

Heats of Formation of Medium-Size Organic Compounds from Contemporary Electronic Structure Methods

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50 KEYWORDS: Formation enthalpies, organic molecules, ab initio, DLPNO-CCSD(T), DFT
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3 ABSTRACT. Computational electronic structure calculations are routinely undertaken to predict
4 thermodynamic properties of the various species. However, the application of highly accurate
5 wave function theory methods, such as the “gold standard” coupled cluster approach including
6 single, double and partly triple excitations in perturbative fashion, CCSD(T), to large molecules
7 is limited due to high computational cost. In this work, the promising domain based local pair
8 natural orbital coupled cluster approach, DLPNO-CCSD(T), has been tested to reproduce 113
9 accurate formation enthalpies of medium-size molecules (few dozens heavy atoms) important for
10 bio- and combustion chemistry via the reaction based Feller-Peterson-Dixon approach. As for
11 comparison, 8 density functional theory (B3LYP, B3LYP-D3, PBE0, PBE0-D3, M06, M06-2X,
12 ω B97X-D3, and ω B97M-V) and MP2-based (B2PLYP-D3, PWPB95-D3, B2T-PLYP, B2T-
13 PLYP-D, B2GP-PLYP, DSD-PBEP86-D3, SCS-MP2, and OO-SCS-MP2) methods have been
14 tested. The worst performance has been obtained for the standard hybrid DFT functionals, PBE0
15 (Mean unsigned error (MUE)/ Mean Signed Error (MSE)=9.1/6.0 kcal/mol) and B3LYP
16 (MUE/MSE=13.5/-13.3 kcal/mol). An influence of an empirical dispersion correction term on
17 these functionals performance is not homogenous: B3LYP performance is improved (B3LYP-D3
18 (MUE/MSE=6.0/0.8 kcal/mol)) meanwhile PBE0 performance is worse (PBE0-D3
19 (MUE/MSE=14.1/13.6 kcal/mol)). The Minnesota functionals, M06 (MUE/MSE=3.8/-2.0
20 kcal/mol) and M06-2X (MUE/MSE=3.5/3.0 kcal/mol), and recently developed ω B97X-D3
21 (MUE/MSE=3.2/0.2 kcal/mol) and ω B97M-V (MUE/MSE=2.2/1.3 kcal/mol) methods provided
22 significantly better formation enthalpies. Enthalpies of similar quality can also be obtained from
23 some double hybrid methods (B2PLYP-D3 (MUE/MSE=4.7/2.0 kcal/mol), PWPB95-D3
24 (MUE/MSE=4.3/3.2 kcal/mol), B2T-PLYP (MUE/MSE=4.1/-3.0 kcal/mol) and B2T-PLYP-D
25 (MUE/MSE=3.3/1.7 kcal/mol)). The two spin component scaled (SCS) MP2 methods resulted in
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3 even smaller errors (SCS-MP2 (MUE/MSE = 1.9/1.2 kcal/mol) and OO-SCS-MP2 (MUE/MSE
4 = 1.6/0.1 kcal/mol)). The best performance was found for the frozen core (FC) DLPNO-
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even smaller errors (SCS-MP2 (MUE/MSE = 1.9/1.2 kcal/mol) and OO-SCS-MP2 (MUE/MSE = 1.6/0.1 kcal/mol)). The best performance was found for the frozen core (FC) DLPNO-CCSD(T) method with MUE/MSE of 1.6/-1.2 kcal/mol. The performance of the DLPNO-CCSD(T) method can be further improved by running the post-SCF calculations on the B3LYP orbitals: the MUE/MSE for DLPNO-CCSD(T, B3LYP) approximation are 1.2/-0.4 kcal/mol. We recommend the DLPNO-CCSD(T, B3LYP) method for the black box applications in thermodynamics of the medium-size organic molecules when the canonical CCSD(T) calculations with the basis sets of the reasonable quality are prohibitively expensive.

1. Introduction

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Gas phase formation enthalpy (ΔH_f) of a chemical substance is a fundamental building block in chemical sciences. When combined with standard molar entropies (S°), heat capacities (C_p), heats of phase change (ΔH_{tr}), and solvation Gibbs free energies (G_s), the formation enthalpies can be used to calculate the equilibrium constant via Hess's Law. In contrast to direct experimental measurements, thermodynamic calculations based on heats of formations can be used to derive the equilibrium constant for *every* reaction at *any* conditions. For example, the equilibrium constant or the reaction heat of the incomplete burning of graphite ($C_{(gr)} + \frac{1}{2} O_2 \rightarrow CO$) cannot be measured, *in principle*, since CO_2 will be always formed as side product along with CO: only thermodynamic calculations can be used to isolate such a process. Similarly, experimentally measuring all the micro-kinetic equilibria of thousands of chemical reactions occurring inside the bulk of the fuel in a nuclear reactor, or more simply in the combustion engines of cars is, *at least*, challenging; thus, leading to exclusive use of thermodynamic

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3 calculations to model these processes. Results of such modelling are often used to design new
4 high temperature materials¹⁻² to satisfy the demands of aerospace³⁻⁵ and nuclear⁶⁻⁸ industries, to
5 unravel the reaction mechanisms and predict the fuel/oxidant efficiency in combustion
6 thermochemistry.⁹⁻¹¹ For instance, Adiabatic Flame Temperature (AFT) is an important
7 combustion property that directly influences other finite rate limited phenomenon, such as
8 laminar burning velocity.¹² AFT can be measured by experiment or by thermodynamic
9 calculations requiring enthalpy of formation, entropy, and heat capacities of species. AFT can be
10 then used to determine the combustion efficiency and heat transfer. Enthalpy of formation
11 significantly affects the equilibrium of reversible reactions in the auto-ignition of fuels, which
12 determines the heat release rate in internal combustion engines.¹³ Enthalpy of formation is also
13 used to calculate hydrocarbon bond dissociation energies, which are needed to estimate the
14 activation energy of combustion reactions.
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33 Apart from this, accurate heats of formation have been actively employed in the development
34 and parameterization of electronic structure theory methods,¹⁴⁻¹⁵ in particular density functional
35 theory (DFT)¹⁶⁻¹⁹ and semi-empirical methods.²⁰⁻²² As an example, one of the most widely used
36 DFT functional, B3LYP,²³⁻²⁵ has been parameterized to reproduce 56 atomization energies
37 derived from corresponding 0 K formation enthalpies.²⁶⁻²⁷ Moreover, the most actively used
38 semi-empirical methods, namely PM3,²⁸⁻³¹ PM6²⁰, and PM7²¹ have
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48 all been parameterized against accurate formation enthalpies.
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51 An interest in accurate formation enthalpies (uncertainty below 1 kcal/mol) stimulated
52 experimental work (particularly in the '50s) to create databases of formation enthalpy for many
53 inorganic and organic compounds. The results have been tabulated in many (online)
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3 thermochemical databases as the NIST-JANAF tables,³²⁻³³ the Glushko/Guvich compilations,³⁴⁻³⁷
4 the handbooks of Krasnov³⁸ and of Baulch,³⁹ the active thermochemical tables (ATcT),⁴⁰⁻⁴¹
5 NASA Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies⁴² and the
6 third millenium thermodynamic database (TMTD).⁴³ However, standard enthalpy measurements
7 do not allow accessing easily this fundamental thermochemical value for compounds of low
8 stability, such as radicals and unstable intermediates of chemical reactions. Moreover, we
9 realized that significant discrepancies exist in the formation enthalpies values for identical
10 compounds tabulated in different compilations. Finally, data in available thermochemical tables
11 are not diverse enough to parameterize and/or validate electronic structure theory methods on a
12 broad enough dataset, thus questioning the applicability of these methods to systems that are
13 significantly different from systems used for validation.
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30 For these reasons, and due to high economic costs related to experimental science in general,
31 computational chemistry is becoming a valuable tool for the prediction of fundamental
32 thermochemical data.⁴⁴⁻⁴⁶ Of course, the possibility of using electronic structure methods in this
33 field relies on their capability to provide formation enthalpies with high accuracy (within 1-2
34 kcal/mol). In this context, the latest versions of the composite schemes,⁴⁷⁻⁵⁰ in particular the
35 correlation consistent composite approach (ccCA) of Wilson and co-workers,⁵¹ the Feller-
36 Peterson-Dixon (FPD) approach^{47-49,52} and the Weizmann-n theories,⁵³ typically provide the gas
37 phase formation enthalpy with the required accuracy for organic and inorganic molecules in the
38 absence of strong multi-reference and spin-orbit effects.^{48-49,54-55} However, the CCSD(T)⁵⁶
39 method, which is the “gold standard” of contemporary theoretical chemistry, and central to all
40 the mentioned composite schemes, is prohibitively expensive even for medium-size organic
41 molecules (few dozens heavy atoms) due to poor scalability of the method (N^7 with N being the
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3 number of electrons in the system) and the requirement of quite large basis sets, as the
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5 calculations converge slowly with respect to the basis set size. This situation has changed
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7 recently, with the advent of resolution of identity (RI) techniques and modern algorithms for the
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9 two-electron integral transformation,⁵⁷⁻⁶⁰ accomplished together with careful exploitation of
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11 localized molecular orbitals⁶¹⁻⁶⁴ to optimize the selection of the most relevant excitations,⁶⁵⁻⁶⁸
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13 such as the local CCSD(T) methods^{58,66-67,69-70} and the domain based pair natural orbitals
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15 DLPNO-CCSD(T),^{62-63,71} that enable accurate energy calculations of molecules containing dozen
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20 to hundreds of heavy atoms.

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23 In the current work, we assess the performance of the DLPNO-CCSD(T) method in reproducing
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25 113 accurate formation enthalpies of medium-size organic molecules containing C, H, N, O, and
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27 S elements. Accurate enthalpies of formation imply that correct energy profiles can be assembled
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29 in reactivity studies, but the large number of structures to be considered prevents systematic use
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31 of the DLPNO-CCSD(T) method; therefore, we also benchmarked a series of computationally
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33 less expensive *popular* contemporary computational chemistry methods ranging from DFT
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35 functionals (B3LYP-D3,^{23-25,72} PBE0-D3,⁷²⁻⁷⁵ M06,⁷⁶⁻⁷⁷ M06-2X⁷⁷ and ω B97X-D3^{72,78-79})
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37 thorough double hybrids (B2PLYP-D3,⁸⁰⁻⁸² PWPB95-D3,⁸² and B2T-PLYP⁸³) and MP2⁸⁴
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39 methods (SCS-MP2⁸⁴⁻⁸⁵ and OO-SCS-MP2^{84,86}).

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42 To derive the formation enthalpies, we used the reaction based Feller-Peterson-Dixon (FPD)
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44 approach.^{47-50,52,87-88} In this approach, the chemical reactions are built in such a way that the
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46 formation enthalpy of one species, for example C in Equation 1, is known with poor accuracy,
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48 while the formation enthalpies for all the other species, A, B and D in Equation 1, are known
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50 with great accuracy. At this point, the formation enthalpy of species C, $\Delta H_f(C)$, is calculated via
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52 the experimental ΔH_f of A, B, D and the theoretical reaction enthalpy of equation 1.
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The reaction-based scheme has several advantages over the atomization energy schemes, where the formation enthalpy is built from assembling the molecule from the individual atoms. First, the formation enthalpies from atomization energies might contain some error because the correlation energy in atoms and molecules is very different, and no full error-compensation can be expected because even the CCSD(T) method does not recover 100 % of the absolute correlation energy.⁸⁹ Hence, it is not surprising that systems containing aromatic rings, such as benzene, turned out to be particularly challenging for the FPD composite approaches based on CCSD(T) atomization energies with large effects arising from the core-valence correlation and higher order correlation terms.⁹⁰ Second, the currently available version of DLPNO-CCSD(T) method is only applicable to closed-shell systems, while the ground state of many atoms is open-shell. Further, since very accurate and precise reference enthalpies can be selected, the performance of the reaction-based scheme is essentially bound by the accuracy of the underlying computational method in predicting the overall reaction enthalpy.

It has to be noted that an idea to use the chemical reactions instead of atomization schemes for calculation of formation enthalpies goes back to 1970s and was pioneered by Pople and co-workers.⁹¹ The suggested isodesmic reactions, in which the number of bonds of each formal type remains the same on each side of the equation, result in the maximum cancelation of errors.⁹¹⁻⁹³ Therefore, even the simplest and computationally affordable methods of computational chemistry, such as the HF method, provide reaction enthalpies of acceptable quality because the change in correlation energy in isodesmic reactions is minimal. When combined with accurate reference experimental formation enthalpies, this approach leads to reliable predicted heats of formation. The downside of this approach is that it is often non-trivial or even impossible to

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compose isodesmic reactions to derive the heat of formation of every organic molecule at hand due to paucity of accurate reference thermochemical values for many organic molecules.¹⁴⁻¹⁵ This highlights the main feature of the reaction-based approach in the present work: despite many of the composed reactions not being isodesmic and having smaller degree of error compensations, there are virtually no errors coming from inaccuracies in reference experimental formation enthalpies. This is because only small organic and inorganic species, for which very accurate experimental formation enthalpies are known, have been used to balance the equations.

2. Computational Details

2.1 Geometry Optimization

All geometry optimizations were performed with the hybrid GGA PBE0⁷³⁻⁷⁵ functional as implemented in the Gaussian 09 suite of programs.⁹⁴ The all-electron def2-tzvp⁹⁵ basis sets of the Karlsruhe group were used on all the elements along with corresponding auxiliary basis functions⁹⁶ needed to fit Coulomb potential to speed up the DFT calculations. The Grimme's D3(BJ) dispersion correction⁷² was applied to arrive at the PBE0-D3(BJ) functional, to account for the possible influence of dispersion interactions on molecular geometries.⁹⁷⁻⁹⁹ Default values were adopted to control the convergence of the SCF iterative steps. Tighter than default, "tight" criteria have been used for geometry optimization: maximum force = $1.5 \cdot 10^{-5}$ a.u., RMS force = $1.0 \cdot 10^{-5}$ a.u., maximum displacement = $6.0 \cdot 10^{-5}$ Å, and RMS displacement = $4.0 \cdot 10^{-5}$ Å. Numerical integration of the exchange-correlation terms was performed using tighter-than-default "ultrafine" option (pruned, 99 radial shells and 590 angular points per shell) to eliminate the potential numerical noise in energy second derivatives. Geometries were characterized as true energy minima by the eigenvalues of the analytically calculated Hessian matrix.

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3 Translational, rotational, and vibrational partition functions for thermal corrections to give total
4 enthalpies were computed within the ideal-gas, rigid-rotor, and harmonic oscillator
5 approximations following standard procedures.¹⁰⁰⁻¹⁰²
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11 If several conformations could be possible for some molecules, the structure of the most stable
12 one was found by geometry optimization with the GGA PBE⁷³⁻⁷⁴ functional and all electron
13 quadruple- ζ quality basis sets $\lambda 3^{103}$ as implemented in PRIRODA 13 suite of programs¹⁰⁴ of
14 manually-generated conformations.
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20 21 22 23 **2.2 Single-Point Energy Evaluation**

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25 Apart from calculations with ω B97M-V functional of Mardirossian and Head-Gordon,¹⁰⁵ the
26 ORCA suite of programs¹⁰⁶ was employed for all the single-point DFT and wavefunction theory
27 (WFT) calculations performed in the present work. First, the DLPNO-CCSD(T) method^{62-63,71}
28 was applied for single-point energy evaluations aimed at getting the most accurate theoretical
29 values for the enthalpies of formation. Tighter than the default “TightPNO” DLPNO settings
30 (TCutPairs = 10^{-5} , TCutPNO = 10^{-7} , and TCutMKN = 10^{-3}) were used, as recommended, for
31 applications where the most accurate values are targeted. To benchmark computationally more
32 convenient methods, enthalpies were reevaluated via single-point energy calculations using the
33 following popular DFT functionals: hybrid GGA B3LYP,²³⁻²⁵ PBE0,⁷³⁻⁷⁵ and hybrid meta-GGA
34 M06,⁷⁶⁻⁷⁷ M06-2X⁷⁶⁻⁷⁷ and ω B97X-D3.^{72,78-79} Apart from M06 and M06-2X, every functional
35 was augmented with Grimme’s empirical correction term with Becke-Johnson damping to arrive
36 at corresponding DFT-D3 functionals. Numerical integration was performed using tighter-than-
37 default “Grid 5 FinalGrid 6” option (Lebedev434 and IntAcc=5.01 for SCF iterations and
38 Lebedev590 and IntAcc=5.34 for the final electronic energy) to eliminate the potential numerical
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3 noise associated with some meta-GGA functionals. Apart from DFT methods, the following
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5 double hybrid methods have been also tested: B2-PLYP-D3,⁸⁰⁻⁸² PWPB95-D3,⁸² B2T-PLYP-D,⁸³
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7 B2GP-PLYP-D3,¹⁰⁷ and DSD-PBEP86-D3.¹⁰⁸⁻¹⁰⁹ Numerical integration grid “Grid 5 FinalGrid
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9 6” was used for the DFT part. Finally, few MP2-based⁸⁴ methods, namely SCS-MP2⁸⁴⁻⁸⁵ and
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11 OO-SCS-MP2^{84,86} have also been employed. All doubly hybrid and MP2-based methods have
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13 been used within the resolution of identity (RI) approximation. Finally, the SP energy
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15 evaluations have also been performed with ω B97M-V method as implemented in QChem 4.4.1
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17 suite of programs.¹¹⁰ The pruned, 99 radial shells and 590 angular points per shell (99, 590)
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19 integration grid has been employed to evaluate the local exchange correlation functional, and the
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21 SG-1 integration grid has been used to evaluate the non-local correlation functional following the
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23 original article of Mardirossian and Head-Gordon.¹⁰⁵
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29 The following triple and quadruple- ζ correlation consistent basis sets were used in the present
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31 work. Hydrogen was described with the cc-pVnZ basis sets of Dunning.¹¹¹ Carbon, nitrogen, and
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33 oxygen were described with the correlation consistent valence cc-pVnZ basis sets of Dunning.¹¹¹
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35 Sulfur atoms were described with the correlation consistent valence cc-pVnZ basis set of Woon
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37 and Dunning.¹¹² The correlation fitting basis sets def2-qzvpp/C developed by Hättig,¹¹³⁻¹¹⁴
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39 necessary for the resolution of identity approximation as a part of DLPNO scheme and for the RI
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41 approximation as part of double hybrid calculations, were used. All def2/C basis sets were
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43 downloaded from the official web page of Turbomole.¹¹⁵
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48 To eliminate the effects of basis set incompleteness, we used the extrapolation schemes for HF
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50 and correlation energies of individual species suggested by Helgaker,¹¹⁶⁻¹¹⁸ see Eqs. 2 and 3. For
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52 two adjacent triple and quadruple- ζ basis sets:
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$$E_{HF}^n = E_{HF}^\infty + \alpha e^{-1.63n} \quad (2)$$

$$E_{corl}^n = E_{corl}^\infty + \beta n^{-3} \quad (3)$$

Where $n = 3$ and 4 for triple and quadruple- ζ basis sets; $E_{HF}^\infty/E_{corl}^\infty$ HF and correlation energies at the complete basis set (CBS) limit; α/β are parameters to be obtained from a system of the two equations. The total enthalpy at CBS limit for each reaction ($A + B \rightarrow C + D$) was evaluated via Eq. 4 for DLPNO-CCSD(T), double hybrids and SCS-MP2 and OO-SCS-MP2 methods:

$$\Delta H_{CCSD(T)}^0 = E_{HF}^\infty(C) + E_{corl}^\infty(C) + H_{corr}^{PBE0-D3}(C) + E_{HF}^\infty(D) + E_{corl}^\infty(D) + H_{corr}^{PBE0-D3}(D) - (E_{HF}^\infty(A) + E_{corl}^\infty(A) + H_{corr}^{PBE0-D3}(A) + E_{HF}^\infty(B) + E_{corl}^\infty(B) + H_{corr}^{PBE0-D3}(B)); \quad (4)$$

where $H_{corr}^{PBE0-D3}$ is the correction to the electronic energy to arrive to the enthalpy obtained with standard harmonic oscillator/rigid rotor/ideal gas approximation, see Section 2.1 for the details.

The total enthalpy at CBS limit for all DFT methods was evaluated via equation 5:

$$\Delta H_{DFT}^0 = E_{DFT}^\infty(C) + H_{corr}^{PBE-D3}(C) + E_{DFT}^\infty(D) + H_{corr}^{PBE-D3}(D) - (E_{DFT}^\infty(A) + H_{corr}^{PBE-D3}(A) + E_{DFT}^\infty(B) + H_{corr}^{PBE-D3}(B)) \quad (5)$$

where E_{DFT}^∞ has been extrapolated via Eq. 2.

In addition to the main protocol introduced above, to explore the effects arising from all electrons included in the correlation treatment, additional DLPNO-CCSD(T) all electron (AE) calculations with different basis sets have been performed. Hydrogen was described with the cc-pVnZ basis sets of Dunning.¹¹¹ Carbon, nitrogen, oxygen and sulfur were described with the correlation consistent weighted core valence cc-pwCVnZ basis sets of Peterson and Dunning.¹¹⁹ Finally, a composite G3(MP2) scheme¹²⁰ as implemented in Gaussian 09 has also been employed to evaluate the enthalpies, as this is often a method of choice for thermochemistry of the moderate-size organic molecules. All the structures were re-optimized according to original

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








10 **2.3 The Benchmark Set**





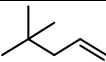


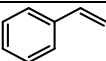
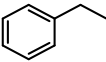



11
12 To accurately test the electronic structure theory methods, high quality gas phase experimental
13 formation enthalpies are of critical importance. Gas phase formation enthalpies of many organic
14 molecules are measured and tabulated^{32-36,38-41,43} and used for benchmarking.^{55,121-143}
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

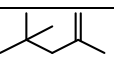
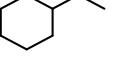


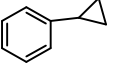

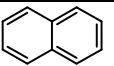
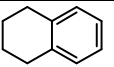

20
21 The enthalpies used for benchmarking electronic structure methods have to be accurate. In this
22 work, we applied the following criteria to the formation enthalpies to ensure their reliability and
23 accuracy: a) data should be obtained from more than one independent measurement; b)
24 measurements from different sources should agree with each other, i.e. do not differ more than
25 by 1-2 kcal/mol ; c) experimental measurements should have uncertainties below 2.0 kcal/mol.
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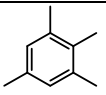
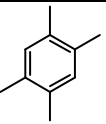
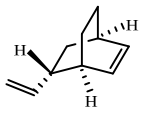
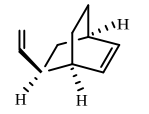
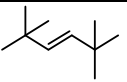
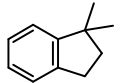
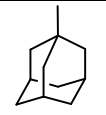
28
29 The chosen set of formation enthalpies used in the present work is given in Table 1, along with
30 recommend average values for each target species and their derived work reactions. There are
31 few peculiarities related to the way we built our reaction set. First, the same number of species
32 has been preserved in both sides of the equations to reduce the influence of the enthalpy
33 correction on the reaction energy. Second, only small organic and inorganic molecules for which
34 accurate formation enthalpies are known have been used to equilibrate the reactions (i.e. were
35 used as A, B and D in Eq. 5), in particular acetylene, ethylene, ethane, CO, methane, H₂, H₂O,
36 H₂S, HCN, N₂, NH₃. We expect under these conditions that the possible cancellations of errors
37 are minimal and better insights in the ability of the electronic structure theory methods to provide
38 accurate reaction enthalpies can be gained.
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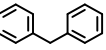
Table 1. Experimental gas phase formation enthalpies used to build the reaction database and chemical reactions used to predict enthalpies.

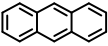
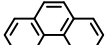
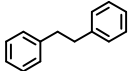

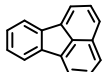
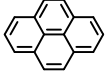
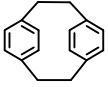
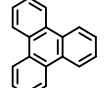
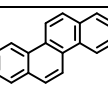
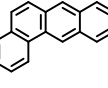
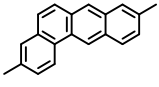
Entry	Structure	Formula	Expt. $\Delta_f H^\circ$ (kcal/mol) ^a	Avg. $\Delta_f H^\circ$ (kcal/mol) ^a	Reaction
M1		C ₆ H ₆	19.8±0.2 ¹⁴⁴ ; 19.8 ¹⁴⁵ ; 19.82±0.12 ¹⁴⁶ ;	19.8	4C ₂ H ₄ → M1 + H ₂ + 2CH ₄
M2		C ₆ H ₁₀	-1.05 ¹⁴⁷ ; -0.86±0.18 ¹⁴⁸ ; -0.60 ¹⁴⁵ ; -0.9±0.5 ¹⁴⁹	-0.9	2C ₂ H ₄ + C ₂ H ₆ → M2 + 2H ₂
M3		C ₆ H ₁₀	2.31 ¹⁴⁷ ; 1.76±0.17 ¹⁴⁸ ; 2.0±0.5 ¹⁴⁹	2.0	2C ₂ H ₄ + C ₂ H ₆ → M3 + 2H ₂
M4		C ₆ H ₁₀	-1.03±0.23 ¹⁵⁰ ; -1.1 ¹⁴⁵ ; -1.3 ¹⁴⁹ ; -1.7 ¹⁵¹	-1.3	2C ₂ H ₄ + C ₂ H ₆ → M4 + 2H ₂
M5		C ₆ H ₁₂	-15.74±0.36 ¹⁵² ; -14.7±0.4 ¹⁵³	-15.2	2C ₂ H ₆ + C ₂ H ₄ → M5 + 2H ₂
M6		C ₆ H ₁₂	-14.56±0.33 ¹⁵⁴ ; -14.39±0.26 ¹⁵⁵	-14.5	2C ₂ H ₆ + C ₂ H ₄ → M6 + 2H ₂
M7		C ₆ H ₁₂	-16.80±0.36 ¹⁵² ; -16.35±0.35 ¹⁵³ ; -16.22±0.25 ¹⁵⁶	-16.5	2C ₂ H ₆ + C ₂ H ₄ → M7 + 2H ₂
M8		C ₇ H ₈	44.6 ¹⁵⁷ ; 43.88±0.38 ¹⁵⁸ ; 43.24±0.50 ¹⁵⁹	43.9	4C ₂ H ₄ → M8 + CH ₄ + 2H ₂
M9		C ₇ H ₈	80.4 ¹⁶⁰ ; 79.5 ¹⁶¹ ; 81.05±0.55 ¹⁶² ; 81.04±0.54 ¹⁶³	80.5	CH ₄ + 2C ₂ H ₄ + C ₂ H ₂ → M9 + 3H ₂

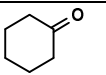
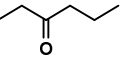
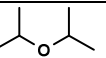
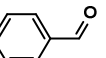
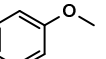
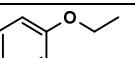

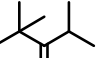
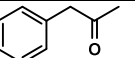
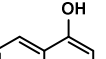
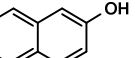
M10		C ₇ H ₈	59.18±0.74 ¹⁶² ;58.4 ¹⁶⁰ ;57.4 ¹⁶¹ ;58.5±1.4 ¹⁶⁴ ; 58.64±0.64 ¹⁶⁵	58.4	CH ₄ + 2C ₂ H ₄ + C ₂ H ₂ → M10 + 3H ₂
M11		C ₇ H ₁₀	18.7 ¹⁶⁶ ;20.2 ¹⁶¹ ;19.6±0.5 ¹⁶²	19.5	3C ₂ H ₄ + CH ₄ → M11 + 3H ₂
M12		C ₇ H ₁₀	19.7±0.5 ¹⁶⁷ ;20.4 ¹⁶⁰ ;21.4 ¹⁶¹ ;21.65±0.81 ¹⁶² ; 21.1±0.65 ¹⁶⁸	20.9	3C ₂ H ₄ + CH ₄ → M12 + 3H ₂
M13		C ₇ H ₁₂	-13.13±0.25 ¹⁶⁹ ;-13.1±1.1 ¹⁶² ;-12.4 ¹⁷⁰ ; 12.4 ¹⁷¹	-12.8	2C ₂ H ₄ + C ₂ H ₆ + CH ₄ → M13 + 3H ₂
M14		C ₇ H ₁₄	-18.96±0.43 ¹⁷² ;-19.91±0.37 ¹⁵⁵	-19.4	C ₂ H ₄ + 2C ₂ H ₆ + CH ₄ → M14 + 3H ₂
M15		C ₇ H ₁₄	-36.99±0.25 ¹⁷³ ;-38.22 ¹⁷⁴	-37.6	C ₂ H ₄ + 2C ₂ H ₆ + CH ₄ → M15 + 3H ₂
M16		C ₈ H ₈	71.13±0.31 ¹⁷⁵ ; 71.13±0.31 ¹⁷⁶	71.13	3C ₂ H ₄ + C ₂ H ₂ → M16 + 3H ₂
M17		C ₈ H ₈	35.11±0.24 ¹⁷⁷ ; 35.47±0.46 ¹⁵⁵	35.3	3C ₂ H ₄ + C ₂ H ₂ → M17 + 3H ₂
M18		C ₈ H ₁₀	7.15±0.40 ¹⁵⁵ ;7.12±0.20 ¹⁷⁸	7.1	4C ₂ H ₄ → M18 + 3H ₂
M19		C ₈ H ₁₀	5.38±0.48 ¹⁵⁵ ;4.54±0.26 ¹⁷⁸	5.0	4C ₂ H ₄ → M19 + 3H ₂
M20		C ₈ H ₁₀	37.7±0.2 ¹⁶⁰ ;38.0±1.5 ¹⁷⁹	37.9	4C ₂ H ₄ → M20 + 3H ₂
M21		C ₈ H ₁₂	6.3 ¹⁸⁰ ;4.88±0.19 ¹⁸¹	5.6	3C ₂ H ₄ + C ₂ H ₆ → M21 + 3H ₂

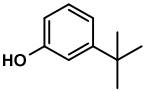
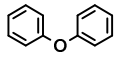
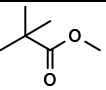
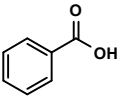
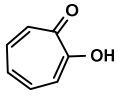
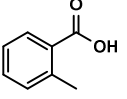
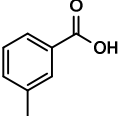
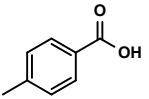
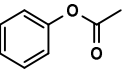
M22		C ₈ H ₁₂	24.16±0.32 ¹⁸²	24.2	3C ₂ H ₄ + C ₂ H ₆ → M22 + 3H ₂
M23		C ₈ H ₁₄	-23.72±0.30 ¹⁷⁰ ; -23.67±0.23 ¹⁸¹	-23.7	2C ₂ H ₄ + 2C ₂ H ₆ → M23 + 3H ₂
M24		C ₈ H ₁₆	-23.95±0.33 ¹⁵⁵ ; -26.55±0.36 ¹⁷²	-25.3	C ₂ H ₄ + 3C ₂ H ₆ → M24 + 3H ₂
M25		C ₈ H ₁₆	-41.25 ¹⁸³ ; -41.05±0.37 ¹⁷³	-41.2	C ₂ H ₄ + 3C ₂ H ₆ → M25 + 3H ₂
M26		C ₉ H ₈	39.08±0.43 ¹⁸⁴ ; 38.53±0.55 ¹⁴⁴	39.03±0.62 ¹⁵⁵ ; 38.9	2C ₂ H ₂ + 2C ₂ H ₄ + CH ₄ → M26 + 4H ₂
M27		C ₉ H ₁₀	14.55±0.55 ¹⁸⁴ ; 14.6±0.5 ¹⁴⁴ ; 14.5±0.4 ¹⁸⁵	14.6	3C ₂ H ₄ + C ₂ H ₂ + CH ₄ → M27 + 4H ₂
M28		C ₉ H ₁₀	36.02±0.24 ¹⁸⁶ ; 35.9±0.2 ¹⁸⁷	36.0	3C ₂ H ₄ + C ₂ H ₂ + CH ₄ → M28 + 4H ₂
M29		C ₁₀ H ₈	73.53±0.82 ¹⁸⁸ ; 73.5 ¹⁵⁷	73.5	3C ₂ H ₄ + 2C ₂ H ₂ → M29 + 4H ₂
M30		C ₁₀ H ₈	36.08±0.30 ¹⁸⁹ ; 35.99±0.26 ¹⁹⁰ ; 38.26 ¹⁹¹ ; 36.25±0.45 ¹⁹²	36.6	3C ₂ H ₄ + 2C ₂ H ₂ → M30 + 4H ₂
M31		C ₁₀ H ₁₂	7.13±1.25 ¹⁹³ ; 7.17 ¹⁹⁴	7.2	5C ₂ H ₄ → M31 + 4H ₂
M32		C ₁₀ H ₁₄	-8.61±0.34 ¹⁹⁵ ; -8.99±0.29 ¹⁹⁶	-8.8	4C ₂ H ₄ + C ₂ H ₆ → M32 + 4H ₂

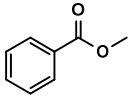
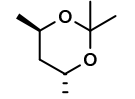
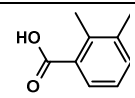
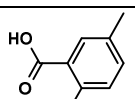
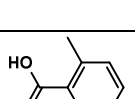
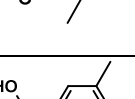
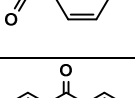
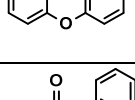
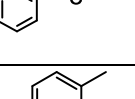
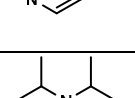
M33		C ₁₀ H ₁₄	-10.33 ± 0.30 ¹⁹⁵ ; -10.6 ± 0.30 ¹⁹⁶ ; -11.1 ± 0.72 ¹⁴⁶	-10.7	4C ₂ H ₄ + C ₂ H ₆ → M33 + 4H ₂
M34		C ₁₀ H ₁₄	-10.8 ¹⁹⁶ ; -11.3 ± 0.45 ¹⁹⁷ ; -11.21 ± 0.43 ¹⁹⁵	-11.1	4C ₂ H ₄ + C ₂ H ₆ → M34 + 4H ₂
M35		C ₁₀ H ₁₄	25.2 ± 1.0 ¹⁹⁸ ; 25.4 ¹⁹⁹	25.3	4C ₂ H ₄ + C ₂ H ₆ → M35 + 4H ₂
M36		C ₁₀ H ₁₄	25.6 ± 1.0 ¹⁹⁸ ; 25.1 ¹⁹⁹	25.4	4C ₂ H ₄ + C ₂ H ₆ → M36 + 4H ₂
M37		C ₁₀ H ₁₆	-30.8 ± 0.9 ²⁰⁰ ; -32.12 ± 0.56 ²⁰¹ ; -31.93 ± 0.60 ¹⁷⁰	-31.6	3C ₂ H ₄ + 2C ₂ H ₆ → M37 + 4H ₂
M38		C ₁₀ H ₁₈	-43.07 ²⁰² ; -43.54 ± 0.55 ¹⁹²	-43.3	2C ₂ H ₄ + 3C ₂ H ₆ → M38 + 4H ₂
M39		C ₁₀ H ₂₀	-39.9 ²⁰³ ; -39.56 ± 0.64 ¹⁴⁸	-39.7	C ₂ H ₄ + 4C ₂ H ₆ → M39 + 4H ₂
M40		C ₁₁ H ₁₄	-0.38 ± 0.45 ¹⁸⁵ ; -0.45 ± 0.24 ²⁰⁴	-0.4	5C ₂ H ₄ + CH ₄ → M40 + 5H ₂
M41		C ₁₁ H ₁₈	-40.99 ± 0.69 ²⁰⁵ ; -41.04 ± 0.63 ²⁰¹	-41.0	3C ₂ H ₄ + 2C ₂ H ₆ + CH ₄ → M41 + 5H ₂

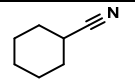
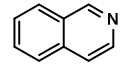
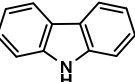
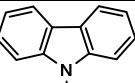
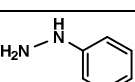
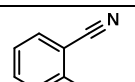
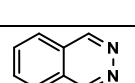
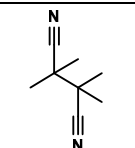
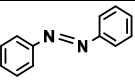
M42		C ₁₁ H ₁₈	-36.34±1.04 ²⁰¹ ; -36.18±0.96 ²⁰⁵	-36.3	3C ₂ H ₄ + 2C ₂ H ₆ + CH ₄ → M42 + 5H ₂
M43		C ₁₂ H ₈	105.2 ²⁰⁶ ; 99.71±0.45 ¹⁴⁴ ; 100.48±0.46 ²⁰⁷	101.8	3C ₂ H ₄ + 3C ₂ H ₂ → M43 + 5H ₂
M44		C ₁₂ H ₈	62.91±0.88 ¹⁴⁴ ; 63.10 ²⁰⁸ ; 61.7±1.4 ²⁰⁹	62.6	3C ₂ H ₄ + 3C ₂ H ₂ → M44 + 5H ₂
M45		C ₁₂ H ₁₀	43.09±0.79 ¹⁴⁴ ; 43.5±0.2 ²¹⁰ ; 43.29±0.42 ²¹¹ ; 43.52±0.63 ¹⁹⁰ ; 42.73 ²¹²	43.2	2C ₂ H ₂ + 4C ₂ H ₄ → M45 + 5H ₂
M46		C ₁₂ H ₁₀	37.48 ± 0.74 ¹⁴⁴ ; 37.4±0.9 ²⁰⁹	37.4	4C ₂ H ₄ + 2C ₂ H ₂ → M46 + 5H ₂
M47		C ₁₂ H ₁₂	26.00 ± 0.72 ²¹³ ; 25.96 ²¹⁴	26.0	5C ₂ H ₄ + C ₂ H ₂ → M47 + 5H ₂
M48		C ₁₂ H ₁₂	18.2 ± 0.48 ²¹⁵ ; 19.1 ²¹⁴	18.7	5C ₂ H ₄ + C ₂ H ₂ → M48 + 5H ₂
M49		C ₁₂ H ₁₄	65.97 ¹⁶⁰ ; 66.11 ²¹⁶	66.0	6C ₂ H ₄ → M49 + 5H ₂
M50		C ₁₂ H ₁₆	-3.39 ¹⁹⁴ ; -3.98±0.35 ²¹¹	-3.7	5C ₂ H ₄ + C ₂ H ₆ → M50 + 5H ₂
M51		C ₁₂ H ₁₈	-18.5 ± 0.60 ¹⁹⁷ ; -18.7 ²¹⁷	-18.6	4C ₂ H ₄ + 2C ₂ H ₆ → M51 + 5H ₂
M52		C ₁₂ H ₂₂	-51.46 ¹⁹⁴ ; -52.19±0.74 ²¹¹	-51.8	2C ₂ H ₄ + 4C ₂ H ₆ → M52 + 5H ₂
M53		C ₁₃ H ₁₂	38.79±0.55 ¹⁴⁴ ; 39.39±0.38 ²¹⁸ ; 37.43 ²¹⁹	38.5	2C ₂ H ₂ + 4C ₂ H ₄ + CH ₄ → M53 + 6H ₂

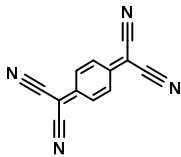
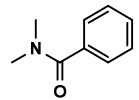
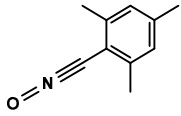
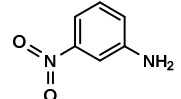
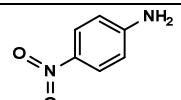
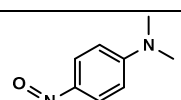
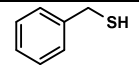
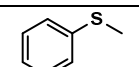
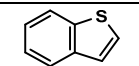
M54		C ₁₄ H ₁₀	52.96 ²²⁰ ; 54.83±0.69 ¹⁴⁴ ;54.28 ¹⁹¹ ;55.2±1.1 ¹⁹⁰ ;	54.3	4C ₂ H ₄ + 3C ₂ H ₂ → M54 + 6H ₂
M55		C ₁₄ H ₁₀	50.67±0.77; 48.33±0.55 ¹⁴⁴ ;49.5±1.1 ¹⁹⁰ ; 48.71 ²²⁰	49.3	4C ₂ H ₄ + 3C ₂ H ₂ → M55 + 6H ₂
M56		C ₁₄ H ₁₄	32.41±0.31 ¹⁹⁰ ; 30.83 ²¹⁷ ; 34.16±0.31 ²²¹	32.5	6C ₂ H ₄ + C ₂ H ₂ → M56 + 6H ₂
M57		C ₁₄ H ₂₄	-67.42±1.67 ²⁰⁵ ; -68.0±1.7 ²⁰¹	-67.7	4C ₂ H ₆ + 3C ₂ H ₄ → M57 + 6H ₂
M58		C ₁₆ H ₁₀	69.78±0.52 ²⁰⁹ ; 69.65±0.96 ¹⁴⁴ ; 69.26 ²²²	69.6	4C ₂ H ₄ + 4C ₂ H ₂ → M58 + 7H ₂
M59		C ₁₆ H ₁₀	53.94±0.29 ²²³ ; 53.90±0.60 ¹⁴⁴	53.9	4C ₂ H ₄ + 4C ₂ H ₂ → M59 + 7H ₂
M60		C ₁₆ H ₁₆	58.48±0.50 ²²⁴ ; 57.6±1.0 ²²⁵ ; 57.7±1.0 ²²⁶	57.9	7C ₂ H ₄ + C ₂ H ₂ → M60 + 7H ₂
M61		C ₁₈ H ₁₂	66.51±1.01 ²²⁷ ; 64.6±1.1 ¹⁴⁴	65.6	5C ₂ H ₄ + 4C ₂ H ₂ → M61 + 8H ₂
M62		C ₁₈ H ₁₂	66.03±1.09 ²²⁷ ; 64.2±1.1 ¹⁴⁴	65.1	5C ₂ H ₄ + 4C ₂ H ₂ → M62 + 8H ₂
M63		C ₁₈ H ₁₂	70.30±0.92 ²²⁷ ; 69.4±1.4 ¹⁴⁴	69.9	5C ₂ H ₄ + 4C ₂ H ₂ → M63 + 8H ₂
M64		C ₂₀ H ₁₆	45.20 ²²⁸ ; 45.1±0.8 ²²⁹	45.2	7C ₂ H ₄ + 3C ₂ H ₂ → M64 + 9H ₂

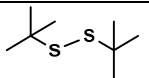
M65		C ₆ H ₁₀ O	-53.23±0.51 ¹⁵⁸ ; -53.94 ²³⁰ ; -54.43±0.45 ²³¹	-53.9	C ₂ H ₆ + 2C ₂ H ₄ + H ₂ O → M65 + 3H ₂
M66		C ₆ H ₁₂ O	-66.51±0.22 ²³² ; -66.50±0.21 ²³³	-66.5	2C ₂ H ₆ + C ₂ H ₄ + H ₂ O → M66 + 3H ₂
M67		C ₆ H ₁₄ O	-76.20±0.45 ²³⁴ ; -76.1±0.6 ²³⁵	-76.2	3C ₂ H ₆ + H ₂ O → M67 + 3H ₂
M68		C ₇ H ₆ O	-8.90±0.22 ²³⁶ ; -8.80±0.72 ²³⁷ ; -7.95 ²³⁸ ; -8.9±1.0 ²³⁹	-8.6	3C ₂ H ₄ + CO → M68 + 3H ₂
M69		C ₇ H ₈ O	-16.24±0.29 ²⁴⁰ ; -16.9 ²⁴¹ ; -18.33±0.22 ²³⁶ ; -17.9 ²⁴²	-17.3	C ₂ H ₆ + 2C ₂ H ₄ + CO → M69 + 3H ₂
M70		C ₈ H ₁₀ O	-24.28±0.28 ²⁴⁰ ; -25.91 ²⁴²	-25.1	4C ₂ H ₄ + H ₂ O → M70 + 4H ₂
M71		C ₈ H ₁₂ O	-52.2 ± 2.0 ²⁴³ ; -53.1 ± 1.3 ²⁴⁴	-52.7	C ₂ H ₆ + 3C ₂ H ₄ + H ₂ O → M71 + 4H ₂
M72		C ₈ H ₁₆ O	-80.86±0.30 ²⁴⁵	-80.9	3C ₂ H ₆ + C ₂ H ₄ + H ₂ O → M72 + 4H ₂
M73		C ₉ H ₁₀ O	-22.62 ²⁴⁶	-22.6	3C ₂ H ₄ + C ₂ H ₆ + CO → M73 + 4H ₂
M74		C ₁₀ H ₈ O	-7.14±0.25 ²⁴⁷ ; -7.36±0.38 ²⁴⁸	-7.3	3C ₂ H ₄ + 2C ₂ H ₂ + H ₂ O → M74 + 5H ₂
M75		C ₁₀ H ₈ O	-7.18±0.27 ²⁴⁷ ; -7.15±0.41 ²⁴⁸	-7.2	3C ₂ H ₄ + 2C ₂ H ₂ + H ₂ O → M75 + 5H ₂

M76		C ₁₀ H ₁₄ O	-44.26 ²⁴⁹ , -44.0 ²⁵⁰	-44.1	4C ₂ H ₄ + C ₂ H ₆ + H ₂ O → M76 + 5H ₂	
M77		C ₁₂ H ₁₀ O	12.43±0.37 ²²¹	12.4	4C ₂ H ₄ + 2C ₂ H ₂ + H ₂ O → M77 + 6H ₂	
M78		C ₆ H ₁₂ O ₂	-117.48±0.42 ²³⁴ , 122.8±1.8 ²⁵²	-118.16 ²⁵¹ , -	-119.5	2C ₂ H ₆ + C ₂ H ₄ + 2H ₂ O → M78 + 4H ₂
M79		C ₇ H ₆ O ₂	-69.48±0.14 ²⁵³ , 70.67±0.14 ²²¹	-70.22±0.17 ²⁵⁴ , -	-70.1	3C ₂ H ₄ + CO + H ₂ O → M79 + 4H ₂
M80		C ₇ H ₆ O ₂	-37.1 ²⁵⁵ , -37.2±0.3 ²⁵⁶ , -37.09±0.35 ²⁵⁷	-37.1	3C ₂ H ₄ + CO + H ₂ O → M80 + 4H ₂	
M81		C ₈ H ₈ O ₂	-76.63 ± 0.36 ²⁵⁸ , -76.63 ²⁵⁹	-76.6	3C ₂ H ₄ + CO + CH ₄ + H ₂ O → M81 + 5H ₂	
M82		C ₈ H ₈ O ₂	-78.37 ± 0.33 ²⁵⁸ , -78.66 ²⁵⁹	-78.5	3C ₂ H ₄ + CO + CH ₄ + H ₂ O → M82 + 5H ₂	
M83		C ₈ H ₈ O ₂	-77.56 ²⁶⁰ , -78.97±0.36 ²⁵⁸ , -78.97 ²⁵⁹	-78.5	3C ₂ H ₄ + CO + CH ₄ + H ₂ O → M83 + 5H ₂	
M84		C ₈ H ₈ O ₂	-66.84±0.29 ²³⁶ , -67.0±0.5 ²⁶¹	-66.9	3C ₂ H ₄ + CO + CH ₄ + H ₂ O → M84 + 5H ₂	

M85		C ₈ H ₈ O ₂	-64.4±1.2 ²⁶²	-64.4	3C ₂ H ₄ + CO + CH ₄ + H ₂ O → M85 + 5H ₂
M86		C ₈ H ₁₆ O ₂	-115.8 ± 1.2 ²⁶³ ; -116.0± 0.8 ²⁶⁴	-115.9	3C ₂ H ₆ + C ₂ H ₄ + 2H ₂ O → M86 + 5H ₂
M87		C ₉ H ₁₀ O ₂	-82.65 ± 0.41 ²⁶⁵ ; -82.65 ²⁵⁹	-82.7	3C ₂ H ₄ + CO + C ₂ H ₆ + H ₂ O → M87 + 5H ₂
M88		C ₉ H ₁₀ O ₂	-83.91 ± 0.41 ²⁶⁵ ; -83.91 ²⁵⁹	-83.9	3C ₂ H ₄ + CO + C ₂ H ₆ + H ₂ O → M88 + 5H ₂
M89		C ₉ H ₁₀ O ₂	-81.64 ± 0.41 ²⁶⁵ ; -81.64 ²⁵⁹	-81.6	3C ₂ H ₄ + CO + C ₂ H ₆ + H ₂ O → M89 + 5H ₂
M90		C ₉ H ₁₀ O ₂	-86.62 ± 0.41 ²⁶⁵ ; -86.62 ²⁵⁹	-86.6	3C ₂ H ₄ + CO + C ₂ H ₆ + H ₂ O → M90 + 5H ₂
M91		C ₁₃ H ₈ O ₂	-22.2 ²⁶⁶ ; -23.5± 0.86 ²⁶⁷	-22.9	4C ₂ H ₄ + 2C ₂ H ₂ + CO + H ₂ O → M91 + 7H ₂
M92		C ₁₃ H ₁₀ O ₂	-34.09±0.52 ²⁶⁸ ; -36.3±1.1 ²⁶⁹	-35.2	5C ₂ H ₄ + C ₂ H ₂ + CO + H ₂ O → M92 + 7H ₂
M93		C ₆ H ₇ N	24.98±0.23 ²⁷⁰ ; 24.80±0.22 ²⁷¹ ; 24.41±0.15 ²⁷⁰ ; 24.43±0.15 ²⁷²	24.7	2C ₂ H ₄ + C ₂ H ₂ + NH ₃ → M93 + 3H ₂
M94		C ₆ H ₁₅ N	-32.58±0.62 ²⁷³ ; -34.35 ²⁷⁴ ;	-33.5	3C ₂ H ₆ + NH ₃ → M94 + 3H ₂

M95		C ₇ H ₁₁ N	1.14±0.16 ²⁷⁵ ; -1.73 ²⁷⁶ ; -0.85 ²⁵¹	-0.5	2C ₂ H ₆ + C ₂ H ₄ + HCN → M95 + 3H ₂
M96		C ₉ H ₇ N	48.903 ²⁷⁷ ; 48.76 ²⁷¹	48.8	3C ₂ H ₄ + C ₂ H ₂ + HCN → M96 + 4H ₂
M97		C ₁₂ H ₉ N	53.27 ²⁷⁸ ; 49.00±0.72 ²⁷⁹ ; 50.10±0.84 ²⁸⁰	50.8	3C ₂ H ₄ + 3C ₂ H ₂ + NH ₃ → M97 + 6H ₂
M98		C ₁₃ H ₁₁ N	48.04 ²⁷¹ ; 47.6±0.1 ²⁸¹ ; 47.61±0.57 ²⁷⁹	47.8	3C ₂ H ₄ + 3C ₂ H ₂ + CH ₄ + NH ₃ → M98 + 7H ₂
M99		C ₆ H ₈ N ₂	48.9±3.0 ²⁸² ; 48.78 ²⁸³	48.8	2C ₂ H ₄ + C ₂ H ₂ + 2NH ₃ → M99 + 4H ₂
M100		C ₈ H ₄ N ₂	88.03 ²⁸⁴ ; 87.83±0.45 ²⁸⁵ ; 86.52 ²⁸⁶	87.5	2C ₂ H ₄ + C ₂ H ₂ + 2HCN → M100 + 4H ₂
M101		C ₈ H ₆ N ₂	82.5 ± 4.3 ²⁸⁷	82.5	3C ₂ H ₄ + 2HCN → M101 + 4H ₂
M102		C ₈ H ₁₂ N ₂	24.05 ²⁸⁸ ; 24.2±0.4 ²⁸⁹	24.1	3C ₂ H ₆ + 2HCN → M102 + 4H ₂
M103		C ₁₂ H ₁₀ N ₂	98.85 ²⁸³ ; 96.92±0.31 ¹⁶⁷ ; 96.13±0.65 ²⁹⁰ ; 96.51 ²⁹¹ ; 98.14 ²⁹²	97.3	5C ₂ H ₄ + C ₂ H ₂ + N ₂ → M103 + 6H ₂

M104		$C_{12}H_4N_4$	184.3^{191} ; 184.0 ± 2.5^{293}	184.2	$3C_2H_4 + C_2H_2 + 4HCN \rightarrow M104 + 7H_2$
M105		$C_9H_{11}NO$	-19.9 ± 2.1^{294} ; -20.60 ± 0.53^{295}	-20.3	$3C_2H_4 + C_2H_6 + CO + NH_3 \rightarrow M105 + 5H_2$
M106		$C_{10}H_{11}NO$	32.74 ± 0.96^{296} ; 31.88 ± 0.96^{297}	32.3	$4C_2H_4 + H_2O + HCN + CH_4 \rightarrow M106 + 6H_2$
M107		$C_6H_6N_2O_2$	14.9 ± 0.43 ; 14.15 ± 1.01	14.5	$C_2H_4 + 2C_2H_2 + 2H_2O + 2NH_3 \rightarrow M107 + 6H_2$
M108		$C_6H_6N_2O_2$	16.06 ± 1.02^{298} ; 13.2 ± 0.4^{299}	14.6	$C_2H_4 + 2C_2H_2 + 2H_2O + 2NH_3 \rightarrow M108 + 6H_2$
M109		$C_8H_{10}N_2O_2$	16.1 ± 0.41^{300} ; 15.0 ± 0.62^{301}	15.6	$3C_2H_4 + C_2H_2 + 2H_2O + 2NH_3 \rightarrow M109 + 7H_2$
M110		C_7H_8S	22.26 ± 0.27^{302} ; 20.96 ± 0.48^{303}	21.6	$2C_2H_4 + C_2H_2 + CH_4 + H_2S \rightarrow M110 + 4H_2$
M111		C_7H_8S	23.25 ± 0.20^{302} ; 23.5 ± 0.7^{303}	23.4	$2C_2H_4 + C_2H_2 + CH_4 + H_2S \rightarrow M111 + 4H_2$
M112		C_8H_6S	39.82^{302} ; 39.74 ± 0.11^{304}	39.8	$2C_2H_4 + 2C_2H_2 + H_2S \rightarrow M112 + 4H_2$

M113		$C_8H_{18}S_2$	-47.8^{305} ; -47.75 ± 0.54^{302} ; -48.29 ± 0.54^{306}	-47.9	$4C_2H_6 + 2H_2S \rightarrow M113 + 5H_2$
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2.4 Calculation of Errors

To gauge the deviation of the theoretical heats of formation from their experimental counterparts, we used the two common protocols based on the mean unsigned error ($MUE = |\Delta H_f(\text{Exp.}) - \Delta H_f(\text{Theo.})|$) and the mean signed error ($MSE = \Delta H_f(\text{Exp.}) - \Delta H_f(\text{Theo.})$). Simultaneous analysis of both MUE and MSE is necessary to make a conclusion on ability of the method to provide absolute formation enthalpies. Clearly, if both MUE and MSE approach to zero, then the method can be recommended for absolute values and thus predictions. This is the best scenario. If MUE is large and MSE is equally large (either positive or negative) then the method cannot be recommended for estimation of absolute formation enthalpies. However, it still can be used for predictions, since in some instances trends are more important than absolute values. Finally, the worst scenario is large MUE and vanishing MSE, rendering the method unacceptable for accurate heats of formation or for the relative values.

3. Results and Discussion

The results and discussion section is organized as follows. First, we assess the ability of the examined DFT methods to reproduce the experimental formation enthalpies. Then, we proceed to the performance of the double hybrid and spin component scaled (SCS) MP2 methods, namely SCS-MP2 and OO-SCS-MP2. Next, the formation enthalpies from the recently developed DLPNO-CCSD(T) methods are discussed. Finally, we discuss the results obtained for large systems with group additivity methods.³⁰⁷ The practical recommendations on the applicability of

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3 these methods to derive accurate formation enthalpies and reaction energies of the medium-size
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5 organic molecules will be listed.
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8 9 **3.1 DFT Methods**

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12 Mean unsigned (MUE) and mean signed (MSE) errors obtained for the 113 formation enthalpies
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14 of medium-size organic molecules with the DFT methods are given in Figure 1. The worst
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16 performer with a MUE of 14.1 kcal/mol turned out to be the PBE0-D3 functional. The large and
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18 positive MSE of 13.6 kcal/mol indicates a systematic tendency of PBE0-D3 towards
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20 underestimation of the reaction enthalpies given in Table 1 and of the corresponding heats of
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22 formation. To explore the influence of the empirical dispersion correction on the quality of the
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24 formation enthalpies, we also performed the calculation with the parent PBE0 functional and we
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26 found that the MUE and the MSE decrease by 5.0 and 7.6 kcal/mol, indicating a clear
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28 improvement over the dispersion-corrected counterpart. An analysis of the individual reaction
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30 enthalpies given in Table 1 indicates a tendency of the PBE0 functional to underestimate the
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32 reaction enthalpies, which leads to too low formation enthalpies. The dispersion correction
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34 merely enforces this tendency as the largest molecular species, for which contribution from the
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36 dispersion correction is largest, are in the right hand side in the chemical equations. Similar
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38 conclusions were obtained by Martin and co-workers when studying the thermochemistry of
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40 C_nH_{2n+2} alkane isomers.³⁰⁸ These findings indicate that an application of the dispersion
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42 correction on the PBE0 functional might result in significantly worse performance, at least in
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44 some applications.³⁰⁸
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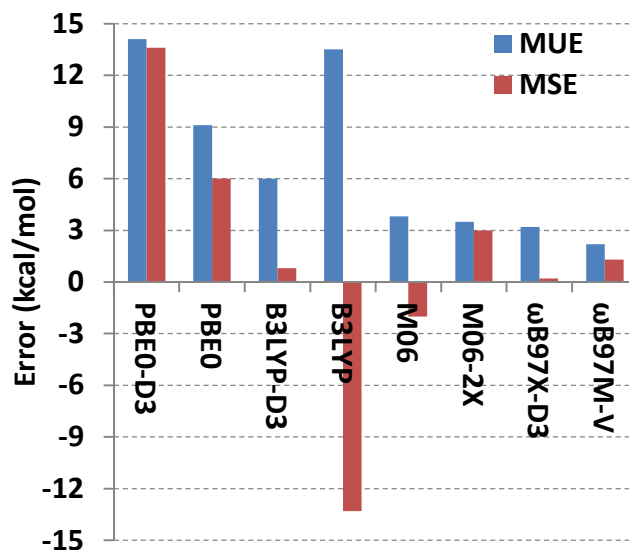


Figure 1. Mean unsigned (MUE) and mean signed (MSE) errors with respect to 113 experimental formation enthalpies obtained with PBE0-D3, PBE0, B3LYP-D3, B3LYP, M06, M06-2X, ω B97XD-D3 and ω B97M-V methods.

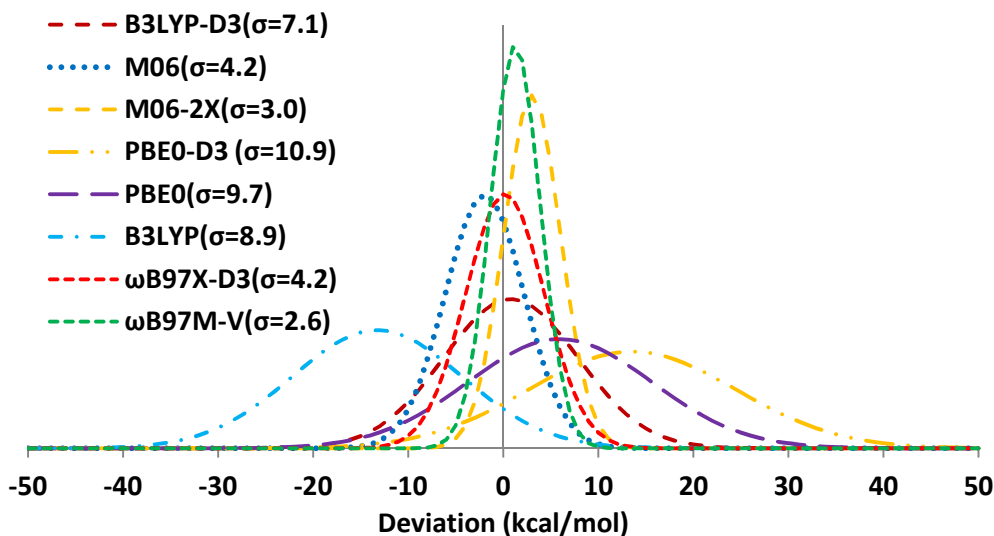
On the contrary, for the B3LYP-D3 functional significantly smaller MUE and MSE of 6.0 and 0.8 kcal/mol have been obtained, while the dispersion free B3LYP calculations result in significantly larger errors, leading to a MUE and MSE of 13.5 kcal/mol and -13.3 kcal/mol. This highlights the importance of including dispersion interaction with the B3LYP functional. Merging together the results obtained for the B3LYP and PBE0 methods with and without an empirical dispersion correction suggests that the influence of an empirical dispersion term on the performance of the parent functionals, which became *de facto* the standard approach in DFT methods, has always to be verified. Interestingly, we reached similar observations in our previous work³⁰⁹ on the performance of the contemporary electronic structure methods in reproducing a set of 111 gas phase reactions of 11 transition metals. A clear improvement is shown upon adding the dispersion correction for the B3LYP method, with the MUE improving

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2
3 by 2.2 kcal/mol. However, for the PBE0 method (and also for M06, M06L, PBE, TPSS, TPSSh)
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5 the MUE was practically unaffected by the dispersion correction. Second, due to the large
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7 MUE/MSE documented for PBE0-D3, PBE0, B3LYP-D3, and B3LYP methods, none of them
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9 are recommended for the prediction of the heats of formation and, consequently, for accurate
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11 thermochemistry of organic reactions, in general. Finally, we would like to highlight the
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13 improved performance of the PBE0 method compared to that of the B3LYP method. This is
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15 quite remarkable, as the former contains no empirical parameters at all, while the latter was
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17 parameterized specifically to reproduce the atomization energies (derived from the heats of
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19 formations) of compounds consisting from the elements of the first three periods of the Periodic
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21 System.
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28 The two Minnesota functionals tested, M06 and M06-2X, have similar MUE, 3.8 and 3.5
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30 kcal/mol. While the M06 method with an MSE of -2.0 kcal/mol tends to overestimate the
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32 reaction enthalpies in Table 1 and the corresponding heats of formation, the M06-2X has a
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34 tendency toward underestimation, with an MSE of 3.0 kcal/mol. For the ω B97X-D3 functional
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36 the MUE and MSE of 3.2 and 0.2 kcal/mol have been found. Finally, the best functional turned
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38 out to be the ω B97M-V with the MUE and MSE of only 2.2 and 1.3 kcal/mol. We recommend
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40 this functional to quantify the thermochemistry of organic reactions when the DLPNO-
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42 CCSD(T)-based ab initio methods listed in Section 3.3 are not applicable.
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48 Kolmogorov-Smirnov test of the errors in reaction enthalpies produced by the standard
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50 functionals PBE0, PBE0-D3, B3LYP, B3LYP-D3 and their modern analogues, M06, M06-2X,
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52 ω B97X-D3 and ω B97M-V has indicated that these can be described by normal distributions. The
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54 normal distributions of errors obtained for all the tested functionals is depicted in Figure 2. The
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3 histograms of raw errors for all the functionals together with the values of Kolmogorov-Smirnov
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5 test, skewness and kurtosis are given in the Figures S1 – S8 in the Supporting Information (SI).
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32 **Figure 2.** Normal distributions of the errors with respect to 113 experimental formation
33 enthalpies obtained with PBE0-D3, PBE0, M06, M06-2X, B3LYP-D3, B3LYP, ω B97XD-D3
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35 and ω B97M-V methods.
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40 An analysis of Figure 2 reveals that all the standard functionals, such as PBE0 and B3LYP with
41 or without an empirical dispersion term, clearly result in wider distributions compared to
42 contemporary DFT functionals developed relatively recently, such as M06, M06-2X, ω B97XD-
43 D3 and ω B97M-V. Indeed, the “classical” DFT functionals with standard deviations (σ) of 10.9
44 kcal/mol (PBE0-D3), 9.7 kcal/mol (PBE0), 8.9 kcal/mol (B3LYP), 7.1 kcal/mol (B3LYP-D3)
45 are remarkably higher those for M06 ($\sigma = 4.2$ kcal/mol), M06-2X ($\sigma = 3.0$ kcal/mol), ω B97XD-
46 D3 ($\sigma = 4.2$ kcal/mol) and ω B97M-V ($\sigma = 2.6$ kcal/mol). All these observations indicate the clear
47 progress in the development of functionals made since mid. 90s.
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3.2 Double Hybrids and MP2

The double hybrid methods, essentially combining a hybrid DFT calculation with a subsequent MP2 step using the DFT orbitals, have first been introduced by Grimme in 2006⁸⁰ following a general framework of application of many-body perturbation theory on Kohn-Sham orbitals pioneered by Görling and Levy in 1994,³¹⁰ and Truhlar and co-workers in 2004.³¹¹ These methods are, in general, claimed to outperform the density functional theory methods in reaction energies.^{83,312} Therefore, we decided to include these methods in our study and compare their performance with the DFT methods introduced in Section 3.1. MUE and MSE errors obtained for the 113 formation enthalpies of medium-size organic molecules with the double hybrid (B2PLYP-D3, PWPB95-D3, B2T-PLYP, B2T-PLYP-D, B2GP-PLYP-D3 and DSD-PBEP86-D3), SCS-MP2/00-SCS-MP2 and G3(MP2) methods are presented in Figure 3.

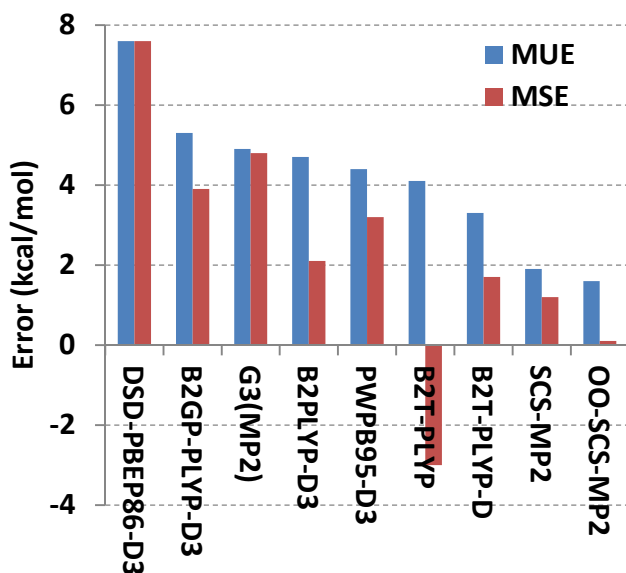


Figure 3. Mean unsigned (MUE) and mean signed (MSE) errors with respect to 113 experimental formation enthalpies obtained with B2PLYP-D3, PWPB95-D3, B2T-PLYP, B2T-

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3 PLYP-D, B2GP-PLYP-D3, DSD-PBEP86-D3, SCS-MP2, OO-SCS-MP2 and G3(MP2)
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5 methods.
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9 For the B2PLYP-D3 and PWPB95-D3 methods, similar MUEs of 4.7 and 4.3 kcal/mol have
10 been obtained. Both methods tend to underestimate the heats of formation and the reaction
11 energies given in Table 1, providing MSEs of 2.0 and 3.2 kcal/mol, respectively. The B2T-PLYP
12 method, designed to reproduce the thermochemistry of the main group elements, resulted in an
13 MUE and MSE of 4.1 and -3.0 kcal/mol, respectively. The D2 dispersion correction improves
14 further on the B2T-PLYP performance leading to MUE and MSE of 3.3 and 1.7 kcal/mol for the
15 B2T-PLYP-D method. The B2GP-PLYP-D3 and DSD-PBEP86-D3 methods of Martin and co-
16 workers both resulted in larger errors. Thus, MUE and MSE for B2GP-PLYP-D3 method turned
17 out to be 5.3 and 3.9 kcal/mol, and MUE and MSE for DSD-PBEP86 are even higher and both
18 equal to 7.6 kcal/mol. The slightly worse performance of B2GP-PLYP-D3 and DSD-PBEP86-
19 D3 comparing to that of B2P-LYP has also been observed recently³¹³ when analyzing
20 performance in ca. reaction 11000 energies generated from W4-11 database.³¹⁴ Comparison of
21 the results plotted in Figures 1 and 3 indicates that all the double hybrid methods outperform the
22 B3LYP and PBE0 methods with or without dispersion correction. However, the other DFT
23 methods tested, such as the M06, M06-2X, and especially the ω B97XD-D3 and ω B97M-V
24 functionals, resulted in smaller errors compared to the double hybrids at somewhat smaller
25 computational costs.
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Apart from the double hybrids, we also tested the spin-component scaled MP2 (SCS-MP2) method. In addition to the standard version,⁸⁵ the orbital optimized version thereof (OO-SCS-MP2)⁸⁶ was also included in the comparison. Both methods outperformed all the DFT and the double-hybrid methods tested, providing a MUE of 1.9 and 1.6 kcal/mol for SCS-MP2 and OO-

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3 SCS-MP2, respectively. While the SCS-MP2 method with the MSE of 1.2 tends to underestimate
4 the formation enthalpies, the orbital optimized version results in a vanishing MSE of 0.1
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6 kcal/mol. Finally, in addition we tested the G3(MP2) composite method, as this is often the
7
8 method of choice for the systems of this size. The MUE from G3(MP2) method is 4.9 kcal/mol
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10 which is comparable to performance of the double-hybrids tested in this study. The MSE turned
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12 out to be positive and only 0.1 kcal/mol smaller than MUE highlighting the tendency of
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14 G3(MP2) method to underestimate the enthalpies of the reactions in Table 1.
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21 Kolmogorov-Smirnov test of the errors in reaction enthalpies produced by tested double hybrid,
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23 G3(MP2) and (OO-)SCS-MP2 methods has revealed that errors from most of the methods can be
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25 described by normal distributions and these are given in Figure 4. The only exception turned out
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27 to be B2T-PLYP. The histograms of raw errors for B2T-PLYP and all other MP2-based methods
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29 together with the values of Kolmogorov-Smirnov test, skewness and kurtosis are given in the
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31 Figures S9 – S17 in the Supporting Information (SI). An analysis of Figure 4 indicates that the
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33 double hybrid methods provide significantly wider error distribution and result in large standard
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35 deviation (σ) values: the largest σ of 5.2 kcal/mol has been obtained for B2GP-PLYP-D3
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37 method and the lowest σ value of 3.5 kcal/mol has been obtained for B2T-PLYP-D method. In
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39 contrast, the SCS-MP2 methods result in narrower error distributions and significantly smaller
40
41 standard deviation values: σ (SCS-MP2) is 2.2 kcal/mol, and σ (OO-SCS-MP2) is 2.0 kcal/mol.
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43 The G3(MP2) method resulted in moderate σ value of 2.6 kcal/mol. Based on these results we
44
45 recommend the SCS-MP2 methods, in particular the OO-SCS-MP2 variant, for accurate
46
47 thermodynamic calculations involving organic molecules of medium size, when the more
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49 expensive DLPNO-CCSD(T) methods discussed below are not affordable.
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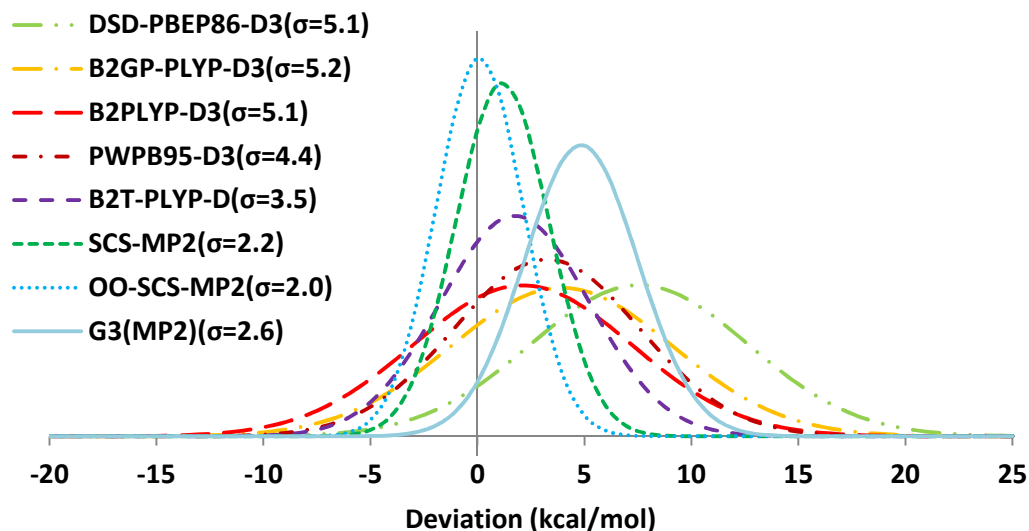


Figure 4. Normal distributions of the errors with respect to 113 experimental formation enthalpies obtained with B2PLYP-D3, PWPB95-D3, B2T-PLYP-D, B2GP-PLYP-D3, DSD-PBEP86-D3, SCS-MP2, OO-SCS-MP2, and G3(MP2) methods.

3.3 DLPNO-CCSD(T)

Mean unsigned (MUE) and mean signed (MSE) errors obtained for the 113 formation enthalpies of medium-size organic molecules with the DLPNO-CCSD(T) method are given in Figure 5.

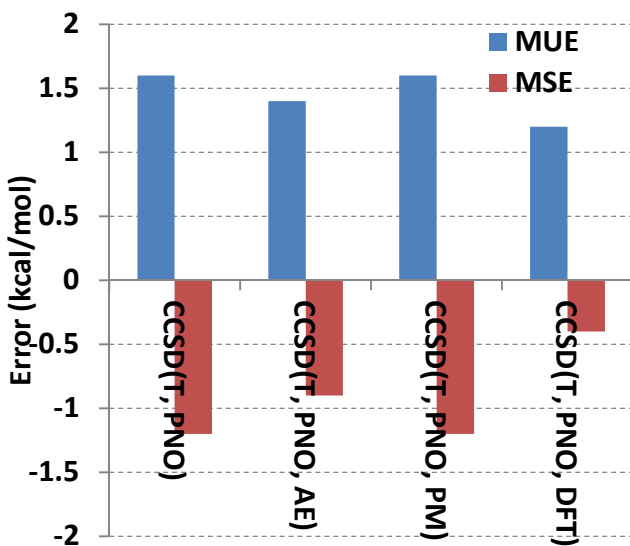


Figure 5. Mean unsigned (MUE) and mean signed (MSE) errors with respect to 113 experimental formation enthalpies obtained with DLPNO-CCSD(T) method. Acronyms used: CCSD(T, PNO) – standard DLPNO-CCSD(T) calculation, CCSD(T, PNO, AE) – DLPNO-CCSD(T) calculation with all electrons included into correlation treatment, CCSD(T, PNO, PM) – standard DLPNO-CCSD(T) calculation with the Pipek-Mezey (PM) scheme to localize the orbitals; CCSD(T, PNO, DFT) – DLPNO-CCSD(T) calculation on the B3LYP orbitals.

The default DLPNO-CCSD(T) calculation results in a MUE of 1.6 kcal/mol, which is equal to what was found for the OO-SCS-MP2 and clearly smaller than that for all other methods tested in the present work. However, comparing to OO-SCS-MP2 method for which the vanishing MSE was found, the -1.2 kcal/mol MSE for the DLPNO-CCSD(T) method indicates systematic overestimation of the heats of formation and reaction energies given in Table 1. To rationalize the origin of this overestimation and to see whether the DLPNO-CCSD(T) performance can be further improved, we carried out additional calculations. First we performed the DLPNO-CCSD(T) calculations with weighted core valence cc-pwCVnZ basis sets and all electrons

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3 included in the correlation treatment, as it was demonstrated that the effects from core –core and
4 the core valence correlation can be large in some cases.^{309,315-321} As a result, the MUE of the
5 DLPNO-CCSD(T) decreased by 0.2 kcal/mol only, although at significantly higher
6 computational costs comparing to the default frozen core calculations. The MSE remained
7 negative and amounts to -0.9 kcal/mol, indicating only limited improvement over the standard
8 frozen core calculation. The tight d core functions which are not the part of the standard cc-pVnZ
9 basis sets have been shown to affect the thermochemistry of Sulfur compounds from CCSD(T)
10 calculations significantly.³²² As these functions are included in cc-pwCVnZ basis sets used for
11 all electron (AE) calculations, comparison of DLPNO-CCSD(T, PNO) and DLPNO-CCSD(T,
12 PNO, AE) heats of formation of M110–M113 compounds should reveal the effects of the tight d
13 functions on the chemical reactions composed for S containing molecules in the present work,
14 see Table 1. The difference between DLPNO-CCSD(T, PNO) and DLPNO-CCSD(T, PNO, AE)
15 formation enthalpies of Sulfur compounds turned out to be only 0.2 kcal/mol indicating the
16 effect of tight d functions to be rather small. This is a consequence of the fact that Sulfur does
17 not change its oxidation state in chemical reactions used to calculate the heats of formation,
18 again highlighting the advantages of using of chemical reactions rather than atomization energies
19 for thermochemistry. The same conclusion on the usefulness of the reaction based-approach can
20 be done by comparing DLPNO-CCSD(T, PNO) and DLPNO-CCSD(T, PNO, AE) formation
21 enthalpies of benzene, which turned out to be 20.2 and 19.8 kcal/mol, correspondingly. Hence,
22 only limited effect of the core-core and core-valence correlation is detected, indicating that
23 significantly more expensive AE calculations might be avoided with only little loss of accuracy.
24 In contrast, the core-valence contribution to heat of formation of benzene through atomization
25 energy based FPD approach was found to be of 7.1 kcal/mol and is definitely non-negligible.⁹⁰
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3 To explore the sensitivity of the enthalpies from the standard DLPNO-CCSD(T) protocol to the
4 localization scheme applied, we also performed additional calculations with the Pipek-Mezey
5 orbital localization procedure (CCSD(T, PNO, PM) in Figure 5), instead of default Foster-Boys
6 scheme. The resulting MUE/MSE values turned out to be identical to the ones from the default
7 DLPNO-CCSD(T) calculation, 1.6/-1.2 kcal/mol. Finally, we performed the DLPNO-CCSD(T)
8 calculations using B3LYP molecular orbitals as reference, see CCSD(T, PNO, DFT) in Figure 5.
9 The MUE was 1.2 kcal/mol, which is the lowest among all the methods tested in the present
10 work, and the MSE as only -0.4 kcal/mol, which is significantly smaller than the MSE of -1.2
11 kcal/mol from the standard DLPNO-CCSD(T) method.
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25 Kolmogorov-Smirnov test of the errors in reaction enthalpies produced by the DLPNO-CCSD(T)
26 methods has revealed that errors from most of the methods cannot be described by normal
27 distributions. Due to these reason we have decided to plot the histograms of raw errors for the
28 DLPNO-CCSD(T) methods. These are given in Figures 6 and 7 together with the values of
29 Kolmogorov-Smirnov test, skewness and kurtosis.
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38 Although the distributions of errors are remarkably similar for the all four variants of DLPNO-
39 CCSD(T) scheme, it can be noted that distribution from the default DLPNO-CCSD(T) method is
40 slightly broader than the others, while a slightly narrower distribution is shown for DLPNO-
41 CCSD(T) calculations using B3LYP molecular orbitals. These observations are confirmed by
42 analysis of the standard deviations: $\sigma = 1.9$ kcal/mol for DLPNO-CCSD(T), $\sigma = 1.8$ kcal/mol for
43 DLPNO-CCSD(T, AE), $\sigma = 1.8$ kcal/mol for DLPNO-CCSD(T, PM), and $\sigma = 1.7$ kcal/mol for
44 DLPNO-CCSD(T, B3LYP). Considering that DFT orbitals often provide better starting orbitals
45 for the CCSD(T) calculation resulting in lower T1 diagnostic value,³²³⁻³²⁴ we recommend the
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DLPNO-CCSD(T) calculation using B3LYP molecular orbitals, DLPNO-CCSD(T, B3LYP) for accurate reaction energies and the heat of formations of medium-size organic molecules.

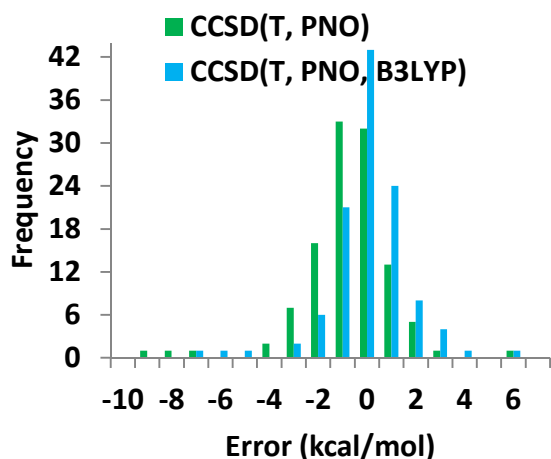


Figure 6. Histogram of errors in 113 formation enthalpies obtained for the standard frozen core DLPNO-CCSD(T) method (CCSD(T, PNO)) and its counterpart on B3LYP orbitals (CCSD(T, PNO, B3LYP)). For CCSD(T, PNO) method: the mean is -1.2 kcal/mol, standard deviation (σ) is 1.9 kcal/mol, skewness is -1.158, kurtosis is 6.330. Kolmogorov-Smirnov normality test: $D = 0.143$, p -value = 0.017. For CCSD(T, PNO, B3LYP) method: the mean is -0.4 kcal/mol, standard deviation (σ) is 1.7 kcal/mol, skewness is -0.773, kurtosis is 5.437. Kolmogorov-Smirnov normality test: $D = 0.116$, p -value = 0.087.

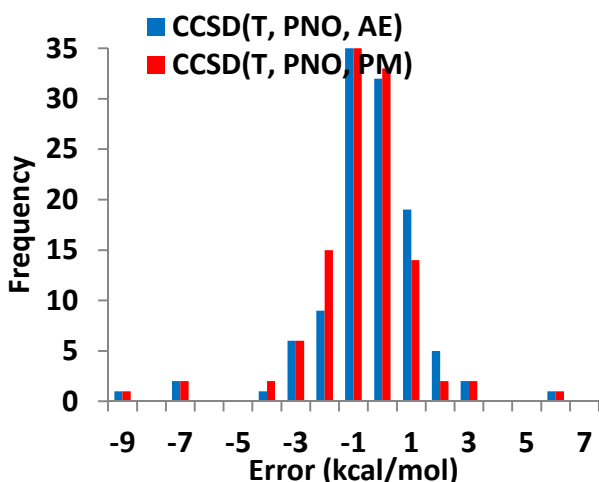


Figure 7. Histogram of errors in 113 formation enthalpies obtained for the all electron DLPNO-CCSD(T) method (CCSD(T, PNO, AE)) and its standard frozen core counterpart on orbitals localized with Pipek-Mezey (PM) scheme (CCSD(T, PNO, PM)). For CCSD(T, PNO, AE) method: the mean is -0.9 kcal/mol, standard deviation (σ) is 1.8 kcal/mol, skewness is -1.148, kurtosis is 6.413. Kolmogorov-Smirnov normality test: $D = 0.134$, p -value = 0.031. For CCSD(T, PNO, PM) method: the mean is -1.2 kcal/mol, standard deviation (σ) is 1.8 kcal/mol, skewness is -1.132, kurtosis is 6.201. Kolmogorov-Smirnov normality test: $D = 0.141$, p -value = 0.020.

3.4 Group Additivity Method

The group additivity (GA) method³⁰⁷ is a straightforward, valuable, and powerful method to estimate the thermodynamic properties (standard enthalpy of formation, standard entropy, and heat capacity as a functional of temperatures) of molecules for reaction analysis. For example, the THERM³²⁵ code is widely used in modeling reactions occurring during combustion to predict the thermochemical properties for hydrocarbons and oxygenated hydrocarbons with acceptable accuracy, especially for which accurate electronic structure theory methods and composite

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3 schemes are prohibitively expensive. Obvious limitations of this method are: a) non-availability
4 of the formation enthalpies for some individual groups; b) the real structure of the molecule is
5 not taken into account, since the only information needed to predict the thermodynamic
6 properties is the molecular topology; c) intra and inter-molecular non-covalent interactions, and
7 hydrogen bonding are ignored.

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10 In the Table S1 the errors from the GA approach are compared with those from the best
11 performing methods in this work, DLPNO-CCSD(T, B3LYP) and OO-SCS-MP2, for a set of
12 molecules for which the GA scheme is applicable (i.e. contributions of all the individual groups
13 in molecule are known and tabulated).³²⁶⁻³²⁷ The MUE of 3.0 kcal/mol obtained for the GA
14 approach is significantly higher compared to the MUEs of 1.1 and 1.3 kcal/mol documented for
15 the DLPNO-CCSD(T, B3LYP) and OO-SCS-MP2 methods. Nevertheless, it has to be mentioned
16 that the GA approach provides a MUE comparable to that of the best performing DFT methods.
17 The MSE for the GA method turned out to be 0.3 kcal/mol, indicating almost complete
18 compensation of overestimated and underestimated enthalpies. The MSEs for the DLPNO-
19 CCSD(T, B3LYP) and OO-SCS-MP2 methods turned out to be -0.8 kcal/mol and -0.1 kcal/mol,
20 i.e. comparable to what was obtained for the GA approach.

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23 Analysis of the deviations of the prediction from the experimental enthalpies indicates that the
24 maximum deviation obtained for the GA method is 10.8 kcal/mol (“M22”), versus maximum
25 deviations of only 2.8 (“M76”) and 2.9 (“M95”) kcal/mol for the DLPNO-CCSD(T, B3LYP) and
26 OO-SCS-MP2 methods. NIST website demonstrated four conformers of M22 as (E,E) 46.9
27 kcal/mol, (Z,Z-chair) 24.2 kcal/mol, (E,Z) 37.8 kcal/mol, and (Z,Z-bent) 13.7 kcal/mol. The
28 structure that was calculated in this work is (Z,Z-chair) conformer, and the enthalpy of formation
29 for M22 is determined as 25.3 kcal/mol under DLPNO-CCSD(T)/CBS level of theory, which has
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3 good agreement with experimental data. GA determined M22 as 13.4 kcal/mol which is close to
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5 the (Z,Z-bent) conformer experimental data on account of its limitation on evaluating the
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7 stereoisomers.
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11 Similarly, the minimum deviation obtained for the GA scheme is -20.1 kcal/mol (M104) because
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13 of its limitation on evaluating high resonance structures, versus minimum deviations of -7.6
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15 (“M104”) and -4.8 (“M76”) kcal/mol for the DLPNO-CCSD(T, B3LYP) and OO-SCS-MP2
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17 methods. This indicates the latter two electronic structure methods to be superior to the GA
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19 approach, and these are in general recommended. One thing attracts our attention as well, which
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21 is the benzyl acid liked group values are needed further improvement since species M81, M82,
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23 M83, M87, M88, M89, and M90, have 3 – 9 kcal/mol discrepancy comparing to experimental
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25 recommend.
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30 31 **3.5 Analysis of Largest Deviations** 32 33

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35 Since the accuracy of DFT methods depends on the particular functional/system under study and
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37 cannot be improved systematically, i.e. for some formation enthalpies simple GGA can be
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39 superior to advanced hybrid-meta GGA or double-hybrids, we only tried to analyze the largest
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41 deviations obtained with the DLPNO-CCSD(T) method using the B3LYP orbitals. In general, we
42
43 expect that an error of 2–3 kcal/mol is acceptable in this study because the average uncertainty
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45 related to the experimental formation enthalpies are ca. 0.5 kcal/mol. Another 1.5–2.5 kcal/mol
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47 error can result from errors in the geometry optimization method, neglecting other low-lying
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49 conformers for Boltzmann averaging, treating the low-lying internal rotations in the harmonic
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51 approximation and some intrinsic errors in the DLPNO-CCSD(T) calculation. Thus, we believe
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53 this level of accuracy can be considered to be close to the so called “chemical accuracy”, since
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3 we have only inspected the experimental formation enthalpies for which errors larger than 3.0
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5 kcal/mol have been obtained with DLPNO-CCSD(T, B3LYP) method.
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9 Out of 113 heats of formation of medium-size organic molecules, only 6 compounds exhibit
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11 deviations of more than 3 kcal/mol with DLPNO-CCSD(T, B3LYP) method. First,
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13 tricyclo[4.4.2.0(1,6)dodeca-2,4,8-triene (“M49”) has a predicted formation enthalpy of 60.3
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15 kcal/mol, which deviates by 5.8 kcal/mol from the two available experimental formation
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17 enthalpies from calorimetry hydrogenation, 66.1 and 66.0 kcal/mol; the OO-SCS-MP2 method
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19 also results in large deviation of 8.1 kcal/mol. As both measurements have been performed in the
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21 same group, it cannot be excluded a systematic error in the experimental values. As much
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23 smaller deviations in DLPNO-CCSD(T, B3LYP) formation enthalpies have been obtained for
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25 structurally similar complexes, i.e., “M21” (-0.5 kcal/mol), we expect re-examination of the
26
27 experimentally measured formation enthalpy of “M49” to be useful.
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34 The DLPNO-CCSD(T) formation enthalpy of benz[a]anthracene (“M63”), 66.7 kcal/mol,
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36 deviates by 3.2 kcal/mol from the two available experimental formation enthalpies of 70.3 ± 0.9
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38 and 69.4 ± 1.4 kcal/mol. As the deviation is only 2.7 kcal/mol for the second experimental
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40 measurement, we believe this accuracy is acceptable. Further, the OO-SCS-MP2 method
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42 provides a deviation of only 0.3 kcal/mol, indicating that the experimental numbers are likely
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44 accurate.
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49 The DLPNO-CCSD(T) formation enthalpy of 3,9-dimethylbenz[a]anthracene (“M64”), 50.9
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51 kcal/mol, deviates by -5.7 kcal/mol from the two available experimental formation enthalpies of
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53 45.1 ± 0.8 and 45.2 kcal/mol. The OO-SCS-MP2 method deviates by -5.5 kcal/mol, which is
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55 practically identical to that obtained for DLPNO-CCSD(T, B3LYP) method. As the same
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3 sublimation enthalpy of dimethylbenz[a]anthracene has been used to derive the two experimental
4 formation enthalpies, the difference between predicted values and their experimental
5 counterparts could be due to error in the sublimation enthalpy of 3,9-dimethylbenz[a]anthracene.
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10 Much smaller deviations in DLPNO-CCSD(T, B3LYP) formation enthalpies have been obtained
11 for structurally similar complexes “M62” (1.1 kcal/mol) and “M63” (3.2 kcal/mol), so we
12 believe experimental re-examination of the sublimation enthalpy of “M64” is worthwhile.
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18 The DLPNO-CCSD(T) formation enthalpy of propanoic acid, 2,2-dimethyl-, methyl ester
19 (“M78”), -116.2 kcal/mol, deviates by -3.3 kcal/mol from the average of the three available
20 experimental formation enthalpies of -117.5±0.4, -118.2 and -122.8±1.8 kcal/mol. As good
21 agreement is obtained with the first two experimental values, it is not unlikely that the third
22 experimental measurement is in error. Furthermore, the OO-SCS-MP2 formation enthalpy, -
23 119.5 kcal/mol, is very close to the second experimental measurement.
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34 The DLPNO-CCSD(T) formation enthalpy of tetracyano-p-quinodimethane (“M104”), 191.8
35 kcal/mol, deviates by -7.6 kcal/mol from the two available experimental formation enthalpies of
36 184.3 and 184.0±2.5 kcal/mol. The OO-SCS-MP2 formation enthalpy, 186.9 kcal/mol, is closer
37 to experimental value but still deviates by -2.7 kcal/mol from the experimental values. On the
38 other hand, the same sublimation enthalpy of this molecule has been used in the derivations of
39 the experimental formation enthalpies, which might suggest that the difference between the
40 predicted values and their experimental counterparts might also be due to inaccuracy in the
41 sublimation enthalpy of tetracyano-p-quinodimethane. However, with the available information
42 it would be speculative to ascribe the deviation between the calculated and the measured values
43 to a weakness of theory and/or experiments. Interestingly, the GA method results in deviation in
44 the formation enthalpy of -20.1 kcal/mol, see Table S1 in the SI.
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3 Finally, the DLPNO-CCSD(T) formation enthalpy of 2,4,6-trimethylbenzonitrile, N-oxide
4 (“M106”), 38.9 kcal/mol, deviates by -6.6 kcal/mol from the two available experimental
5 formation enthalpies of 32.7 ± 1.0 and 31.9 ± 1.0 kcal/mol. On the other hand, the OO-SCS-MP2
6 method results in the fairly small deviation of 1.8 kcal/mol. As both measurements have been
7 performed in the same group, it is not unlikely that the experimental values could be affected by
8 systematic error. However, also in this case it is possible to ascribe the deviation between the
9 calculated and the measured values to a weakness of a theory.

20 21 **4. Conclusions**

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24 In the current work, we assessed the performance of the DLPNO-CCSD(T) method together with
25 a series of contemporary computational chemistry methods ranging from DFT functionals to
26 double hybrids and MP2 methods. A dataset 113 accurate formation enthalpies of medium-size
27 organic molecules containing C, H, N, O, and S elements was used to benchmark the calculation.
28 To derive the formation enthalpies, we used the reaction based Feller-Peterson-Dixon (FPD)
29 approach.
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39 The worst performance was obtained by the standard hybrid DFT functionals, PBE0, PBE0-D3,
40 B3LYP, and B3LYP-D3. Remarkably, the influence of an empirical dispersion term on the
41 performance of the functionals is not homogeneous; it improves the B3LYP performance but
42 leads to significantly larger errors in the case of the PBE0 functional. This suggests that the
43 effect of an empirical dispersion correction, which has become *de facto* standard in DFT, has to
44 be thoroughly validated before using a specific functional in any DFT study. The empirically
45 parameterized Minnesota functionals, M06 and M06-2X, and the ω B97X-D3 functional provided
46 significantly better formation enthalpies comparing to those from the PBE0(-D3) and B3LYP(-
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3 D3) functionals. Enthalpies of similar accuracy can also be obtained from the double hybrid
4 methods (B2PLYP-D3, PWPB95-D3, B2T-PLYP, B2T-PLYP-D, and B2GP-PLYP-D3). Yet
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6 similar accuracy can be obtained with composite G3(MP2) approach. However, these methods
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8 (double hybrids and G3(MP2)) are, in general, not recommended due to higher computational
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10 costs comparing to the M06 type and ω B97X-D3/ ω B97M-V functionals, which will become
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12 especially true if the larger molecule are to be calculated. The few spin component scaled (SCS)
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14 MP2 methods tested were found to perform excellently, with MUEs below 2.0 kcal/mol. The
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16 slightly better performing OO-SCS-MP2 method is recommended. However, the SCS-MP2
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18 method provides only slightly higher deviations, and thus could be method of choice when the
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20 problem is bound by available computational resources.
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28 The best performance was found for the recently developed DLPNO-CCSD(T) method. We
29
30 recommend to use this method in thermochemical calculations of molecules of medium size,
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32 when canonical CCSD(T) calculations with basis sets of reasonable quality are prohibitively
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34 expensive. The performance of the DLPNO-CCSD(T) method can be slightly improved if the
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36 DLPNO-CCSD(T) calculation is performed on the B3LYP orbitals, and we indeed recommend
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38 the DLPNO-CCSD(T, B3LYP) method for completely black box applications in
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40 thermodynamics of medium-size organic molecules as the DFT orbitals are also known to
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42 provide the better orbitals resulting in lower T1 diagnostic values for CCSD(T) calculations. The
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44 group additivity method, widely used for large molecules, turned out to perform significantly
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46 worse compared to the best performers in found in this work, DLPNO-CCSD(T, B3LYP) and
47
48 OO-SCS-MP2 methods, with a very broad distribution in the errors. Thus, GA is not
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50 recommended if accurate heats of formation are targeted. If very large molecules have to be
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3 examined, the recommended method probably is the ω B97M-V functional, which provides
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5 reasonably small MUE and reasonably narrow distribution of the errors.
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8 9 ASSOCIATED CONTENT

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12 **Supporting Information.** Cartesian coordinates (Å) of PBE0-D3/def2-tzvp optimized
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14 structures, B3LYP, B3LYP-D3, PBE0, PBE0-D3, M06, M06-2X, ω B97X-D3, ω B97M-V,
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16 B2PLYP-D3, PWPB95-D3, B2T-PLYP, B2T-PLYP-D, B2GP-PLYP, DSD-PBEP86-D3, SCS-
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18 MP2, OO-SCS-MP2, DLPNO-CCSD(T), DLPNO-CCSD(T, AE), DLPNO-CCSD(T, PM),
19
20 DLPNO-CCSD(T, B3LYP) energies with different basis sets, T1 diagnostic values, T2 (largest
21
22 amplitudes values), enthalpic corrections, Cartesian coordinates tabulated enthalpies and errors
23
24 forming the basis of Figures 1 – 7 and Figures S1-S16, tabulated absolute enthalpies of all 113
25
26 reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.
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8 SYNOPSIS (Word Style "SN_Synopsis_TOC"). If you are submitting your paper to a journal
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10 that requires a synopsis, see the journal's Instructions for Authors for details.
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