

Explicitly correlated benchmark calculations on C₈H₈ isomer energy separations: How accurate are DFT, double-hybrid, and composite ab initio procedures?

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Abstract

Accurate isomerization energies are obtained for a set of 45 C₈H₈ 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, polyynes, 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 (the performance of MP2), namely: 2.9 (B972-D), 2.8 (PW6B95), 2.7 (B3PW91-D), 2.2 (PWPB95-D3), 2.1 (ω B97X-D), and 1.2 (DSD-PBEP86) kcal/mol. 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.

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I. 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 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[1]. 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. They also noted that coupled cluster with singles, doubles, and quasiperturbative 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, 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: 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 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 coworkers[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, 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 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., Refs.[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/naphthacene $C_{18}H_{12}$.

In the present work we introduce a database of highly-accurate energies for 45 C_8H_8 isomers. The isomers that we have examined are shown in Figures 1 and 2. These cover a broad spectrum of C–C bonding situations ($sp^3 - sp^3$, $sp^3 - sp^2$, $sp^3 - sp$, $sp^2 - sp^2$, $sp^2 - sp$, and $sp - sp$) involving polyacetylene, polyyne, 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]. 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.

II. 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.

The geometries of all isomers have been 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]). Benchmark isomerization energies were then obtained by means of our recently-developed W1-F12 thermochemical protocol[36] using the Molpro 2010.1 program suite[41].

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 reference [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 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 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 is obtained.

We shall then use our W1-F12 benchmark isomerization energies for C_8H_8 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 τ (which contains similar information as the Laplacian of the density): M06-L[60], TPSS[61] and τ -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 ω B97[66], and ω B97-X[66].); and (ii) the hybrid meta-GGAs: B98[67], TPSSh[68], B1B95[69], PW6B95[19], τ -HCTHh[62], BMK[8], M05[70], M05-2X[71], M06, M06-2X, and M06-HF[15, 72, 73].
- 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[74], DSD-PBEP86[75], and PWPB95[76].

The conventional DFT calculations (rungs 1–4 of Jacob’s Ladder) are carried out with the

polarization-consistent pc2 basis set of Jensen[77] 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[78] was used is the the PWPB95 spin-component-scaled double hybrid as prescribed in reference[76]). The empirical s_6 pre-factors are taken from references[12, 13, 17], these were, for the most part, optimized against the S22 benchmark set of weakly interacting systems[79].

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[80], G4(MP2)[81], and G4(MP2)-6X[82]). 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[83] and CBS-APNO[84] methods as well as the Wilson correlation-consistent composite approach[85], specifically the ccCA-PS3 variant[86]. In the latter, as advocated by Prascher et al.[87], we applied the resolution of the identity (RI) approximation[88] in the MP2 basis set extrapolation and core-valence correlation steps: auxiliary basis sets from Ref.[89] 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 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[90], SCS-CCSD[91], SCS(MI)CCSD[92], MP2.5[93], and MP4. The PWP95 and PWP95-D3 calculations were carried out using the ORCA 2.9 program system[94], 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[95]. 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 Gn and CBS-like calculations where those were taken as the starting geometry for the optimizations prescribed by their protocol.

III. RESULTS AND DISCUSSION

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

A. 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 I. Energies are given relative to the lowest-energy isomer (styrene, structure **1**, Figure 1). The isomerization energies spread a wide energetic range of up to 124.5 kcal/mol. 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, polyynes, and cumulene moieties.

For the lowest-energy structure, styrene, our W1-F12 computed atomization energy is 1815.89 kcal/mol at the bottom of the well and 1733.61 at 0 K. Using the ‘interim value’s $\Delta_f H_{0K}^\circ[C(g)] = 170.024$ and $\Delta_f H_{0K}^\circ[H(g)] = 51.633$ kcal/mol from version 1.110 α of the Active Thermochemical Tables[96], this leads to heats of formation for styrene of 39.65 kcal/mol at 0 K and 34.38 kcal/mol at 298 K. The latter is in good agreement with the available experimental values of 35.1 ± 0.24 kcal/mol from Prosen and Rossini[97], 35.3 ± 0.4 kcal/mol from Pedley et al.[98], and 35.4 kcal/mol from the TRC tables[99]. Some of the remaining discrepancy is liable to come from the uncertainty in the zero-point vibrational energy[100, 101], 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 nondynamical 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 ~ 1 –3 kJ/mol of the isomerization energies at the full configuration interaction (FCI) basis-set limit[36, 53, 102].

B. Performance of density functional theory for the C_8H_8 isomerization reactions

Table II 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 GGAs and meta-GGAs, the only functionals that yield RMSDs below 4 kcal/mol are PBE-D (3.9) and TPSS-D (3.8 kcal/mol). (ii) A respectable number of the hybrid-GGA functionals result in RMSDs between roughly 3 and 4 kcal/mol (namely, B3P86, B3PW91, B97-1, B97-2, and PBE0), which are lowered slightly further when the ‘-D’ correction is included (reaching 2.7 kcal/mol for B3PW91-D). (iii) Of the hybrid-meta GGAs PW6B95 reaches RMSD=2.8 kcal/mol, followed closely by M06-2X (RMSD=3.1 kcal/mol). (iv) Of the range-separated hybrid GGAs, ω B97X-D shows excellent performance with an RMSD of only 2.1 kcal/mol. (v) With regard to the double hybrids, DSD-PBEP86 gives an exceptionally low RMSD of just 1.2 kcal/mol (and a near-zero MSD of 0.2 kcal/mol), PWPB95-D3 coming in second at RMSD=2.2 kcal/mol. (vi) Finally, we note that inclusion of the D2 dispersion corrections reduces the RMSDs by amounts ranging from 0.1–1.1 kcal/mol: 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 III 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^{2,4}.0^{3,5}.0^{6,8}]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 exception (M06HF and ω B97) all of the DFT functionals overestimate the reaction energy of the **1**→**11** isomerization. For ten functionals deviations larger than 10 kcal/mol 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, specifically, M06HF (-1.8), ω B97 (-0.2), and PWPB95-D3 (1.9 kcal/mol).

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 (BLYP). Cases for which the deviations (in absolute value) are larger than 10 kcal/mol include: ω 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 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).

Moving to the next highly-strained molecule (with the tongue-twister name of pentacyclo[5.1.0.0^{2,4}.0^{3,5}.0^{6,8}]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, from -29.4 to +19.4 kcal/mol (where again the largest deviations are obtained for M05 and BLYP). Notable cases for which the deviations exceed 10 kcal/mol are ω B97, M06, M06L, B1B95-D, B3LYP, and BLYP-D. On the other hand, deviations lower than 1 kcal/mol (in absolute value) are obtained for τ HCTH (-0.4), BPW91 (0.2), and BMK-D (0.4 kcal/mol).

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 (BLYP). Other notable functionals for which the deviations exceed 10 kcal/mol (in absolute value) are: BMK, M05, ω B97, B2T-PLYP, B2-PLYP, B2-PLYP-D, B97D, B3LYP, and B3LYP-D. Notable cases with deviations < 1 kcal/mol 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).

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[103], reference [104], and references within these publications). With very few exceptions, the DFT functionals underestimate the reaction energy of the **1**→**36** isomerization (and do so by over 10 kcal/mol in many cases). However, for five functionals deviations ≤ 1.0 kcal/mol are obtained: These are DSD-BLYP (-0.9), ω B97X-D (-0.8), B2K-PLYP (-0.5), B2K-PLYP-D (0.1), and BMK-D (0.3 kcal/mol).

C. Isomer pairs for which the considered DFT and DHDFE 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)→(cumulenic isomer). Specifically, they are reactions: **27**→**29**, **32**→**33**, and **34**→**36**. The W1-F12 isomerization energies are: +2.59 (**27**→**29**), +1.69 (**32**→**33**), and +6.47 kcal/mol (**34**→**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 DHDFE functionals predict that the cumulenic/linear isomer is energetically more stable. Table IV gives the W1-F12 and DFT isomerization energies for these three reactions. The isomerization energies with the correct (positive) sign are bolded. Before proceeding to a discussion of the individual isomerizations, we note that only the ω 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**→**29** isomerization, 10 out of the 56 functionals in Table IV manage to get the correct energetic order of the isomers. Of these, only PBE0-D, BMK-D, ω B97, and ω B97X reproduce the W1-F12 isomerization energy to within 1 kcal/mol.

For the **32**→**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 are obtained for PBE0, B1B95-D, ω B97X, and ω B97XD.

The **34**→**36** isomerization proves to be a very difficult test for the DFT and DHDFT functionals. Despite the W1-F12 energy separation being as large as +6.5 kcal/mol 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 from the W1-F12 isomerization energy. The four functionals that are within 3 kcal/mol from the W1-F12 value attain the following isomerization energies: +5.7 (ω B97X), +4.9 (DSD-PBEP86), +4.1 (B2K-PLYP-D), and +3.8 (DSD-BLYP) kcal/mol. Thus, among the double-hybrid functionals, the very recent spin-component-scaled double hybrid DSD-PBEP86 acquits itself best.

D. Performance of G4-type composite and lower-level *ab initio* procedures for the C_8H_8 isomerization energies

Table V 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 $\text{RMSD} = 0.8$ kcal/mol). G4(MP2)-6X shows even better performance with an RMSD of 0.6 kcal/mol (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 III), or with the isomerization reactions reported in Table IV). 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. CBS-QB3 has somewhat larger error statistics, but still acquits 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 kcal/mol, the largest deviation (for isomer **40**) being just -0.54 kcal/mol.

We will now consider the performance of more approximate wavefunction methods (see Table V). At the SCF level, we find $\text{RMSD}=9.3$ kcal/mol, 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 RMSD = 3.2 kcal/mol, the largest negative and positive errors being -4.4 and +7.5 kcal/mol, respectively; reducing the basis set to cc-pVTZ only affects the RMSD in the 2nd 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 kcal/mol, 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) kcal/mol.

Full MP4/cc-pVTZ still has an RMSD of 1.4 kcal/mol, which would seem to be a rather modest improvement over the 2.0 kcal/mol 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 kcal/mol, the largest negative and positive errors now being just -1.5 and +1.2 kcal/mol. 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 RMSD=1.9 kcal/mol than MP4(SDQ), while SCS-MP3 slightly improves further on that (1.7 kcal/mol). While MP2.5 — an average of MP2 and MP3, proposed by Hobza and coworkers[93] for weak interactions — does very well on conformer energies of alkanes[105], it clearly is less appropriate here: its RMSD = 2.0 is the same as straight MP3. Finally, and somewhat surprisingly, SCS-CCSD[91] yields a disappointing RMSD = 2.7 kcal/mol. The more recent SCS(MI)CCSD reparametrization for weak interactions[92] does much better (RMSD = 1.4 kcal/mol), but its slight edge over SCS-MP3 (1.7 kcal/mol) hardly justifies the cost. Besides, the even less expensive DSD-PBEP86 double hybrid DFT functional actually offers a superior RMSD = 1.2 kcal/mol.

Arguably, any double-hybrid that is not of at least MP2 quality (RMSD = 3.2 kcal/mol) 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 (RMSD=3.1 kcal/mol), DSD-PWPB95 comfortably so (RMSD=2.3 kcal/mol, which drops slightly further to 2.2 kcal/mol with the D3 dispersion corrections), and finally the very recent DSD-PBEP86 (RMSD=1.2 kcal/mol) by a wide margin — in fact, it outperforms both MP4 and CCSD. Found through an elaborate systematic search of exchange-correlation functional space,[75] DSD-PBEP86

represents a significant improvement over the original spin-component-scaled double hybrid SCS-BLYP[74] for many properties, and this is once again borne out here (RMSD reduced by 60% and MSD/bias nearly eliminated).

IV. CONCLUSIONS

We have obtained benchmark isomerization energies for 45 C_8H_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^{2,4}.0^{3,5}.0^{6,8}]octane (**39**), and cubane (**41**) deviations (in absolute value) larger than 10 kcal/mol are obtained for many functionals (notable examples include: BLYP, B97D, HCTH407, M06L, τ -HCTH, B3LYP, BH&HLYP, ω B97, M05, B1B95, and B2-PLYP);
- The best performing DFT functionals attain the following RMSDs: 2.1 (ω B97X-D), 2.7 (B3PW91-D), 2.8 (PW6B95), 3.0 (B3PW91 and B3P86), 3.1 (M062X), and 3.2 kcal/mol (ω 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, slightly better than MP4 and CCSD;
- Dispersion corrections play a relatively minor role in the C_8H_8 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 be achieved;
- The correlation-consistent composite approach RI-ccCA-PS3 results in an RMSD of just under 1 kJ/mol (specifically, RMSD = 0.23 kcal/mol and MAD = 0.19 kcal/mol);
- 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 (specifically, RMSD = 0.8, 0.8, 0.6, and 0.8 kcal/mol, 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 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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TABLE I: Component breakdown of the benchmark W1-F12 isomerization energies for the 45 C₈H₈ isomers (displayed in Figures 1 and 2). Energies (in kcal/mol) are given relative to the lowest-energy isomer (styrene, structure **1**, Figure 1).

	Δ SCF	Δ CCSD	Δ (T)	Δ CV ^a	Δ Rel. ^b	Δ ZPVE ^c	ΔE_e^d	ΔE_0^e	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-xylene
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-xylene
8	32.84	-7.82	0.19	0.15	0.03	0.11	25.36	25.28	1,6a-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	1,3a-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	<i>f</i>
14	43.90	-2.03	0.90	-0.13	0.00	-2.05	42.65	44.70	<i>f</i>
15	44.48	-1.78	1.14	-0.13	0.00	-2.14	43.71	45.85	<i>f</i>
16	47.69	-2.87	0.97	-0.02	0.00	-1.17	45.78	46.95	<i>f</i>
17	54.53	-6.32	-0.55	-0.05	0.06	-0.53	47.62	48.21	<i>f</i>
18	58.28	-10.40	0.22	0.27	0.02	-0.64	48.37	49.04	<i>f</i>
19	56.25	-7.08	-0.65	-0.09	0.07	-1.01	48.43	49.50	<i>f</i>
20	60.71	-0.84	0.22	0.17	-0.02	-3.05	60.26	63.28	<i>f</i>
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	<i>f</i>
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	<i>f</i>
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	<i>f</i>
32	90.44	-12.66	0.65	0.49	0.04	-0.86	78.92	79.82	<i>f</i>
33	79.69	-0.24	1.56	-0.39	0.03	-2.70	80.61	83.34	<i>f</i>
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	<i>f</i>
36	93.41	-2.75	-2.18	-0.18	-0.03	-4.51	88.29	92.78	1,1-dimethyl[5]cumulene ^f
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	<i>f</i>
39	106.79	-16.07	1.48	-0.10	0.18	-0.41	92.11	92.69	<i>f</i>
40	103.87	-6.11	-1.16	0.35	-0.02	-3.75	96.95	100.69	<i>f</i>
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	<i>f</i>

^aCV = core-valence correction.

^bScalar relativistic correction from second-order Douglas-Kroll CCSD(T) calculations.

^cZero-point vibrational energy correction from B3LYP/A'VTZ harmonic calculations (scaled by 0.985).

^dNonrelativistic, 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).

^eRelativistic, all-electron, ZPVE-inclusive CCSD(T) basis set limit reference isomerization energies from W1-F12 theory (for comparison with experiment).

^fFull IUPAC names: **13** = tricyclo[3.2.1.0^{2,8}]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^{2,7}.0^{4,6}]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^{2,5}]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^{2,4}.0^{3,5}.0^{6,8}]octane, **40** = 1,3-divinylcyclobuta-1,3-dieno[5.1.0.0^{2,4}.0^{3,5}.0^{6,8}]octane, **45** = 6-Ethynylbicyclo[3.1.0]hex-2-ene.

TABLE II: Performance statistics (kcal/mol) of conventional and double-hybrid DFT functionals for the calculation of C₈H₈ isomerization energies.^{a,b,c}

	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
τ -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
ω B97	6.3	4.0	-2.9	-21.9 (39)	3.6 (3)	13
ω B97X-D	2.1	1.7	0.8	-5.3 (41)	4.4 (11)	9
ω 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
τ -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

^aErrors are $E_{\text{isomer}}[\text{level}] - E_{\text{isomer}}[\text{CCSD(T)}]$ in kcal/mol.

^bThe standard DFT calculations were carried out in conjunction with the pc-2 basis set[77], while the DHDFT calculations were carried out in conjunction with the cc-pVQZ basis set.

^cRMSD = 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).

TABLE III: Particularly challenging isomers for DFT and DHDFE (the tabulated values are deviations from W1-F12 reference values, in kcal/mol, for the structures of the isomers see Figures 1 and 2).^a

	11	28	36	39	41
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
τ -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
ω B97	-0.2	-17.6	2.4	-21.9	-17.5
ω B97X	2.7	-7.8	1.4	-10.5	-8.3
ω 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
τ -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

^aFootnotes *a* and *b* to Table II apply.

TABLE IV: 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).

The isomerization energies with the correct (positive) sign are bolded.^a

	27→29	32→33	34→36
Wrong sign ^b	46	46	39
W1-F12	+2.59	+1.69	+6.47
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
τ -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	+0.2	+0.5	-5.3
B3PW91	-3.6	-4.4	-8.4
B98	-3.5	-4.0	-8.5
B971-D	-0.5	+0.4	-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	+2.2	+4.0	-2.4
PBE0	-0.3	+0.9	-4.4
ω B97	+3.6	+4.0	+9.5
ω B97X	+1.9	+1.2	+5.7
ω B97XD	+0.9	+1.8	+1.4
TPSSh-D	-2.0	-0.6	-8.6
TPSSh	-5.1	-4.6	-11.2
B1B95-D	-0.8	+2.1	-3.6
B1B95	-3.5	-1.2	-5.8
τ -HCTHh	-3.3	-4.2	-9.6
BMK-D	+3.3	+13.9	+2.4
BMK	+1.0	+10.9	+0.6
M05	-6.0	-7.0	-4.9
M052X	+1.4	-4.7	+3.5
M06-D	-4.6	-10.1	-4.0
M06	-5.5	-11.2	-4.7
M062X-D	-0.8	-6.9	+2.5
M062X	-1.0	-7.1	+2.3
M06HF	+5.0	-0.7	+13.6
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	+2.1
B2GP-PLYP	-2.9	-6.9	+1.0
B2K-PLYP-D	-1.0	-4.2	+4.1
B2K-PLYP	-2.0	-5.5	+3.3
B2T-PLYP-D	-1.7	-5.7	+0.7
B2T-PLYP	-3.4	-7.9	-0.7
DSD-BLYP	+0.5	-0.7	+4.9
DSD-PBEP86	-1.1	-4.4	+3.8
PWPB95	-1.7	-1.2	-0.1
PWPB95-D3	-0.9	-0.3	+0.5

^aFootnotes *a* and *b* to Table II apply.

^bNumber of functionals (out of 56 functionals) that give the wrong sign for the isomerization reaction.

TABLE V: Statistical analysis for the performance of G4-type and MP n procedures for the calculation of C₈H₈ isomerization energies (in kcal/mol).^a

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

^aFootnotes *a* and *c* to Table II apply.

^bAll isomerization energies are underestimated.

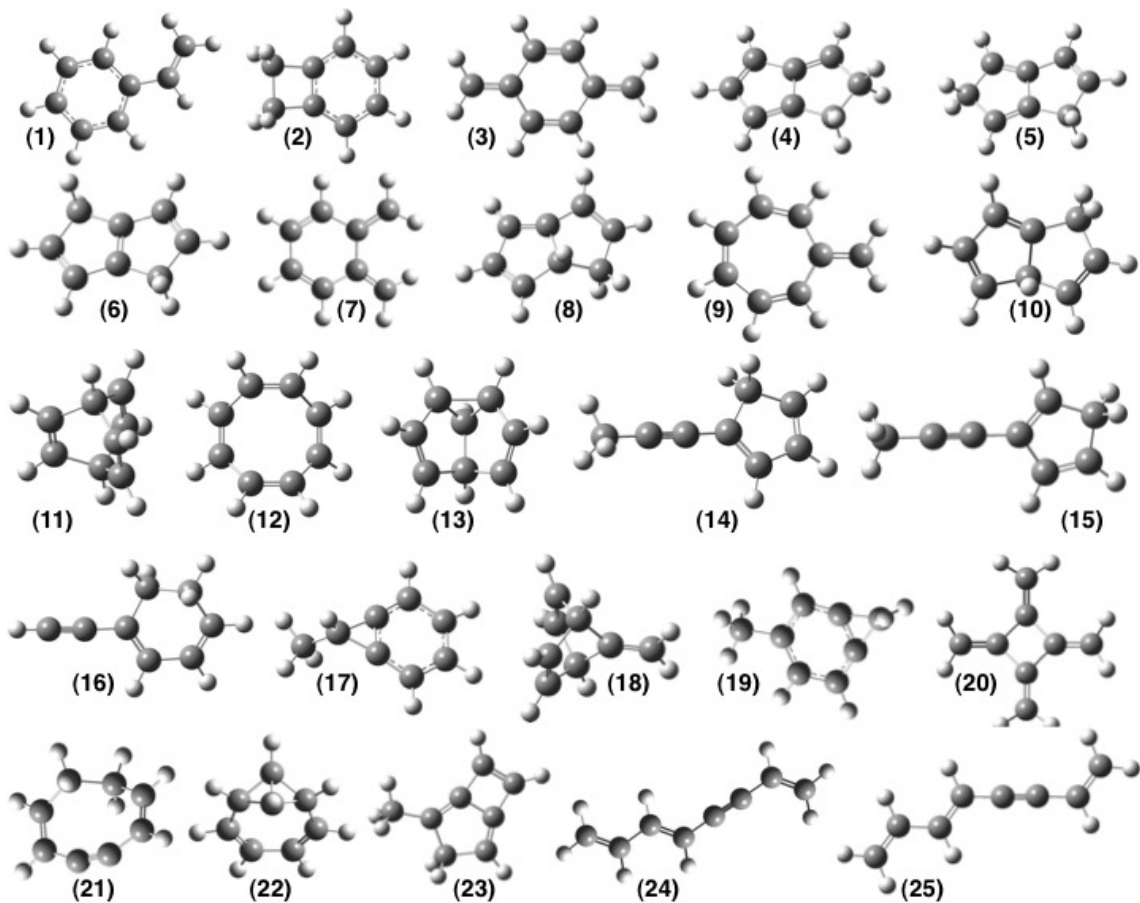


FIG. 1: Twenty five lowest-lying C₈H₈ isomers (ordered according to increasing CCSD(T)/CBS (ΔE_e) energies, given in Table I, for structure names see Table I).

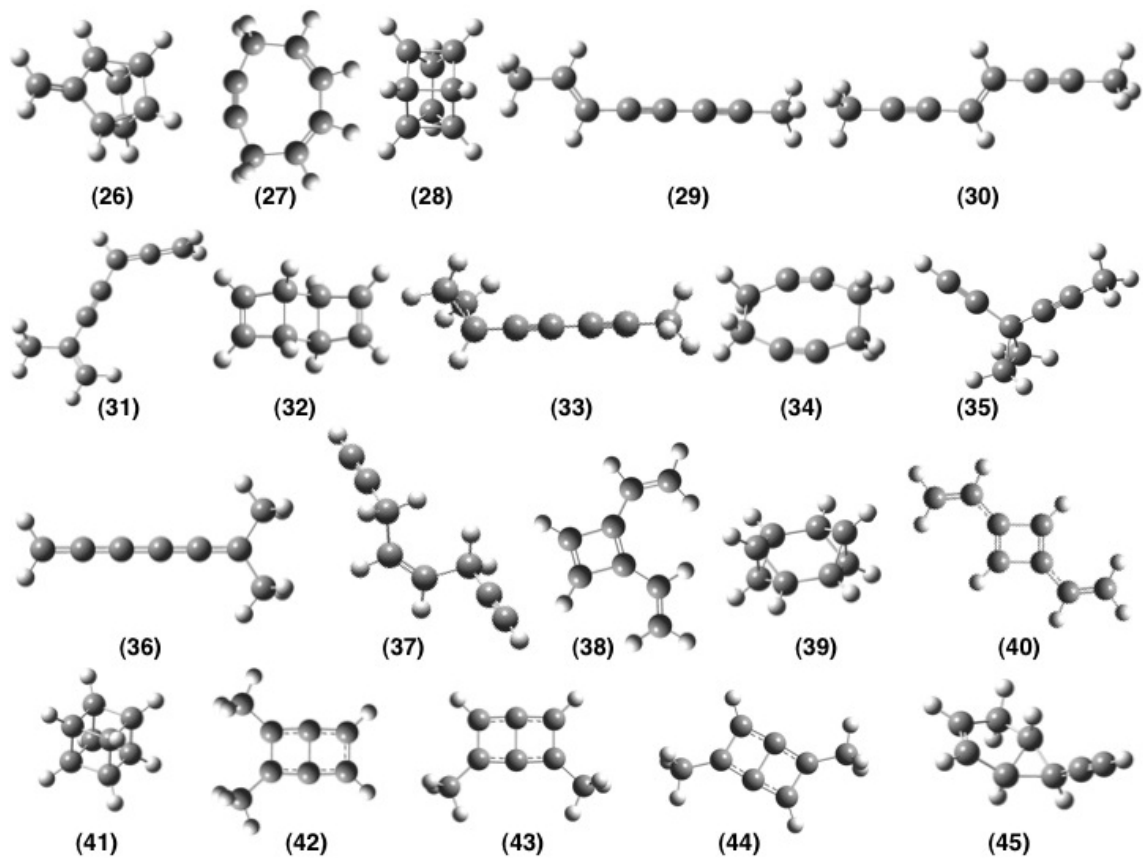


FIG. 2: Twenty higher-energy C_8H_8 isomers (ordered according to increasing CCSD(T)/CBS (ΔE_e) energies, given in Table I, for structure names see Table I)

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