.; Lu, G. Q.; Cheng, H. M. Strain Energies Due to Nonplanar Distortion of Fullerenes and Their Dependence on Structural Motifs. J. Phys. Chem. B 2006, 110, 218–221.

(11) Yu, J.; Sumathi, R.; Green, W. H. Accurate and Efficient Method for Predicting Thermochemistry of Polycyclic Aromatic Hydrocarbons – Bond-Centered Group Additivity. *J. Am. Chem. Soc.* **2004**, *126*, 12685–12700.

(12) Cioslowski, J.; Rao, N.; Moncrieff, D. Standard Enthalpies of Formation of Fullerenes and Their Dependence on Structural Motifs. *J. Am. Chem. Soc.* **2000**, *122*, 8265–8270.

(13) Manna, D.; Martin, J. M. L. What Are the Ground State Structures of C_{20} and C_{24} ? An Explicitly Correlated Ab Initio Approach. *J. Phys. Chem. A* **2016**, *120*, 153–160.

(14) Jin, Y.; Perera, A.; Lotrich, V. F.; Bartlett, R. J. Coupled Cluster Geometries and Energies of C_{20} Carbon Cluster Isomers – a New Benchmark Study. *Chem. Phys. Lett.* **2015**, *629*, 76–80.

(15) An, W.; Gao, Y.; Bulusu, S.; Zeng, X. C. Ab initio calculation of bowl, cage, and ring isomers of C_{20} and C_{20}^{-} . J. Chem. Phys. 2005, 122, 204109.

(16) Karton, A.; Waite, S. L.; Page, A. J. Performance of DFT for C_{60} Isomerization Energies: A Noticeable Exception to Jacob's Ladder. *J. Phys. Chem. A* **2019**, *123*, 257–266.

(17) Martin, J. M. L.; de Oliveira, G. Towards Standard Methods for Benchmark Quality Ab Initio thermochemistry W1 and W2 Theory. *J. Chem. Phys.* **1999**, *111*, 1843–1856.

(18) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **2013**, *139*, 134101.

(19) Kruse, H.; Mladek, A.; Gkionis, K.; Hansen, A.; Grimme, S.; Sponer, J. Quantum Chemical Benchmark Study on 46 RNA Backbone Families Using a Dinucleotide Unit. *J. Chem. Theory Comput.* **2015**, *11*, 4972–4991.

(20) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gaussian-4 theory using reduced order perturbation theory. *J. Chem. Phys.* 2007, 127, 124105.

(21) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gn theory. WIREs Comput. Mol. Sci. 2011, 1, 810–825.

(22) Karton, A. How reliable is DFT in predicting the relative energies of polycyclic aromatic hydrocarbon isomers? Comparison of functionals from different rungs of Jacob's Ladder. *J. Comput. Chem.* **2017**, 38, 370–382.

(23) Yu, L.-J.; Karton, A. Assessment of theoretical procedures for a diverse set of isomerization reactions involving double-bond migration in conjugated dienes. *Chem. Phys.* **2014**, *441*, 166–177.

(24) Karton, A.; Martin, J. M. L. Explicitly correlated benchmark calculations on C_8H_8 isomer energy separations: How accurate are DFT, double-hybrid and composite ab initio procedures? *Mol. Phys.* **2012**, *110*, 2477–2491.

(25) Karton, A.; Daon, S.; Martin, J. M. L. W4–11: A high-confidence dataset for computational thermochemistry derived from W4 ab initio data. *Chem. Phys. Lett.* **2011**, *510*, 165–178.

(26) Sarrami, F.; Yu, L.-J.; Karton, A. Thermochemistry of icosahedral closo-dicarboranes: A composite ab initio quantum-chemical perspective. *Can. J. Chem.* **2016**, *94*, 1082–1089.

(27) Karton, A.; Schreiner, P. R.; Martin, J. M. L. Heats of formation of platonic hydrocarbon cages by means of high-level thermochemical procedures. *J. Comput. Chem.* **2016**, *37*, 49–58.

(28) Karton, A. A computational chemist's guide to accurate thermochemistry for organic molecules. *WIREs Comput. Mol. Sci.* **2016**, *6*, 292–310.

(29) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schutz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; et al. *MOLPRO* (ver. 2016.1) is a package of ab initio programs. Available online at http://www.molpro.net.

(30) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schutz, M. Molpro: a generalpurpose quantum chemistry program package. *WIREs Comput. Mol. Sci.* **2012**, *2*, 242–253.

(31) Perdew, J. P.; Schmidt, K. Jacob's ladder of density functional approximations for the exchange-correlation energy. *AIP Conf. Proc.* **2000**, *577*, 1.

(32) Gáspár, R. Statistical exchange for electron in shell and the $X\alpha$ method. *Acta Phys. Hung.* **1974**, 35, 213–218.

(33) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(34) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.

(35) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(36) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(37) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986**, 33, 8822–8824.

(38) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46*, 6671–6687.

(39) Zhao, Y.; Truhlar, D. G. A new local density functional for maingroup thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, *125*, 194101.

(40) Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(41) Mardirossian, N.; Head-Gordon, M. Systemping the genome of meta-generalized gradient approximation density functionals: The search for B97M-V. *J. Chem. Phys.* **2015**, *142*, 074111.

(42) Yu, H. S.; He, X.; Truhlar, D. G. MN15-L: a new local exchangecorrelation functional for Kohn–Sham density functional theory with broad accuracy for atoms, molecules, and solids. *J. Chem. Theory Comput.* **2016**, *12*, 1280–1293. (43) Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372.

(44) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648.

(45) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, 98, 11623–11627.

(46) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158.

(47) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(48) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* **2003**, *119*, 12129.

(49) Zhao, Y.; Truhlar, D. G. Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions. J. Phys. Chem. A **2005**, *109*, 5656–5667.

(50) Yu, H. S.; He, X.; Li, S. L.; Truhlar, D. G. MN15: a Kohn–Sham global-hybrid exchange–correlation density functional with broad accuracy for multi-reference and single-reference systems and non-covalent interactions. *Chem. Sci.* **2016**, *7*, 5032–5051.

(51) Yanai, T.; Tew, D.; Handy, N. A new hybrid exchange correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, 393, 51–57.

(52) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106.

(53) Vydrov, O. A.; Scuseria, G. E. Assessment of a long-range corrected hybrid functional. J. Chem. Phys. **2006**, 125, 234109.

(54) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(55) Peverati, R.; Truhlar, D. G. Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation. *J. Phys. Chem. Lett.* **2011**, *2*, 2810–2817.

(56) Peverati, R.; Truhlar, D. G. Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16187–16191.

(57) Grimme, S. Semiempirical hybrid density functional with perturbative second-order correlation. *J. Chem. Phys.* **2006**, *124*, 034108.

(58) Schwabe, T.; Grimme, S. Towards chemical accuracy for the thermodynamics of large molecules: new hybrid density functionals including non-local correlation effects. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398–4401.

(59) Karton, A.; Tarnopolsky, A.; Lamere, J.–F.; Schatz, G. C.; Martin, J. M. L. Highly accurate first-principles benchmark datasets for the parametrization and validation of density functional and other approximate methods. Derivation of a robust, generally applicable, double-hybrid functional for thermochemistry and thermochemical kinetics. J. Phys. Chem. A 2008, 112, 12868–12886.

(60) Tarnopolsky, A.; Karton, A.; Sertchook, R.; Vuzman, D.; Martin, J. M. L. Double-hybrid functionals for thermochemical kinetics. *J. Phys. Chem. A* **2008**, *112*, 3–8.

(61) Kozuch, S.; Martin, J. M. L. Spin-component-scaled double hybrids: An extensive search for the best fifth-rung functionals blending DFT and perturbation theory. *J. Comput. Chem.* **2013**, *34*, 2327–2344.

(62) Kozuch, S.; Martin, J. M. L. DSD-PBEP86: in search of the best double-hybrid DFT with spin-component scaled MP2 and dispersion corrections. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20104–20107.

(63) Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. J. Chem. Theory Comput. 2011, 7, 291–309.

(64) Caldeweyher, E.; Bannwarth, C.; Grimme, S. Extension of the D3 dispersion coefficient model. *J. Chem. Phys.* **2017**, *147*, 34112.

(65) Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A generally applicable atomiccharge dependent London dispersion correction. *J. Chem. Phys.* **2019**, *150*, 154112.

(66) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(67) Neese, F. The ORCA Program System. WIREs Comput. Mol. Sci. 2012, 2, 73–78.

(68) Neese, F. Software update: the ORCA program system, version 4.0. WIREs Comput. Mol. Sci. 2018, 8, e1327.

(69) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. *Gaussian 16*, rev. A.03; Gaussian, Inc.: Wallingford, CT, 2016.

(70) Kesharwani, M. K.; Brauer, B.; Martin, J. M. L. Frequency and Zero-Point Vibrational Energy Scale Factors for Double-Hybrid Density Functionals (and Other Selected Methods): Can Anharmonic Force Fields Be Avoided? J. Phys. Chem. A **2015**, 119, 1701–1714.

(71) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. Density Functionals for Inorganometallic and Organometallic Chemistry. J. Phys. Chem. A 2005, 109, 11127–11143.

(72) Zhao, Y.; Tishchenko, O.; Gour, J. R.; Li, W.; Lutz, J. J.; Piecuch, P.; Truhlar, D. G. Thermochemical Kinetics for Multireference Systems: Addition Reactions of Ozone. *J. Phys. Chem. A* **2009**, *113*, 5786–5799.

(73) Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. Exchange and correlation energy in density functional theory: Comparison of accurate density functional theory quantities with traditional Hartree–Fock based ones and generalized gradient approximations for the molecules Li₂, N₂, F₂. *J. Chem. Phys.* **1997**, *107*, 5007.

(74) Becke, A. D. Simulation of delocalized exchange by local density functionals. *J. Chem. Phys.* **2000**, *112*, 4020.

(75) Handy, N. C.; Cohen, A. J. A dynamical correlation functional. *J. Chem. Phys.* **2002**, *116*, 5411.

(76) Becke, A. D. A real-space model of nondynamical correlation. *J. Chem. Phys.* **2003**, *119*, 2972.

(77) Polo, V.; Grafenstein, J.; Kraka, E.; Cremer, D. Long-range and short-range Coulomb correlation effects as simulated by Hartree–Fock, local density approximation, and generalized gradient approximation exchange functionals. *Theor. Chem. Acc.* **2003**, *109*, 22.

(78) Peverati, R.; Truhlar, D. G. The Quest for a Universal Density Functional: The Accuracy of Density Functionals Across a Broad Spectrum of Databases in Chemistry and Physics. *Philos. Trans. R. Soc.* A **2014**, 372, 20120476.

(79) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. W4 theory for computational thermochemistry: in pursuit of confident sub-kJ/mol predictions. *J. Chem. Phys.* **2006**, *125*, 144108.

(80) Karton, A.; Parthiban, S.; Martin, J. M. L. Post-CCSD(T) ab initio thermochemistry of halogen oxides and related hydrides XOX, XOOX, HOX, XO_n, and HXO_n (X = F, Cl), and evaluation of DFT methods for these systems. *J. Phys. Chem. A* **2009**, *113*, 4802.

(81) Lee, J.; Head-Gordon, M. Distinguishing artificial and essential symmetry breaking in a single determinant: approach and application to the C_{60} , C_{36} , and C_{20} fullerenes. *Phys. Chem. Chem. Phys.* **2019**, *21*, 4763–4778.

(82) Kroto, H. W. The stability of the fullerenes Cn, with n = 24, 28, 32, 36, 50, 60 and 70. *Nature* **1987**, 329, 529–531.

(83) Tan, Y. Z.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. The stabilization of fused-pentagon fullerene molecules. *Nat. Chem.* **2009**, *1*, 450–460. (84) Tan, Y.-Z.; Li, J.; Zhu, F.; Han, X.; Jiang, W.-S.; Huang, R.-B.; Zheng, Z.; Qian, Z.-Z.; Chen, R.-T.; Liao, Z.-J.; Xie, S.-Y.; Lu, X.; Zheng, L.-S. Chlorofullerenes featuring triple sequentially fused pentagons. *Nat. Chem.* **2010**, *2*, 269–273.

(85) Schreiner, P. R.; Fokin, A. A.; Pascal, R. A.; de Meijere, A. Many Density Functional Theory Approaches Fail To Give Reliable Large Hydrocarbon Isomer Energy Differences. *Org. Lett.* **2006**, *8*, 3635– 3638.

(86) Grimme, S.; Steinmetz, M.; Korth, M. How to Compute Isomerization Energies of Organic Molecules with Quantum Chemical Methods. *J. Org. Chem.* **2007**, *72*, 2118–2126.

(87) Wodrich, M. D.; Corminboeuf, C.; Schreiner, P. R.; Fokin, A. A.; Schleyer, P. v. R. How Accurate Are DFT Treatments of Organic Energies? *Org. Lett.* **2006**, No. 9, 1851–1854.

(88) Baric, D.; Maksic, Z. B. On the origin of Baeyer strain in molecules – an ab initio and DFT analysis. *Theor. Chem. Acc.* **2005**, *114*, 222–228.

(89) Karton, A.; Martin, J. M. L. Explicitly correlated Wn theory: W1-F12 and W2-F12. J. Chem. Phys. 2012, 136, 124114.

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