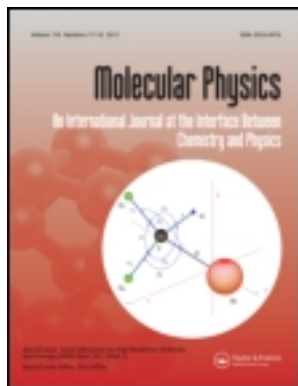


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## INVITED ARTICLE

### Explicitly correlated benchmark calculations on C<sub>8</sub>H<sub>8</sub> isomer energy separations: how accurate are DFT, double-hybrid, and composite *ab initio* procedures?

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Accurate isomerization energies are obtained for a set of 45 C<sub>8</sub>H<sub>8</sub> isomers by means of the high-level, *ab initio* W1-F12 thermochemical protocol. The 45 isomers involve a range of hydrocarbon functional groups, including (linear and cyclic) polyacetylene, polyyne, and cumulene moieties, as well as aromatic, anti-aromatic, and highly-strained rings. Performance of a variety of DFT functionals for the isomerization energies is evaluated. This proves to be a challenging test: only six of the 56 tested functionals attain root mean square deviations (RMSDs) below 3 kcal mol<sup>-1</sup> (the performance of MP2, namely: 2.9 (B972-D), 2.8 (PW6B95), 2.7 (B3PW91-D), 2.2 (PWPB95-D3), 2.1 ( $\omega$ B97X-D), and 1.2 (DSD-PBEP86) kcal mol<sup>-1</sup>). Isomers involving highly-strained fused rings or long cumulenic chains provide a 'torture test' for most functionals. Finally, we evaluate the performance of composite procedures (e.g. G4, G4(MP2), CBS-QB3, and CBS-APNO), as well as that of standard *ab initio* procedures (e.g. MP2, SCS-MP2, MP4, CCSD, and SCS-CCSD). Both connected triples and post-MP4 singles and doubles are important for accurate results. SCS-MP2 actually outperforms MP4(SDQ) for this problem, while SCS-MP3 yields similar performance as CCSD and slightly bests MP4. All the tested empirical composite procedures show excellent performance with RMSDs below 1 kcal mol<sup>-1</sup>.

**Keywords:** C<sub>8</sub>H<sub>8</sub>; isomerization; unsaturated hydrocarbons; CCSD(T); explicitly-correlated; W1-F12; DFT; double-hybrid; G4, and G4(MP2)

#### 1. Introduction

In recent years, a number of studies have shown that many commonly used density functional theory (DFT) methods are unable to accurately reproduce isomer energy differences of organic molecules [1–4]. Grimme [1] has shown that (without including the empirical dispersion correction) nearly all DFT functionals predict the wrong sign for the isomerization energy from *n*-octane to hexamethylethane. Schreiner *et al.* [2,3] have shown that B3LYP [5–7] has particular difficulties in cases involving small-ring systems and saturated hydrocarbons. They also noted that, generally, the deviations relative to experiment increase with the size of the isomers. Grimme *et al.* [4] have evaluated the performance of several DFT and wave-function theory (WFT) methods for a set of 34 isomerization reactions of small organic molecules (a.k.a. the ISO34 test set). They have shown that BMK [8], mPW2-PLYP [9], and B2-PLYP [10] outperform the other tested functionals with root mean square deviations (RMSDs) of 1.8–1.9 kcal mol<sup>-1</sup>. They also noted that coupled cluster with singles, doubles, and quasi-perturbative triple excitations (CCSD(T)) and spin-component scaled MP2 (SCS-MP2 [11])

calculations in conjunction with a triple-zeta quality basis set resulted in the lowest RMSDs relative to experiment (specifically, RMSD = 1.0 and 1.3 kcal mol<sup>-1</sup>, respectively). Similar conclusions were reached by our own group for the isomerization energies of saturated (linear and branched) alkanes with up to eight carbons [12]. More specifically, we have shown that relative to reference isomerization energies from W1h theory, the following functionals (in conjunction with the 'D2' dispersion correction [13]) attain RMSDs below 1 kJ mol<sup>-1</sup>: X3LYP [14], M06-2X [15], B2K-PLYP [16], and B2GP-PLYP [17]. We have also shown [18] that the following functionals attain RMSDs below 1 kJ mol<sup>-1</sup> for conformation energies of linear alkanes of up to *n*-hexane: PW6B95 [19], BMK, B3PW91-D [6,20], B2K-PLYP-D, and B2GP-PLYP-D. Grimme and co-workers [21] have also introduced a dataset of 24 isomerization reactions of much larger organic molecules calculated at the SCS-MP2 level (a.k.a. the ISOL test set). They concluded that empirical dispersion corrections significantly improve the performance of the DFT methods, and that PBE0-D [22] and B2GP-PLYP-D give the best performance with RMSDs of 3.4 and 3.9 kcal mol<sup>-1</sup>,

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respectively (note however, that the latter method and the reference values should be of similar accuracy).

Evaluating more approximate methods requires benchmark data: if experimental data are absent, of dubious value, or difficult to extract in a manner that can be directly compared with the calculations (e.g. due to phase changes with poorly known transition enthalpies), one willy-nilly resorts to highly accurate first-principles calculations instead. Modern high-accuracy computational thermochemistry methods [23–26] are, for small molecules (up to 4–5 nonhydrogen atoms) capable of even sub-kJ mol<sup>-1</sup> accuracy. However, the high-order coupled cluster methods required exhibit such steep system size scaling that medium-sized organic molecules are effectively out of reach. Even with sophisticated basis set extrapolation methods [27] calculations using conventional one-particle basis functions quickly become intractable.

Explicitly correlated methods [28,29] offer one way out of this predicament, as they exhibit dramatically faster basis set convergence. Following the pioneering work of Persson and Taylor [30] which introduced fixed linear combinations of Gaussian-type geminals,

on fixed Gaussian-type geminals, nonlinear correlation factors were considered, which eventually led to the ‘F12’ methods [31,32] with a Slater-type correlation factor [33] becoming a de facto standard: see, e.g. [34,35] for successful thermochemical applications. Very recently, we proposed [36] a F12-based modification of our W1 thermochemical method [37,38] and showed that it in fact yielded similar (for first-row systems, superior) accuracy as the original at greatly reduced computational cost: the largest system which we were able to treat [36] with commodity cluster hardware was tetracene/naphthalene C<sub>18</sub>H<sub>12</sub>.

In the present work we introduce a database of highly-accurate energies for 45 C<sub>8</sub>H<sub>8</sub> isomers. The isomers that we have examined are shown in Figures 1 and 2. These cover a broad spectrum of C–C bonding situations (*sp*<sup>3</sup>–*sp*<sup>3</sup>, *sp*<sup>3</sup>–*sp*<sup>2</sup>, *sp*<sup>3</sup>–*sp*, *sp*<sup>2</sup>–*sp*<sup>2</sup>, *sp*<sup>2</sup>–*sp*, and *sp*–*sp*) involving polyacetylene, polyene, and cumulene moieties, as well as aromatic, anti-aromatic, and strained rings. Reference isomerization energies at the CCSD(T)/CBS level (i.e. complete basis set limit CCSD(T)) are obtained by means of the recently-developed W1-F12 procedure [36].

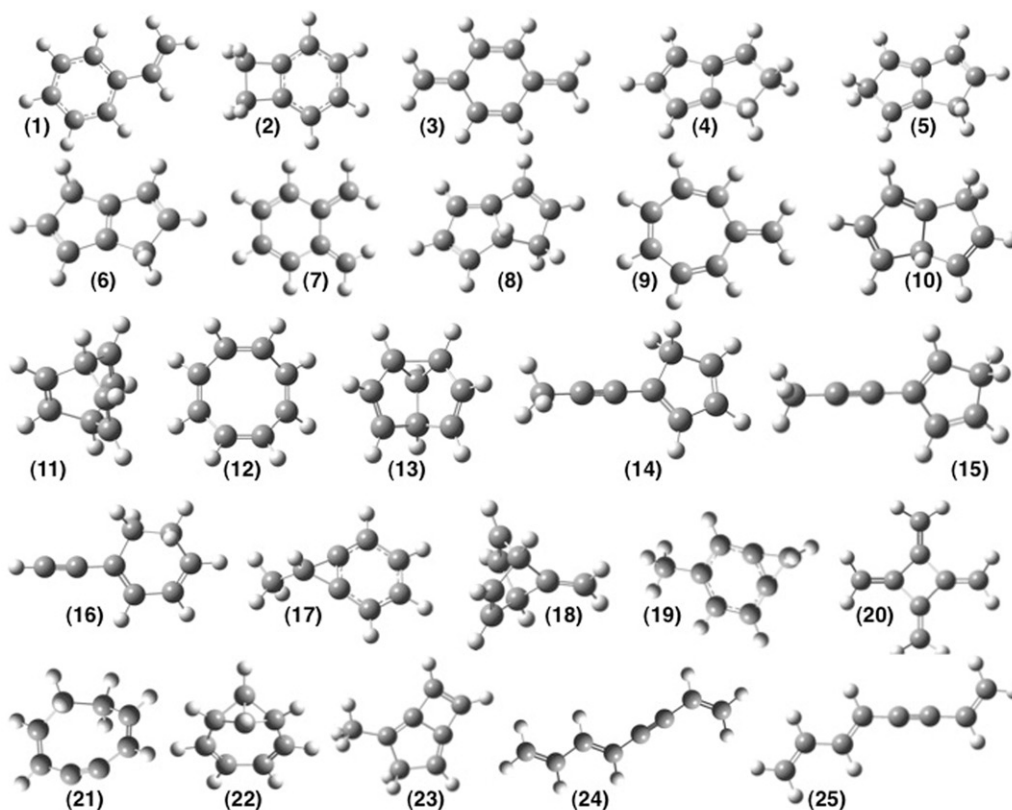


Figure 1. Twenty-five lowest-lying C<sub>8</sub>H<sub>8</sub> isomers ordered by increasing CCSD(T)/CBS  $\Delta E_e$  energies as given in Table 1. See there for structure names.

These benchmark values allow us to assess the performance of more approximate theoretical procedures. Specifically, we examine the performance of a variety of contemporary density functional theory (DFT) and double-hybrid DFT (DHDFT) methods, as well as a number of composite thermochemistry procedures, and several conventional *ab initio* methods.

## 2. Computational details

Virtually all calculations were run on the CRUNTCh (Computational Research at UNT in Chemistry) Linux farm at the University of North Texas. Some additional calculations were carried out on the CFARM2 cluster of the Faculty of Chemistry at the Weizmann Institute of Science and on the authors' personal Apple Macbook Pro laptop computers.

Benchmark isomerization energies were obtained by means of our recently-developed W1-F12 thermochemical protocol [36] using the Molpro 2010.1 program suite [41]. As specified in the W1-F12 protocol [36], the geometries of all isomers were obtained at the B3LYP/A'VTZ level of theory (where A'VTZ indicates the combination of the standard correlation-consistent

cc-pVTZ basis set on hydrogen [39] and the aug-cc-pVTZ basis set on carbon [40]).

W1-F12 combines F12 methods [42] with extrapolation techniques in order to reproduce the CCSD(T) basis set limit energy. Due to the drastically accelerated basis set convergence of the F12 methods [43,44], W1-F12 is superior to the original W1 method not only in terms of performance but also in terms of computational cost (for further details see [36]). In brief, the Hartree–Fock component is extrapolated from the VDZ-F12 and VTZ-F12 basis sets, using the  $E(L) = E_\infty + A/L^\alpha$  two-point extrapolation formula, with  $\alpha = 5$  (VnZ-F12 denotes the cc-pVnZ-F12 basis sets of Peterson *et al.* [43] which were developed for explicitly correlated calculations). The valence CCSD-F12 correlation energy is extrapolated from the same basis sets, using the said two-point extrapolation formula with  $\alpha = 3.67$ . In all of the explicitly correlated coupled cluster calculations the diagonal, fixed-amplitude 3C(FIX) ansatz [45–47] and the CCSD-F12b approximation [48,49] are employed. The (T) valence correlation energy is obtained in the same way as in the original W1 theory, i.e. extrapolated from the A'VDZ and A'VTZ basis sets using the above two-point extrapolation formula with  $\alpha = 3.22$ . The CCSD

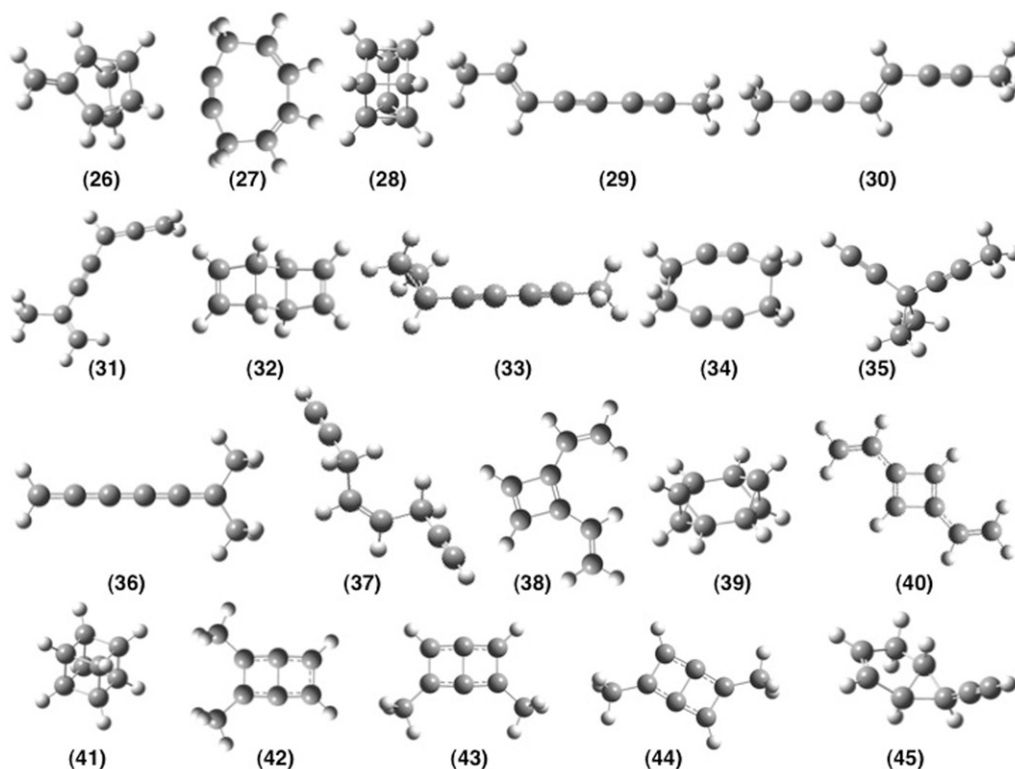


Figure 2. Twenty higher-energy  $C_8H_8$  isomers ordered by increasing CCSD(T)/CBS  $\Delta E_c$  energies as given in Table 1. See there for structure names.



inner-shell contribution is calculated with the core-valence weighted correlation-consistent A'PWCVTZ basis set of Peterson and Dunning [50], whilst the (T) inner-shell contribution is calculated with the PWCVTZ(no *f*) basis set (where A'PWCVTZ indicates the combination of the cc-pVTZ basis set on hydrogen and the aug-cc-pwCVTZ basis set on carbon, and 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 [51]) is obtained as the difference between non-relativistic CCSD(T)/A'VDZ and relativistic CCSD(T)/A'VDZ-DK calculations [52] (where A'VDZ-DK indicates the combination of the cc-pVDZ-DK basis set on H and aug-cc-pVDZ-DK basis set on C). W1-F12 shows excellent performance for systems containing only first-row elements (and H). Specifically, over the 97 first-row systems in the W4-11 dataset [53], W1-F12 attains a RMSD of 0.19 kcal mol<sup>-1</sup> against all-electron, relativistic CCSD(T) reference atomization energies at the infinite basis set limit. When considering reference atomization energies at the FCI basis set limit an RMSD of 0.45 kcal mol<sup>-1</sup> is obtained.

We shall then use our W1-F12 benchmark isomerization energies for C<sub>8</sub>H<sub>8</sub> to evaluate the performance of a variety of DFT exchange-correlation functionals in predicting isomerization energies for unsaturated hydrocarbons. The exchange-correlation functionals employed include the following classes (numbered by the rungs on Perdew's 'Jacob's Ladder of DFT' [54] they belong to):

- The pure generalized gradient approximation (GGA) functionals, employing both the local density and the reduced density gradient: BP86 [55,56], BPW91 [20,55], B97-D [57], BLYP [5,55], HCTH407 [58], and PBE [59].
- The meta-GGAs, additionally employing the kinetic energy density  $\tau$  (which contains similar information as the Laplacian of the density): M06-L [60], TPSS [61] and  $\tau$ -HCTH [62].
- Functionals involving the occupied orbitals, specifically hybrid functionals (involving HF-like exchange) subdivided into: (i) the hybrid GGAs (which one might term 'imperfect fourth-rung functionals'): BH&HLYP [63], B3LYP [5–7], B3P86 [6,56], B3PW91 [6,20], B97-1 [64], B97-2 [65], and PBE0 [22]. (We also consider the range-separated hybrid GGAs  $\omega$ B97 [66], and  $\omega$ B97-X [66].) (ii) The hybrid meta-GGAs: B98 [67], TPSSh [68], B1B95,<sup>1</sup> PW6B95 [19],  $\tau$ -HCTHh [62],

BMK [8], M05 [69], M05-2X [70], M06, M06-2X, and M06-HF [15,71,72].

- Functionals employing also virtual orbital information, specifically 'double-hybrid [10] functionals' (involving both HF-like exchange and MP2-like correlation): B2-PLYP [10], B2T-PLYP [16], B2K-PLYP [16], B2GP-PLYP [17], as well as the spin-component-scaled double hybrids DSD-BLYP [73], DSD-BPEP86 [74], and PWPB95 [75].

The conventional DFT calculations (rungs 1–4 of Jacob's Ladder) are carried out with the polarization-consistent pc2 basis set of Jensen [76] specifically designed for DFT calculations. The DHDFT calculations, which inherit the slow basis-set convergence of MP2 to some degree, are carried out with the cc-pVQZ basis set.

Dispersion corrections for the DFT energies (denoted by the suffix -D) were applied using our implementation of Grimme's 'D2' correction [13] (one exception in which the 'D3' correction [77] was used is the the PWPB95 spin-component-scaled double hybrid as prescribed in [75]). The empirical  $s_6$  pre-factors are taken from [12,13,17], these were, for the most part, optimized against the S22 benchmark set of weakly interacting systems [78].

For a rigorous comparison with the DFT data, secondary effects that are not explicitly included in the DFT calculations, such as relativity, and zero-point vibrational energy (ZPVE) corrections, are excluded from the W1-F12 reference values.

We proceed to evaluate the performance of a number of G4-type compound thermochemistry methods (G4 [79], G4(MP2) [80], and G4(MP2)-6X [81]). Note that for isomerization energies these procedures become nonempirical as the empirical higher-level-correction term is the same for both reactants and products. We further considered the CBS-QB3 [82] and CBS-APNO [83] methods as well as the Wilson correlation-consistent composite approach [84], specifically the ccCA-PS3 variant [85]. In the latter, as advocated by Prascher *et al.* [86], we applied the resolution of the identity (RI) approximation [87] in the MP2 basis set extrapolation and core-valence correlation steps: auxiliary basis sets from [88] were used for this purpose. (For a selection of structures, we compared with ccCA-PS3 calculations using conventional MP2, and found insignificant differences of at most 0.01 kcal mol<sup>-1</sup> in the relative energies.)

These procedures are evaluated against the same reference values as the DFT functionals, and accordingly they do not include ZPVE corrections. In addition, we evaluate the performance of MP2,

SCS-MP2 [11], SCS-MP3 [89], SCS-CCSD [90], SCS(MI)CCSD [91], MP2.5 [92], and MP4. The PWPB95 and PWPB95-D3 calculations were carried out using the ORCA 2.9 program system [93], the RI-ccCA-PS3 calculations performed using MOLPRO 2010.1 [41] and a script in the program's scripting language, while all remaining DFT, MP $n$ , and composite *ab initio* (both  $G_n$  and CBS-like) results were obtained using the Gaussian 09 program suite [94]. The B3LYP/A'VTZ optimized geometries (given in the Supporting Information to the present paper) that were used for the W1-F12 calculations were employed throughout, except for the  $G_n$  and CBS-like calculations where those were taken as the starting geometry for the optimizations prescribed by their respective protocols.

### 3. Results and discussion

Section 3.1 gives a brief overview of the CCSD(T)/CBS benchmark reference data from W1-F12 theory. In Section 3.2 we will assess the performance of a wide range of DFT and DHDFT functionals relative to the W1-F12 isomerization energies with emphasis on isomers that pose a significant challenge for DFT. Section 3.3 identifies three isomerization reactions for which most of the DFT and DHDFT functionals predict the wrong sign (i.e. reverse the energy order of the isomers). Finally, in Section 3.4 we assess the performance of a number G4-type (and CBS-type) composite and standard *ab initio* procedures.

#### 3.1. W1-F12 benchmark isomerization energies

Figures 1 and 2 display the 45  $C_8H_8$  isomers, whilst the all-electron, nonrelativistic, vibrationless CCSD(T)/CBS benchmark reference values from W1-F12 theory are given in Table 1. Energies are given relative to the lowest-energy isomer (styrene, structure **1**, Figure 1). The isomerization energies are spread over a wide energetic range of up to  $124.5 \text{ kcal mol}^{-1}$ . In addition the isomers involve a plethora of hydrocarbon functional groups including aromatic rings, highly-stained 3- and 4-membered rings, as well as polyacetylene, polyene, and cumulene moieties.

For the lowest-energy structure, styrene, our W1-F12 computed atomization energy is  $1815.89 \text{ kcal mol}^{-1}$  at the bottom of the well and  $1733.61$  at 0 K. Using the 'interim values'  $\Delta_f H_{0\text{K}}^\circ[C(g)] = 170.024 \pm 0.014 \text{ kcal mol}^{-1}$ , and  $\Delta_f H_{298\text{K}}^\circ[C(g)] = 171.336 \pm 0.014 \text{ kcal mol}^{-1}$  from [95], besides the established  $\Delta_f H_{0\text{K}}^\circ[H(g)] = 51.633 \text{ kcal mol}^{-1}$  and  $\Delta_f H_{298\text{K}}^\circ[H(g)] = 52.103 \text{ kcal mol}^{-1}$  from the same source, this leads to

heats of formation for styrene of  $39.65 \text{ kcal mol}^{-1}$  at 0 K and  $34.38 \text{ kcal mol}^{-1}$  at 298 K. The latter is in good agreement with the available experimental values of  $35.1 \pm 0.24 \text{ kcal mol}^{-1}$  from Prosen and Rossini [96],  $35.3 \pm 0.4 \text{ kcal mol}^{-1}$  from Pedley *et al.* [97], and  $35.4 \text{ kcal mol}^{-1}$  from the TRC tables [98]. Some of the remaining discrepancy is liable to come from the uncertainty in the zero-point vibrational energy [99,100], which will mostly cancel between structures in the isomer comparison.

Since W1-F12 represents a layered extrapolation 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. The percentage of the atomization energy accounted for by parenthetical connected triple excitations,  $\%TAE_e[(T)]$ , has been shown to be a reliable energy-based diagnostic indicating the importance of non-dynamical correlation effects [23]. 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 include mild non-dynamical correlation. Table S1 of the Supporting Information gathers the  $\%TAE_e[(T)]$  values for the  $C_8H_8$  isomers. The  $\%TAE_e[(T)]$  values range between 2.0–2.5% (note also that in all cases the SCF component accounts for 74–76% of the total atomization energy). These values suggest that our all-electron, nonrelativistic, vibrationless benchmark isomerization energies should, in principle, be within  $\sim 1\text{--}3 \text{ kJ mol}^{-1}$  of the isomerization energies at the full configuration interaction (FCI) basis-set limit [36,53,101].

#### 3.2. Performance of density functional theory for the $C_8H_8$ isomerization reactions

Table 2 gives the RMSD, mean signed deviations (MSD), and mean average deviations (MAD) from our benchmark W1-F12 results for a large variety of contemporary DFT and DHDFT functionals (with and without empirical dispersion corrections). We start by making the following general observations. (i) Of the pure GGA and meta-GGAs, the only functionals that yield RMSDs below  $4 \text{ kcal mol}^{-1}$  are PBE-D (3.9) and TPSS-D ( $3.8 \text{ kcal mol}^{-1}$ ). (ii) A respectable number of the hybrid-GGA functionals result in RMSDs between roughly 3 and  $4 \text{ kcal mol}^{-1}$  (namely, B3P86, B3PW91, B97-1, B97-2, and PBE0), which are lowered slightly further when the '-D' correction is included (reaching  $2.7 \text{ kcal mol}^{-1}$  for B3PW91-D). (iii) Of the hybrid-meta GGAs PW6B95 reaches  $\text{RMSD} = 2.8 \text{ kcal mol}^{-1}$ , followed closely by M06-2X

Table 1. Component breakdown of the benchmark W1-F12 isomerization energies for the 45 C<sub>8</sub>H<sub>8</sub> isomers (displayed in Figures 1 and 2). Energies (in kcal mol<sup>-1</sup>) are given relative to the lowest-energy isomer (styrene, structure 1, Figure 1).

	$\Delta$ SCF	$\Delta$ CCSD	$\Delta$ (T)	$\Delta$ CV <sup>a</sup>	$\Delta$ Rel. <sup>b</sup>	$\Delta$ ZPVE <sup>c</sup>	$\Delta E_e$ <sup>d</sup>	$\Delta E_0$ <sup>e</sup>	Structure Name
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	styrene
2	15.60	-4.35	0.19	0.08	0.04	0.59	11.52	10.97	benzocyclobutane
3	20.22	-1.50	-0.36	0.07	-0.01	-0.61	18.42	19.02	p-xylylene
4	25.52	-6.16	0.19	0.12	0.03	0.19	19.68	19.52	1,2-dihydropentalene
5	26.33	-6.62	0.61	0.06	0.03	-0.24	20.39	20.65	1,5-dihydropentalene
6	28.92	-8.13	0.16	0.02	0.04	-0.47	20.97	21.48	1,4-dihydropentalene
7	28.39	-3.10	-0.53	0.09	0.00	-0.78	24.85	25.63	o-xylylene
8	32.84	-7.82	0.19	0.15	0.03	0.11	25.36	25.28	1,6 a-dihydropentalene
9	30.39	-2.11	-0.41	0.13	0.00	-0.01	28.00	28.01	heptafulvene
10	35.56	-7.61	0.69	0.15	0.03	-0.10	28.79	28.92	1,3 a-dihydropentalene
11	48.98	-12.99	-0.06	0.15	0.04	0.10	36.08	36.02	barrelene
12	37.76	-1.82	0.84	0.12	0.00	-0.46	36.90	37.35	cyclooctatetraene
13	49.23	-12.52	0.22	0.15	0.07	0.31	37.09	36.85	f
14	43.90	-2.03	0.90	-0.13	0.00	-2.05	42.65	44.70	f
15	44.48	-1.78	1.14	-0.13	0.00	-2.14	43.71	45.85	f
16	47.69	-2.87	0.97	-0.02	0.00	-1.17	45.78	46.95	f
17	54.53	-6.32	-0.55	-0.05	0.06	-0.53	47.62	48.21	f
18	58.28	-10.40	0.22	0.27	0.02	-0.64	48.37	49.04	f
19	56.25	-7.08	-0.65	-0.09	0.07	-1.01	48.43	49.50	f
20	60.71	-0.84	0.22	0.17	-0.02	-3.05	60.26	63.28	f
21	70.62	-9.04	-0.76	0.10	0.01	-0.42	60.92	61.34	cycloocta-1,5-dien-3-yne
22	70.99	-9.47	0.66	0.00	0.09	0.00	62.19	62.28	octavalene
23	72.64	-9.14	-0.37	0.25	0.03	-1.40	63.39	64.82	f
24	59.45	3.40	0.63	-0.01	-0.05	-3.06	63.46	66.48	1,3,7-octatrien-5-yne
25	59.46	3.39	0.62	-0.01	-0.05	-3.06	63.46	66.48	octa-1,3,7-trien-5-yne
26	79.09	-12.68	1.43	-0.01	0.13	-0.62	67.83	68.58	f
27	73.47	-5.61	0.68	0.05	0.01	-0.49	68.59	69.09	1,3-cyclooctadien-6-yne
28	87.63	-18.16	1.33	0.19	0.15	0.28	70.99	70.86	cuneane
29	68.33	2.24	0.91	-0.30	-0.02	-3.66	71.18	74.82	octa-2-en-4,6-diyne
30	67.79	3.40	1.59	-0.27	-0.03	-3.88	72.50	76.35	oct-4-en-2,6-diyne
31	74.63	2.11	1.07	-0.12	-0.04	-3.95	77.69	81.60	f
32	90.44	-12.66	0.65	0.49	0.04	-0.86	78.92	79.82	f
33	79.69	-0.24	1.56	-0.39	0.03	-2.70	80.61	83.34	f
34	89.49	-8.42	0.76	-0.02	0.02	-0.70	81.82	82.54	1,5-cyclooctadiyne
35	86.98	-0.66	2.18	-0.28	0.01	-3.39	88.22	91.62	f
36	93.41	-2.75	-2.18	-0.18	-0.03	-4.51	88.29	92.78	1,1-dimethyl[5]cumulene <sup>f</sup>
37	84.33	1.98	2.36	-0.09	-0.05	-3.59	88.58	92.12	4-Octene-1,7-diyne
38	99.99	-6.66	-1.79	0.35	-0.02	-3.32	91.88	95.18	f
39	106.79	-16.07	1.48	-0.10	0.18	-0.41	92.11	92.69	f
40	103.87	-6.11	-1.16	0.35	-0.02	-3.75	96.95	100.69	f
41	128.04	-20.21	1.41	0.68	0.13	-0.15	109.92	110.20	cubane
42	135.99	-17.10	-3.81	0.41	0.03	-3.46	115.49	118.98	2,3-dimethylbicyclo[2.2.0]
43	135.82	-16.73	-3.77	0.41	0.03	-3.46	115.73	119.23	2,6-dimethylbicyclo[2.2.0]
44	136.31	-16.93	-3.79	0.42	0.03	-3.49	116.00	119.53	2,5-dimethylbicyclo[2.2.0]
45	138.58	-14.10	-0.27	0.25	0.03	-1.90	124.46	126.39	f

Notes: <sup>a</sup>CV = core–valence correction.<sup>b</sup>Scalar relativistic correction from second-order Douglas–Kroll CCSD(T) calculations.<sup>c</sup>Zero-point vibrational energy correction from B3LYP/A'VTZ harmonic calculations (scaled by 0.985).<sup>d</sup>Nonrelativistic, all-electron, vibrationless CCSD(T) basis set limit reference isomerization energies from W1-F12 theory (these are used for the evaluation of the DFT and composite *ab initio* procedures).<sup>e</sup>Relativistic, all-electron, ZPVE-inclusive CCSD(T) basis set limit reference isomerization energies from W1-F12 theory (for comparison with experiment).<sup>f</sup>Full IUPAC names: 13 = tricyclo[3.2.1.0<sup>2,8</sup>]octa-2,6-diene, 14 = 1-(1-Propyn-1-yl)-1,3-cyclopentadiene, 15 = 2-prop-1-ynylcyclopenta-1,3-diene, 16 = 1-ethynylcyclohexa-1,3-dienecyclo[3.1.0]hex-2-ene, 17 = 7-methylbicyclo[4.1.0]hepta-1,3,5-triene, 18 = tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane,3-methylene, 19 = 3-methylbicyclo[4.1.0]hepta-1,3,5-triene, 20 = cyclobutane,tetrakis(methylene)-, 23 = 2-methylbicyclo[3.2.0]hepta-1,4-dienecyclo[3.1.0]hex-2-ene, 26 = 7-methylenebicyclo[2.2.1]hepta-2,5-diene, 31 = 6-methyl-1,2,6-heptatrien-4-yne, 32 = tricyclo[4.2.0.0<sup>2,5</sup>]octa-3,7-diene, 33 = 1-cyclopropylpenta-1,3-diyne, 35 = 1-ethynyl-1-(1-propyn-1-yl)cyclopropane, 36 = 6-methylhepta-1,2,3,4,5-pentaene, 38 = 1,2-divinylcyclobuta-1,3-dienecyclo[2.2.1]hepta-2,5-diene, 39 = pentacyclo[5.1.0.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>]octane, 40 = 1,3-divinylcyclobuta-1,3-dieneo[5.1.0.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>]octane, 45 = 6-Ethynylbicyclo[3.1.0]hex-2-ene.

Table 2. Performance statistics ( $\text{kcal mol}^{-1}$ ) of conventional and double-hybrid DFT functionals for the calculation of  $\text{C}_8\text{H}_8$  isomerization energies.<sup>a,b,c</sup>

	RMSD	MAD	MSD	LND	LPD	WO
BP86	4.5	3.5	-0.4	-15.9 (36)	7.5 (11)	14
BLYP-D	8.7	6.5	2.7	-19.1 (36)	21.9 (28)	14
BLYP	9.9	7.3	2.5	-21.6 (36)	24.1 (28)	14
B97D	7.1	5.4	1.4	-18.3 (36)	16.2 (41)	15
BPW91	4.7	3.6	-1.1	-16.7 (36)	7.3 (11)	15
HCTH407-D	5.7	4.4	-1.9	-16.7 (36)	10.7 (11)	15
HCTH407	6.5	5.1	-2.0	-18.9 (36)	11.5 (11)	15
PBE-D	3.9	2.8	-1.2	-12.8 (36)	6.7 (37)	15
PBE	4.2	3.1	-1.3	-14.3 (36)	6.2 (37)	13
M06L	6.1	4.8	-2.1	-17.0 (36)	10.6 (11)	14
TPSS-D	3.8	3.0	-0.3	-12.9 (36)	7.4 (11)	12
TPSS	4.5	3.5	-0.4	-15.0 (36)	8.1 (11)	12
$\tau$ -HCTH	5.8	4.6	-0.1	-17.6 (36)	11.1 (11)	15
BH&HLYP	6.8	5.6	5.3	-1.2 (36)	14.4 (41)	9
B3LYP-D	6.5	5.1	3.8	-9.9 (36)	15.4 (28)	12
B3LYP	7.3	5.7	3.6	-12.1 (36)	17.7 (41)	13
B3P86	3.0	2.2	1.2	-6.8 (36)	7.4 (37)	11
B3PW91-D	2.7	2.2	0.7	-6.1 (36)	6.6 (37)	9
B3PW91	3.0	2.4	0.5	-8.3 (36)	6.6 (34)	14
B971-D	3.3	2.6	2.0	-6.6 (36)	7.7 (39)	12
B971	3.7	2.9	1.9	-7.9 (36)	9.0 (39)	13
B972-D	2.9	2.4	0.6	-6.5 (36)	7.3 (11)	11
B972	3.4	2.7	0.5	-8.7 (36)	8.0 (11)	11
PBE0-D	3.7	3.0	0.2	-9.2 (39)	8.7 (37)	13
PBE0	3.5	2.8	0.1	-7.9 (39)	8.2 (37)	13
$\omega$ B97	6.3	4.0	-2.9	-21.9 (39)	3.6 (3)	13
$\omega$ B97X-D	2.1	1.7	0.8	-5.3 (41)	4.4 (11)	9
$\omega$ B97X	3.2	2.1	-0.4	-10.5 (39)	4.0 (38)	13
B98	4.6	3.5	2.6	-8.2 (36)	12.6 (39)	14
TPSSh-D	3.2	2.6	0.2	-9.0 (36)	6.7 (11)	13
TPSSh	3.6	2.8	0.0	-10.9 (36)	7.3 (11)	12
B1B95-D	4.1	2.9	-1.2	-12.4 (39)	5.4 (37)	12
B1B95	4.0	3.0	-1.3	-10.9 (39)	5.4 (34)	12
$\tau$ -HCTHh	3.9	3.1	1.6	-9.7 (36)	7.8 (11)	14
BMK-D	4.8	3.1	-0.4	-22.1 (41)	5.6 (37)	14
BMK	4.5	2.9	-0.5	-20.4 (41)	5.2 (37)	13
M05	9.9	7.3	-6.8	-29.4 (39)	5.2 (11)	14
M052X	4.5	3.8	3.6	-1.4 (19)	10.8 (41)	10
M06-D	5.1	3.8	-2.8	-14.7 (39)	5.5 (11)	12
M06	5.2	3.8	-2.8	-14.2 (39)	5.7 (11)	12
M062X-D	3.1	2.4	-0.1	-10.2 (39)	4.1 (38)	10
M062X	3.1	2.5	-0.2	-10.1 (39)	4.1 (38)	10
M06HF	3.5	2.6	2.0	-2.6 (35)	9.1 (43)	12
PW6B95	2.8	2.4	0.2	-7.3 (36)	5.6 (34)	10
B2-PLYP-D	4.3	3.4	2.7	-5.3 (36)	11.1 (41)	9
B2-PLYP	4.7	3.7	2.6	-6.4 (36)	12.5 (41)	12
B2GP-PLYP-D	3.6	2.9	2.7	-1.8 (36)	8.9 (41)	11
B2GP-PLYP	3.8	3.1	2.7	-2.7 (36)	9.9 (41)	9
B2K-PLYP-D	3.3	2.8	2.7	-0.7 (29)	7.6 (41)	10
B2K-PLYP	3.5	2.9	2.7	-1.6 (29)	8.4 (41)	10
B2T-PLYP-D	3.9	3.2	2.8	-3.0 (36)	9.8 (41)	9
B2T-PLYP	4.2	3.5	2.8	-4.0 (36)	11.0 (41)	10
DSD-BLYP	3.1	2.5	2.3	-1.4 (29)	7.4 (41)	11
DSD-PBEP86	1.2	1.0	0.2	-2.0 (33)	3.2 (40)	11
PWPB95	2.3	1.8	-1.2	-6.0 (39)	2.0 (11)	11
PWPB95-D3	2.2	1.7	-1.1	-5.9 (39)	1.9 (11)	10

Notes: <sup>a</sup>Errors are  $E_{\text{isomer}}[\text{level}] - E_{\text{isomer}}[\text{CCSD(T)}]$  in  $\text{kcal mol}^{-1}$ .

<sup>b</sup>The standard DFT calculations were carried out in conjunction with the pc-2 basis set [76], while the DHDFE calculations were carried out in conjunction with the cc-pVQZ basis set.

<sup>c</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation, LND = largest negative deviation, LPD = largest positive deviation, and WO = number of isomers predicted to be in the wrong order (the structures with the LND and LPD are given in parentheses).



(RMSD = 3.1 kcal mol<sup>-1</sup>). (iv) Of the range-separated hybrid GGAs,  $\omega$ B97X-D shows excellent performance with an RMSD of only 2.1 kcal mol<sup>-1</sup>. (v) With regard to the double hybrids, DSD-PBEP86 gives an exceptionally low RMSD of just 1.2 kcal mol<sup>-1</sup> (and a near-zero MSD of 0.2 kcal mol<sup>-1</sup>), PWPB95-D3 coming in second at RMSD = 2.2 kcal mol<sup>-1</sup>. (vi) Finally, we note that inclusion of the D2 dispersion corrections reduces the RMSDs by amounts ranging from 0.1–1.1 kcal mol<sup>-1</sup>: more significant contributions were found [21] for isomerization energies in larger molecules.

It is worthwhile examining in greater detail isomers that are particularly challenging for most of the DFT functionals. Table 3 gives the deviations from our W1-F12 benchmark reference values for the five most taxing isomers. These are: **11** (barrelene), **28** (cuneane), **36** (1,1-dimethyl[5]cumulene or 6-methylhepta-1,2,3,4,5-pentaene), **39** (pentacyclo[5.1.0.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>]octane), and **41** (cubane). Four isomers (**11**, **28**, **39**, and **41**) involve highly-strained ring systems, whereas isomer **36** is a linear cumulene.

Beginning with barrelene (structure **11**, Figure 1), with two minor exceptions (M06HF and  $\omega$ B97), all of the DFT functionals overestimate the reaction energy of the **1** → **11** isomerization. For ten functionals deviations larger than 10 kcal mol<sup>-1</sup> are obtained (including, M06L, B3LYP, B3LYP-D, B97D, BLYP, and BLYP-D). Only three functionals (out of the 56 functionals considered) give deviations (in absolute value) that are smaller than 2 kcal mol<sup>-1</sup>, specifically, M06HF (-1.8),  $\omega$ B97 (-0.2), and PWPB95-D3 (1.9 kcal mol<sup>-1</sup>).

Cuneane (from the Latin *cuneum* = wedge, structure **28**, Figure 2) is a highly strained system that involves two 3-membered rings, two 4-membered rings, and two 5-membered rings. The deviations for the DFT functionals spread over a wide range, from -21.3 (M05) to +24.1 kcal mol<sup>-1</sup> (BLYP). Cases for which the deviations (in absolute value) are larger than 10 kcal mol<sup>-1</sup> include:  $\omega$ B97, BMK-D, B2-PLYP, B97D, B3LYP, and B3LYP-D. Nevertheless, for a number of functionals the energy of the **1** → **28** isomerization reaction is obtained within 1 kcal mol<sup>-1</sup> from the W1-F12 value: these are PBE and DSD-PBEP86 (-0.8), TPSSh (-0.3), B3PW91 (0.0), B972 (0.2), TPSS-D (0.5), HCTH407 (0.6), and B3P86 (0.7 kcal mol<sup>-1</sup>).

Moving to the next highly-strained molecule (with the tongue-twister name of pentacyclo[5.1.0.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>]octane, structure **39**, Figure 2), we note that this system involves two sets of fused 3-membered rings. Similarly to cuneane, the deviations for the DFT functionals span a wide range,

Table 3. Particularly challenging isomers for DFT and DHDF (the tabulated values are deviations from W1-F12 reference values, in kcal mol<sup>-1</sup>, for the structures of the isomers see Figures 1 and 2).<sup>a</sup>

	<b>11</b>	<b>28</b>	<b>36</b>	<b>39</b>	<b>41</b>
BP86	7.5	5.3	-15.9	2.6	4.4
BLYP-D	13.5	21.9	-19.1	17.0	20.0
BLYP	14.4	24.1	-21.6	19.4	23.1
B97D	13.0	15.2	-18.3	7.3	16.2
BPW91	7.3	2.9	-16.7	0.2	2.0
HCTH407-D	10.7	-1.4	-16.7	-10.6	1.4
HCTH407	11.5	0.6	-18.9	-8.5	4.3
PBE-D	5.4	-2.2	-12.8	-4.9	-3.2
PBE	5.9	-0.8	-14.3	-3.4	-1.2
M06L	10.6	-5.7	-17.0	-13.8	-3.1
TPSS-D	7.4	0.5	-12.9	-3.0	-0.6
TPSS	8.1	2.3	-15.0	-1.0	2.0
$\tau$ -HCTH	11.1	7.5	-17.6	-0.4	10.6
BH&HLYP	11.0	12.9	-1.2	10.7	14.4
B3LYP-D	11.6	15.4	-9.9	11.7	14.9
B3LYP	12.4	17.3	-12.1	13.7	17.7
B3P86	6.4	0.7	-6.8	-1.1	1.3
B3PW91-D	5.8	-2.0	-6.1	-4.2	-2.6
B3PW91	6.6	0.0	-8.3	-2.0	0.3
B971-D	7.1	5.4	-6.6	7.7	0.7
B971	7.6	6.6	-7.9	9.0	2.4
B972-D	7.3	-1.7	-6.5	-5.9	-0.9
B972	8.0	0.2	-8.7	-3.8	1.8
PBE0-D	3.8	-7.8	-2.7	-9.2	-7.6
PBE0	4.3	-6.5	-4.2	-7.9	-5.8
$\omega$ B97	-0.2	-17.6	2.4	-21.9	-17.5
$\omega$ B97X	2.7	-7.8	1.4	-10.5	-8.3
$\omega$ B97XD	4.4	-2.0	-0.8	-1.2	-5.3
B98	8.3	9.8	-8.2	12.6	5.5
TPSSh-D	6.7	-1.9	-9.0	-4.8	-2.4
TPSSh	7.3	-0.3	-10.9	-3.0	-0.1
B1B95-D	3.0	-10.3	-5.3	-12.4	-9.8
B1B95	3.6	-8.9	-6.9	-10.9	-7.9
$\tau$ -HCTHh	7.8	7.0	-9.7	7.4	4.4
BMK-D	2.7	-10.2	0.3	0.4	-22.1
BMK	3.2	-9.0	-1.0	1.7	-20.4
M05	5.2	-21.3	-13.0	-29.4	-17.6
M052X	3.7	4.9	1.3	-1.2	10.8
M06-D	5.5	-7.0	-11.9	-14.7	-3.8
M06	5.7	-6.5	-12.4	-14.2	-3.1
M062X-D	3.8	-2.5	-4.2	-10.2	2.4
M062X	3.8	-2.4	-4.4	-10.1	2.5
M06HF	-1.8	2.4	4.6	-1.6	7.7
PW6B95	5.6	-2.7	-7.3	-4.9	-1.8
B2-PLYP-D	7.5	10.0	-5.3	7.7	11.1
B2-PLYP	7.9	11.0	-6.4	8.8	12.5
B2GP-PLYP-D	6.3	7.0	-1.8	5.3	8.9
B2GP-PLYP	6.6	7.8	-2.7	6.1	9.9
B2K-PLYP-D	5.6	5.3	0.1	3.9	7.6
B2K-PLYP	5.8	5.9	-0.5	4.5	8.4
B2T-PLYP-D	6.9	8.2	-3.0	6.3	9.8
B2T-PLYP	7.2	9.1	-4.0	7.3	11.0
DSD-BLYP	5.3	5.4	-0.9	3.9	7.4
DSD-PBEP86	2.4	-0.8	-1.2	-1.9	0.0
PWPB95	2.0	-4.6	-4.9	-6.0	-4.3
PWPB95-D3	1.9	-4.6	-4.4	-5.9	-4.5

Note: <sup>a</sup>Footnotes a and b to Table 2 apply.

from  $-29.4$  to  $+19.4$  kcal mol $^{-1}$  (where again the largest deviations are obtained for M05 and BLYP). Notable cases for which the deviations exceed 10 kcal mol $^{-1}$  are  $\omega$ B97, M06, M06L, B1B95-D, B3LYP, and BLYP-D. On the other hand, deviations lower than 1 kcal mol $^{-1}$  (in absolute value) are obtained for  $\tau$ HCTH ( $-0.4$ ), BPW91 (0.2), and BMK-D (0.4 kcal mol $^{-1}$ ).

The last highly-strained system is the famous cubane molecule (structure **41**, Figure 2). Again, the deviations for the DFT functionals spread over a wide range, from  $-22.1$  (BMK-D) to  $+23.1$  kcal mol $^{-1}$  (BLYP). Other notable functionals for which the deviations exceed 10 kcal mol $^{-1}$  (in absolute value) are: BMK, M05,  $\omega$ B97, B2T-PLYP, B2-PLYP, B2-PLYP-D, B97D, B3LYP, and B3LYP-D. Notable cases with deviations  $< 1$  kcal mol $^{-1}$  are: B972-D ( $-0.9$ ), TPSS-D ( $-0.6$ ), TPSSh ( $-0.1$ ), DSD-PBEP86 (0.0), B3PW91 (0.3), and B971-D (0.7 kcal mol $^{-1}$ ).

Last but not least, 1,1-dimethyl[5]cumulene (systematic name: 6-methylhepta-1,2,3,4,5-pentaene, structure **36** in Figure 2) is clearly a taxing isomer. This is hardly surprising since long cumulenic chains are a well-known ‘torture test’ for almost any DFT functional (see, for example, Yousaf and Taylor [102], also [103], and references within these publications). With very few exceptions, the DFT functionals underestimate the reaction energy of the **1**  $\rightarrow$  **36** isomerization (and do so by over 10 kcal mol $^{-1}$  in many cases). However, for five functionals deviations  $\leq 1.0$  kcal mol $^{-1}$  are obtained: these are DSD-BLYP ( $-0.9$ ),  $\omega$ B97X-D ( $-0.8$ ), B2K-PLYP ( $-0.5$ ), B2K-PLYP-D (0.1), and BMK-D (0.3 kcal mol $^{-1}$ ).

### 3.3. Isomer pairs for which the considered DFT and DHDFT functionals systematically predict the wrong energetic order

In the previous subsection we have seen that highly-strained isomers and long cumulenic chains pose a particular challenge for many DFT functionals. It is therefore not surprising that the three isomerization reactions for which nearly all DFT functionals predict the wrong sign involve these two types of species, i.e. they are of the form: (strained/cyclic isomer)  $\rightarrow$  (cumulenic isomer). Specifically, they are reactions: **27**  $\rightarrow$  **29**, **32**  $\rightarrow$  **33**, and **34**  $\rightarrow$  **36**. The W1-F12 isomerization energies are:  $+2.59$  (**27**  $\rightarrow$  **29**),  $+1.69$  (**32**  $\rightarrow$  **33**), and  $+6.47$  kcal mol $^{-1}$  (**34**  $\rightarrow$  **36**). That is, at the CCSD(T)/CBS level the strained/cyclic isomer is energetically more stable than the cumulenic/linear one. Nevertheless, 70–80% of the considered DFT and DHDFT functionals predict that the cumulenic/linear isomer is energetically more stable. Table 4 gives the

Table 4. Three isomer pairs for which 70–80% of the considered DFT/DHDFT functionals predict the wrong energetic order (the tabulated values are isomerization energies, in kcal mol $^{-1}$ ). The isomerization energies with the correct (positive) sign are given in bold<sup>a</sup>.

	<b>27</b> $\rightarrow$ <b>29</b>	<b>32</b> $\rightarrow$ <b>33</b>	<b>34</b> $\rightarrow$ <b>36</b>
Wrong sign <sup>b</sup>	46	46	39
W1-F12	<b>+2.59</b>	<b>+1.69</b>	<b>+6.47</b>
BP86	$-5.4$	$-7.3$	$-14.9$
BLYP-D	$-7.0$	$-13.9$	$-17.3$
BLYP	$-11.2$	$-19.3$	$-20.8$
BPW91	$-6.6$	$-7.6$	$-15.7$
HCTH407-D	$-5.9$	$-6.9$	$-16.8$
HCTH407	$-9.8$	$-11.9$	$-19.9$
PBE-D	$-1.0$	$-0.5$	$-11.3$
PBE	$-3.7$	$-3.8$	$-13.4$
M06L	$-9.0$	$-12.3$	$-14.1$
TPSS-D	$-3.2$	$-2.3$	$-12.0$
TPSS	$-6.7$	$-6.8$	$-14.9$
$\tau$ -HCTH	$-8.2$	$-13.2$	$-17.6$
BH&HLYP	$-3.4$	$-8.8$	$-2.9$
B3LYP-D	$-3.6$	$-9.1$	$-9.5$
B3LYP	$-7.3$	$-13.7$	$-12.5$
B3P86	$-2.0$	$-3.3$	$-7.2$
B3PW91-D	<b>+0.2</b>	<b>+0.5</b>	$-5.3$
B3PW91	$-3.6$	$-4.4$	$-8.4$
B98	$-3.5$	$-4.0$	$-8.5$
B971-D	$-0.5$	<b>+0.4</b>	$-6.1$
B971	$-2.8$	$-2.5$	$-8.0$
B972-D	$-0.9$	$-1.2$	$-6.3$
B972	$-4.6$	$-5.8$	$-9.3$
B97D	$-7.1$	$-12.9$	$-17.4$
PBE0-D	<b>+2.2</b>	<b>+4.0</b>	$-2.4$
PBE0	$-0.3$	<b>+0.9</b>	$-4.4$
$\omega$ B97	<b>+3.6</b>	<b>+4.0</b>	<b>+9.5</b>
$\omega$ B97X	<b>+1.9</b>	<b>+1.2</b>	<b>+5.7</b>
$\omega$ B97XD	<b>+0.9</b>	<b>+1.8</b>	<b>+1.4</b>
TPSSh-D	$-2.0$	$-0.6$	$-8.6$
TPSSh	$-5.1$	$-4.6$	$-11.2$
B1B95-D	$-0.8$	<b>+2.1</b>	$-3.6$
B1B95	$-3.5$	$-1.2$	$-5.8$
$\tau$ -HCTHh	$-3.3$	$-4.2$	$-9.6$
BMK-D	<b>+3.3</b>	<b>+13.9</b>	<b>+2.4</b>
BMK	<b>+1.0</b>	<b>+10.9</b>	<b>+0.6</b>
M05	$-6.0$	$-7.0$	$-4.9$
M052X	<b>+1.4</b>	$-4.7$	<b>+3.5</b>
M06-D	$-4.6$	$-10.1$	$-4.0$
M06	$-5.5$	$-11.2$	$-4.7$
M062X-D	$-0.8$	$-6.9$	<b>+2.5</b>
M062X	$-1.0$	$-7.1$	<b>+2.3</b>
M06HF	<b>+5.0</b>	$-0.7$	<b>+13.6</b>
PW6B95	$-3.9$	$-3.8$	$-6.4$
B2-PLYP-D	$-2.5$	$-6.9$	$-1.5$
B2-PLYP	$-4.4$	$-9.4$	$-3.1$
B2GP-PLYP-D	$-1.5$	$-5.2$	<b>+2.1</b>
B2GP-PLYP	$-2.9$	$-6.9$	<b>+1.0</b>
B2K-PLYP-D	$-1.0$	$-4.2$	<b>+4.1</b>
B2K-PLYP	$-2.0$	$-5.5$	<b>+3.3</b>
B2T-PLYP-D	$-1.7$	$-5.7$	<b>+0.7</b>
B2T-PLYP	$-3.4$	$-7.9$	$-0.7$
DSD-BLYP	<b>+0.5</b>	$-0.7$	<b>+4.9</b>
DSD-PBEP86	$-1.1$	$-4.4$	<b>+3.8</b>
PWPB95	$-1.7$	$-1.2$	$-0.1$
PWPB95-D3	$-0.9$	$-0.3$	<b>+0.5</b>

Notes: <sup>a</sup>Footnotes a and b to Table 2 apply.

<sup>b</sup>Number of functionals (out of 56 functionals) that give the wrong sign for the isomerization reaction.

Table 5. Statistical analysis for the performance of G4-type and MP $n$  procedures for the calculation of C<sub>8</sub>H<sub>8</sub> isomerization energies (in kcal mol<sup>-1</sup>).<sup>a</sup>

	RMSD	MAD	MSD	LND	LPD
ccCA-PS3-RI	0.23	0.19	-0.12	-0.54 ( <b>40</b> )	0.31 ( <b>2</b> )
G4	0.80	0.63	-0.50	-1.76 ( <b>38</b> )	0.69 ( <b>41</b> )
G4MP2	0.83	0.67	-0.16	-2.19 ( <b>38</b> )	1.14 ( <b>41</b> )
G4MP2-6X	0.64	0.52	0.03	-1.30 ( <b>38</b> )	1.21 ( <b>33</b> )
CBS-QB3	1.1	0.9	0.8	-1.0 ( <b>44</b> )	2.4 ( <b>41</b> )
CBS-APNO	0.77	0.61	0.31	-1.14 ( <b>36</b> )	2.00 ( <b>41</b> )
HF/VQZ	9.3	7.4	6.2	-4.8 ( <b>30</b> )	20.6 ( <b>42</b> )
MP2/VQZ	3.2	2.6	1.2	-4.4 ( <b>42</b> )	7.5 ( <b>40</b> )
SCS-MP2/VQZ	1.9	1.5	-0.9	-4.7 ( <b>33</b> )	1.9 ( <b>40</b> )
MP2.5/VQZ	2.0	1.6	1.3	-1.9 ( <b>39</b> )	5.0 ( <b>40</b> )
MP3/VQZ	2.0	1.4	1.3	-0.4 ( <b>39</b> )	6.0 ( <b>42</b> )
SCS-MP3/VQZ	1.7	1.1	-0.9	-4.1 ( <b>35</b> )	0.9 ( <b>38</b> )
MP4(SDQ)/VTZ	2.0	1.7	-1.2	-4.1 ( <b>35</b> )	2.8 ( <b>42</b> )
MP4/VTZ	1.4	1.0	-0.3	-3.6 ( <b>44</b> )	1.5 ( <b>40</b> )
CCSD/VTZ	1.4	1.0	-0.4	-2.8 ( <b>37</b> )	3.5 ( <b>42</b> )
SCS-CCSD/VTZ	2.7	2.4	-2.4	-5.9 ( <b>41</b> )	<sup>b</sup>
SCS(MI)CCISD/VTZ	1.4	1.1	-0.8	-3.6 ( <b>41</b> )	1.2 ( <b>38</b> )
CCSD(T)/VTZ	0.60	0.46	-0.25	-1.51 ( <b>36</b> )	1.20 ( <b>39</b> )

Notes: <sup>a</sup>Footnotes a and c to Table 2 apply.

<sup>b</sup>All isomerization energies are underestimated.

W1-F12 and DFT isomerization energies for these three reactions. The isomerization energies with the correct (positive) sign are given in bold. Before proceeding to a discussion of the individual isomerizations, we note that only the  $\omega$ B97X functional seems to handle all three isomerization reactions, i.e. to obtain the reaction energy with the correct sign and in reasonable agreement with the W1-F12 results.

Starting with the **27**  $\rightarrow$  **29** isomerization, 10 out of the 56 functionals in Table 4 manage to get the correct energetic order of the isomers. Of these, only PBE0-D, BMK-D,  $\omega$ B97, and  $\omega$ B97X reproduce the W1-F12 isomerization energy to within 1 kcal mol<sup>-1</sup>.

For the **32**  $\rightarrow$  **33** isomerization, again, only 10 functionals manage to get the correct sign for the reaction energy. Deviations from the W1-F12 value of less than 1 kcal mol<sup>-1</sup> are obtained for PBE0, B1B95-D,  $\omega$ B97X, and  $\omega$ B97XD.

The **34**  $\rightarrow$  **36** isomerization proves to be a very difficult test for the DFT and DHDFE functionals. Despite the W1-F12 energy separation being as large as +6.5 kcal mol<sup>-1</sup> only 17 out of the 56 considered functionals manage to reproduce the correct energetic order of the isomers. More than half of these functionals deviate by three or more kcal mol<sup>-1</sup> from the W1-F12 isomerization energy. The four functionals that are within 3 kcal mol<sup>-1</sup> from the W1-F12 value attain the following isomerization energies: +5.7 ( $\omega$ B97X), +4.9 (DSD-PBEP86), +4.1 (B2K-PLYP-D), and +3.8 (DSD-BLYP) kcal mol<sup>-1</sup>. Thus, among

the double-hybrid functionals, the very recent spin-component-scaled double hybrid DSD-PBEP86 acquires itself best.

### 3.4. Performance of G4-type composite and lower-level *ab initio* procedures for the C<sub>8</sub>H<sub>8</sub> isomerization energies

Table 5 gives an overview of the performance of the composite G4, G4(MP2), G4(MP2)-6X, CBS-QB3, and CBS-APNO procedures, as well as of standard *ab initio* procedures (MP2, SCS-MP2, MP2.5, MP3, SCS-MP3, MP4, CCSD, and SCS-CCSD). G4 and G4(MP2) show excellent performance with RMSDs below the threshold of chemical accuracy (namely, for both RMSD = 0.8 kcal mol<sup>-1</sup>). G4(MP2)-6X shows even better performance with an RMSD of 0.6 kcal mol<sup>-1</sup> (also note that the MSD for this procedure is essentially zero). It is worth mentioning that the G4-type procedures do not have any difficulty with the isomers that are problematic for the DFT functionals (reported in Table 3), or with the isomerization reactions reported in Table 4). For example, for these three protocols the largest deviation is obtained for isomer **38**, specifically it is: -1.8 (G4), -2.2 (G4(MP2)), and -1.3 (G4(MP2)-6X) kcal mol<sup>-1</sup>. CBS-QB3 has somewhat larger error statistics, but still acquires itself well, whilst CBS-APNO shows similar performance to that of G4. Finally, we note

that the RI-ccCA-PS3 method results in an RMSD of just  $0.23 \text{ kcal mol}^{-1}$ , the largest deviation (for isomer **40**) being just  $-0.54 \text{ kcal mol}^{-1}$ . From the raw data in the W4-11 paper, we find that the ccCA error statistics, relative to TAEs at the relativistic FCI limit, for just the first-row systems (excluding  $\text{Be}_2$  and  $\text{BeF}_2$ , 97 molecules) are RMSD 0.75, MSD  $-0.19$  MAD  $0.54 \text{ kcal mol}^{-1}$ , compared to the corresponding W1-F12 statistics [36] of RMSD 0.45, MSD  $-0.31$ , and MAD  $0.33 \text{ kcal mol}^{-1}$ . These latter statistics drop [36] to RMSD 0.19, MSD  $-0.09$ , MAD  $0.13 \text{ kcal mol}^{-1}$  if CCSD(T) limits are considered instead. While W1-F12 would seem to be the superior method to ccCA for TAEs, the two methods appear to agree to within overlapping uncertainties for the  $\text{C}_8\text{H}_8$  isomerization energies.

We will now consider the performance of more approximate wavefunction methods (see Table 5). At the SCF level, we find  $\text{RMSD} = 9.3 \text{ kcal mol}^{-1}$ , which is not so interesting in itself as for the fact that several DFT methods (notably BLYP and M05) fail to make even that modest grade. At the MP2/cc-pVQZ level, we find an  $\text{RMSD} = 3.2 \text{ kcal mol}^{-1}$ , the largest negative and positive errors being  $-4.4$  and  $+7.5 \text{ kcal mol}^{-1}$ , respectively; reducing the basis set to cc-pVTZ only affects the RMSD in the second decimal place, and likewise at the MP3 level. MP3, MP4(SDQ), and CCSD with the cc-pVTZ basis set reduce the RMSD successively to 2.0, 2.0, and  $1.4 \text{ kcal mol}^{-1}$ , indicating that higher-order  $T_1$  and  $T_2$  terms are relatively important here: this is further highlighted by the drop in the mean signed error from  $-1.2$  (MP4(SDQ)) to  $-0.4$  (CCSD)  $\text{kcal mol}^{-1}$ .

Full MP4/cc-pVTZ still has an RMSD of  $1.4 \text{ kcal mol}^{-1}$ , which would seem to be a rather modest improvement over the  $2.0 \text{ kcal mol}^{-1}$  found for MP4(SDQ). However, going from CCSD to CCSD(T) with the cc-pVTZ basis represents a dramatic improvement from 1.4 to  $0.6 \text{ kcal mol}^{-1}$ , the largest negative and positive errors now being just  $-1.5$  and  $+1.2 \text{ kcal mol}^{-1}$ . The importance of connected triples for processes in which multiple bonds are broken and formed should not come as a surprise.

Let us now turn to some modified *ab initio* methods. SCS-MP2, which has the same computational cost as MP2, actually yields a better  $\text{RMSD} = 1.9 \text{ kcal mol}^{-1}$  than MP4(SDQ), while SCS-MP3 slightly improves further on that ( $1.7 \text{ kcal mol}^{-1}$ ). While MP2.5 – an average of MP2 and MP3, proposed by Hobza and co-workers [92] for weak interactions – does very well on conformer energies of alkanes [104], it clearly is less appropriate here: its  $\text{RMSD} = 2.0$  is the

same as straight MP3. Finally, and somewhat surprisingly, SCS-CCSD [90] yields a disappointing  $\text{RMSD} = 2.7 \text{ kcal mol}^{-1}$ . The more recent SCS(MI)CCSD reparametrization for weak interactions [91] does much better ( $\text{RMSD} = 1.4 \text{ kcal mol}^{-1}$ ), but its slight edge over SCS-MP3 ( $1.7 \text{ kcal mol}^{-1}$ ) hardly justifies the cost. Besides, the even less expensive DSD-PBEP86 double hybrid DFT functional actually offers a superior  $\text{RMSD} = 1.2 \text{ kcal mol}^{-1}$ .

Arguably, any double-hybrid that is not of at least MP2 quality ( $\text{RMSD} = 3.2 \text{ kcal mol}^{-1}$ ) would be a waste of CPU time for this problem. Out of the ordinary double hybrids only B2K-PLYP-D meets that test. All three spin-component-scaled double hybrids considered meet this criterion, DSD-BLYP barely so ( $\text{RMSD} = 3.1 \text{ kcal mol}^{-1}$ ), DSD-PWPB95 comfortably so ( $\text{RMSD} = 2.3 \text{ kcal mol}^{-1}$ , which drops slightly further to  $2.2 \text{ kcal mol}^{-1}$  with the D3 dispersion corrections), and finally the very recent DSD-PBEP86 ( $\text{RMSD} = 1.2 \text{ kcal mol}^{-1}$ ) by a wide margin – in fact, it outperforms both MP4 and CCSD. Found through an elaborate systematic search of exchange-correlation functional space [74], DSD-PBEP86 represents a significant improvement over the original spin-component-scaled double hybrid SCS-BLYP [73] for many properties, and this is once again borne out here ( $\text{RMSD}$  reduced by 60% and MSD/bias nearly eliminated).

#### 4. Conclusions

We have obtained benchmark isomerization energies for 45  $\text{C}_8\text{H}_8$  isomers at the CCSD(T)/CBS limit by means of the high-level W1-F12 composite thermochemistry protocol. The considered isomers involve a range of hydrocarbon functional groups, including (linear and cyclic) polyacetylene, polyynes, and cumulene moieties, as well as aromatic, anti-aromatic, and highly-strained rings. We use these to evaluate the performance of a variety of DFT functionals in predicting the isomerization energies. With regard to the performance of DFT and DHDFT we draw the following conclusions:

- Highly-strained (e.g. involving multiple 3- and 4-membered fused rings) and cumulenic systems pose a formidable challenge to many DFT functionals.
- Specifically, for isomers such as barrelene (**11**), cuneane (**28**), 1,1-dimethyl[5]cumulene (**36**), pentacyclo[5.1.0.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>]octane (**39**), and cubane (**41**) deviations (in absolute value) larger than  $10 \text{ kcal mol}^{-1}$  are obtained for many functionals (notable examples



include: BLYP, B97D, HCTH407, M06L,  $\tau$ -HCTH, B3LYP, BH&HLYP,  $\omega$ B97, M05, B1B95, and B2-PLYP).

- The best performing DFT functionals attain the following RMSDs: 2.1 ( $\omega$ B97X-D), 2.7 (B3PW91-D), 2.8 (PW6B95), 3.0 (B3PW91 and B3P86), 3.1 (M062X), and 3.2 kcal mol<sup>-1</sup> ( $\omega$ B97X and TPSSh-D), thus meeting or exceeding the performance of MP2.
- Performance is quite sensitive to the quality of the correlation functional, with LYP putting in an especially poor performance.
- Of the considered DHDFT functionals, the novel spin-component-scaled double hybrid DSD-PBEP86 exhibits the best performance with an RMSD of 1.2 kcal mol<sup>-1</sup>, slightly better than MP4 and CCSD.
- Dispersion corrections play a relatively minor role in the C<sub>8</sub>H<sub>8</sub> isomerization reactions. That is, the RMSDs are reduced by 10% or less upon inclusion of the D2 dispersion correction.

The performance of a number of lower-level *ab initio* methods as well as G4-type and CBS-type composite procedures was also evaluated for the calculation of the isomerization energies. We make the following observations:

- Post-MP4  $T_1$  and  $T_2$  terms do have an influence on the energetics, but (T) triples are important as well, and only at the CCSD(T) level can RMS errors below 1 kcal mol<sup>-1</sup> be achieved.
- The correlation-consistent composite approach RI-ccCA-PS3 results in an RMSD of just under 1 kJ mol<sup>-1</sup> (specifically, RMSD = 0.23 kcal mol<sup>-1</sup> and MAD = 0.19 kcal mol<sup>-1</sup>).
- G4, G4(MP2), G4(MP2)-6X, and CBS-APNO, all being additivity approximations to the CCSD(T) basis set limit, show excellent performance with RMSDs below 1 kcal mol<sup>-1</sup> (specifically, RMSD = 0.8, 0.8, 0.6, and 0.8 kcal mol<sup>-1</sup>, respectively).
- The G4-type and CBS-type procedures do not seem to have any difficulties with highly-strained or cumulenic isomers, e.g. for all the isomers deviations (in absolute value) below 2.4 kcal mol<sup>-1</sup> are obtained.
- SCS-MP2 and SCS-MP3 outperform standard MP2 and MP3, respectively, and in fact

SCS-MP3 affords an RMSD comparable to CCSD for this problem set.

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### Note

1. Combines Becke88 [55] exchange functional (28% HF exchange) and Becke95 correlation functional [105].

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