Chapter

Quantum Calculations to Estimate the Heat of Hydrogenation Theoretically

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Abstract

Standard enthalpies of hydrogenation of 29 unsaturated hydrocarbon compounds were calculated in the gas phase by CCSD(T) theory with complete basis set cc-pVXZ, where X = DZ, TZ, as well as by complete basis set limit extrapolation. Geometries of reactants and products were optimized at the M06-2X/6-31g(d) level. This M06-2X geometries were used in the CCSD(T)/cc-pVXZ//M06-2X/6-31g (d) and cc-pV(DT)Z extrapolation calculations. (MAD) the mean absolute deviations of the enthalpies of hydrogenation between the calculated and experimental results that range from 8.8 to 3.4 kJ mol^{-1} based on the Comparison between the calculation at CCSD(T) and experimental results. The MAD value has improved and decreased to 1.5 kJ mol^{-1} after using complete basis set limit extrapolation. The deviations of the experimental values are located inside the "chemical accuracy" ($\pm$1 kcal mol^{-1} $\approx$ $\pm$4.2 kJ mol^{-1}) as some results showed. A very good linear correlations between experimental and calculated enthalpies of hydro-genation have been obtained at CCSD(T)/cc-pVTZ//M06-2X/6-31g(d) level and CCSD (T)/cc-pV(DT)Z extrapolation levels (SD =2.11 and 2.12 kJ mol^{-1}, respectively).

Keywords: complete basis set (CBS), density functional theory (DFT), CCSD (T), extrapolated method, molecules, energy, enthalpy, hydrocarbons

1. Introduction

The calculation of enthalpies of formation for the large unsaturated molecules, some of which are not included in the practical range of combustion thermochemistry, based on quantum mechanical first principles which have been possible basing on the recent important advances in computational chemistry. Necessary, Quantum mechanical calculations of molecular thermochemical properties are approximate. Approximations may be employed by the Composite quantum mechanical procedures at each of several computational steps and in the same time it may have an empirical factor to correct the cumulative error. When the error of the various approximations is known within narrow limits, but the question about the accuracy of the "known" value is noticed immediately because the uncertainty of the comparison between the approximate quantum mechanical result and the standard to which it is compared.

The most correct quantum mechanical procedure is been established after its ability to reproduce various accurate experimental results to calculate unknown

thermochemical values of explosive compounds or unstable, unsuited to classical thermochemical methods, or to calculate thermochemical properties of radicals, molecules, or ions of fleeting existence [1–15]. Here where a major advantage to create the accuracy of inherent hydrogen thermochemical results lies, and it works for encouraging and renewing interest in the diverse literature devoted to hydrogen thermochemistry.

The main part of the quantum chemistry is contended in the total electronic energy of a molecule. And this total electronic energy is a function of the nuclear geometric configuration after Born-Oppenheimer separation of electronic and nuclear motion, therefore generating hyper surfaces of potential energy–for electronically excited states as well as for the ground state.

At the end of this work a very important fact is clear now which clarify that wave function-based quantum-chemical methods can produce molecular electronic energies with an accuracy that surpasses that of experimental measurements of molecular energies (in terms of enthalpies of formation).

An important feature of the wavefunction-based quantum-chemical methodology is the ability to access the exact characterizing of the molecular electronic structure in a systematic manner. To achieve systematic approach two basic steps have been taken, the first step using advanced hierarchy of wavefunction models and the second step using systematic sequence of basis sets – or a nearly complete basis set – of atomic orbitals.

2. Basis-set convergence

It is noted that the type of wavefunction model used, or density functional, plays an important role in determining accuracy of computed molecular_electronic energies. In addition to the important role played by the flexibility of the one electron basis set of atomic orbitals (AOs) by which the molecular orbitals (MOs) are expanded. It is worth noting that Slater's determinants are constructed using MOs for use in Kohn - Sham theory or to expand the n-electron wavefunction.

Different ways can be chosen from basis sets of AOs (the literature [16–18]). As for the approach followed in study of molecular electronic-structure based on wavefunction methods, a well-defined procedure must have been used in order to generating sequences of the basis sets in order to increase flexibility. This way is very useful by generating hierarchies for basis sets, Each next higher level describes an improved systematically of the molecular electronic structure compared to the next lower level. Within the hierarchy the calculated results converge within a prescribed accuracy, and then the basis-set hierarchy ends up effectively complete basis [16]. Therein lies the problem where approaches of wavefunction that depend on the electron-correlation effects of the convergence to an effectively complete basis are very slow. When increasing the number N of AOs in the basis according to an optimal manner, it reduces the basis-set error as $\propto N^{-1}$, thus obtaining a good approximation. It is often noticed that the accuracy of the electronic correlation calculations is limited by computational technical constraints. This is due to computing times growing at least as N4 and the computational effort grows more quickly compared to gain in accuracy.

2.1 Correlation-consistent basis sets

The correlation-consistent basis sets from Dunning and his co-workers [19, 20] represent a popular hierarchy of basis sets. When the valence orbitals are

correlated in a calculations only then can the expansion mainly in the Limit extrapolation, until it ends to an effectively complete basis [21–26]. The term X-tuple zeta basis sets represents to correlation-consistent polarized valence, denoted by cc-pVXZ, and is used in the calculations of this work, where X = D, T, (double, triple zeta). It should be noted that when all the electrons are correlated (core as well as valence orbitals), the cc-pCVXZ basis sets must be used provided $2 \leq X \leq 5$.

Reactions	$\Delta_{hyd}H^0_{298}(\exp.)$
Ethyne +2 H_2 → ethane	−312.0 ± 0.63
Ethene + H_2 → ethane	−136.3 ± 0.3
Propadiene +2 H_2 → propane	−295.1 ± 0.1
Prop-1-yne + 2 H_2 → propane	−289.6 ± 0.63
Prop-1-ene + H_2 → propane	−125.0 ± 0.42
But-2-yne + 2 H_2 → butane	−272.4 ± 1.3
Isobutene + H_2 → isobutane	−117.8 ± 0.42
(2E)-but-2-ene + H_2 → butane	−118.5 ± 0.42
(2Z)-but-2-ene + H_2 → butane	−114.6 ± 0.42
(2E)-pent-2-ene + H_2 → pentane	−113.8 ± 0.8
(2Z)-pent-2-ene + H_2 → pentane	−117.7 ± 0.8
2-Methylbut-1-ene + H_2 → 2-methylbutane	−118.2 ± 0.42
2-Methylbut-2-ene + H_2 → 2-methylbutane	−111.6 ± 0.3
3-Methylbut-1-ene + H_2 → 2-methylbutane	−126.3 ± 0.3
Cyclopenta-1,3-diene +2 H_2 → cyclopentane	−210.8 ± 0.84
Hex-1,5-diene +2 H_2 → hexane	−251.2 ± 0.42
Hex-1-ene + H_2 → hexane	−126.0 ± 2.0
2,3-Dimethylbuta-1,3-diene +2 H_2 → 2,3-dimethylbutane	−223.4 ± 0.63
2,3-Dimethylbuta-1-ene + H_2 → 2,3-dimethylbutane	−116.1 ± 0.4
2,3-Dimethylbuta-2-ene + H_2 → 2,3-dimethylbutane	−110.4 ± 0.42
3,3-Dimethylbuta-1-ene + H_2 → 2,2-dimethylbutane	−125.9 ± 0.63
Benzene +3 H_2 → cyclohexane	−205.3 ± 0.6
Cyclohexa-1,3-diene +2 H_2 → cyclohexane	−229.6 ± 0.42
Cyclohexene + H_2 → cyclohexane	−118.6 ± 0.42
Hept-1-ene + H_2 → heptane	−125.1 ± 0.3
4,4-Dimethylpent-1-ene + H_2 → 2,2-dimethylpentane	−122.5 ± 0.42
Cyclohepta-1,3,5-triene +3 H_2 → cycloheptane	−301.7 ± 1.3
Cyclohepta-1,3-diene +2 H_2 → cycloheptane	−212.4 ± 0.63
Cycloheptene + H_2 → cycloheptane	−108.9 ± 0.63
NIST - JANAF thermochemical tables, Ref. [33]	

Table 1.
Experimental values of hydrogenation enthalpy of some unsaturated hydrocarbons in the gas phase (in kJ Mol^{-1}).

2.2 Basis-set extrapolation

The correlation-consistent basis sets form a basis-set hierarchy well suited for complete basis-set limit extrapolations of the correlation-energy. Then the correlation energy can have been determined depending on X when $X \rightarrow \infty$.

In 1977, 27 formulas for two-point linear extrapolation were introduced by Helgaker et al. [27] via the basis sets cc-pCVXZ and cc-pCVYZ, the electron-correlation energies and are computed E_X and E_Y, and the $C_{XY} = X^3/(X^3\ Y^3)$ coefficient is determined in Eq. (1),

$$E_{XY} = \left(E_X X^3 - E_Y Y^3\right)/\left(X^3 - Y^3\right) = C_{XY}E_X + (1 - C_{XY})E_Y \quad (1)$$

The EX correlation energy can be recovered in correlation-consistent basis of cc-pVXZ via the Eq. (2), When performing calculations according to the basis sets, cc-pVXZ and cc-pVYZ, two equations with two unknowns are obtained, a and E, whose Solving leads to Eq. (2), with that in mind $E = E_{XY}$

$$E_X = E_\infty + aX^3 \quad (2)$$

Note that through experience [28–32] that the best estimate of complete basis set limit extrapolation is by using two consecutive basis set when X = Y - 1, for example the pair cc-pCVDZ/cc-pCVTZ, and so on).

The level at which the results were obtained by extrapolation is denoted by cc-pCV(XY)Z, where XY = DT, TQ, and so forth. It is only at this level that the correlation energy is extrapolated.

The CCSD(T)/cc-pV(XY)Z extrapolation will be applied to obtain estimates of the basis-set limit of corrections for M06-2X/6-31g(d) level of theory by calculations of hydrogenation enthalpies of some unsaturated hydrocarbon compounds (**Table 1**).

In Section 3, we shall describe the methods used, the molecular equilibrium geometries, and the basis sets. Results will be shown in Section 3.2, including molecular electronic energies, enthalpies of hydrogenation, and statistical analysis of the computational results.

3. Computational details

3.1 Computational methods

Electronic energies were computed by the density-functional (M06-2X) [34] approach with 6-31g(d) basis set. The M06-2X/6-31g(d) equilibrium geometries of the reactants and products was optimized with the Gaussian 09 program [35]. All CCSD(T)/cc-pV(DT)Z calculations were performed at fixed molecular equilibrium geometries that were optimized at the M06-2X/6-31g(d) level can be found in supporting information.

3.2 Results and discussion

3.2.1 Nonrelativistic electronic energies

The total electronic M06-2X/6-31g(d) energies, $H_{corr,}$ G_{corr}, and the zero-point vibrational energies (ZPE) are reported in **Table 2**, while **Table 3** shows CCSD

Compounds	M06-2X/6-3g(d)			
	E_o	H_{corr}	G_{corr}	*ZPE*
H_2	−1.1635655	0.013609	−0.001167	0.010304
Ethane	−79.771814	0.080116	0.054255	0.075684
Ethyne	−77.287772	0.031118	0.008428	0.027383
Ethene	−78.536836	0.055732	0.030890	0.051757
Propane	−119.064602	0.110657	0.080306	0.105246
Propadiene	−116.591917	0.060782	0.033335	0.056103
Prop-1-yne	−116.591781	0.061355	0.033375	0.056509
Prop-1-ene	−117.834775	0.085736	0.055653	0.080695
Cis- butane	−158.357373	0.140439	0.106229	0.133684
But-2-yne	−155.894141	0.091157	0.060488	0.085379
Isobutene	−158.359492	0.139891	0.105558	0.133229
Isobutane	−157.133592	0.115796	0.083003	0.109592
Trans-butane	−158.356612	0.140562	0.106344	0.133858
(2E)-but-2-ene	−157.132136	0.116000	0.083013	0.109658
(2Z)-but-2-ene	−157.130271	0.115947	0.081911	0.109398
pentane	−197.650150	0.171137	0.133095	0.163224
(2E)-pent-2-ene	−196.424444	0.146203	0.108344	0.138462
(2Z)-pent-2-ene	−196.422473	0.146538	0.108366	0.138911
2-Methylbutane	−197.650616	0.170492	0.132540	0.162599
2-Methylbut-1-ene	−196.425399	0.145953	0.108348	0.138377
2-Methylbut-2-ene	−196.428427	0.145977	0.108516	0.138233
3-Methylbut-1-ene	−196.421594	0.146029	0.109827	0.138805
Cyclopentane	−196.447999	0.148834	0.115170	0.142836
Cyclopenta-1,3-diene	−194.004693	0.099092	0.067447	0.094033
Hexane	−236.942859	0.201129	0.159944	0.191831
Hex-1,2-diene	−234.482131	0.151996	0.111965	0.143762
Hex-1-ene	−235.712709	0.176575	0.135740	0.167804
2,3-Dimethylbutane	−236.944627	0.200377	0.160337	0.191276
2,3-Dimethylbuta-1,3-diene	−234.499027	0.152102	0.114663	0.144198
2,3-Dimethylbuta-1-ene	−235.719209	0.176092	0.136350	0.167500
2,3-Dimethylbuta-2-ene	−235.721700	0.175800	0.134436	0.166165
2,2-Dimethylbutane	−236.946825	0.199906	0.159467	0.190810
3,3-Dimethylbuta-1-ene	−235.717309	0.175580	0.136683	0.167108
Cyclohexane	−235.752287	0.179349	0.145101	0.172770
Benzene	−232.136474	0.107012	0.076593	0.101699
Cyclohexa-1,3-diene	−233.301453	0.130219	0.096574	0.124132
Cyclohexene	−234.525715	0.154825	0.119853	0.148434
Heptane	−276.235598	0.231328	0.186546	0.220693
Hept-1-ene	−275.005449	0.206749	0.162214	0.196621

Compounds	M06-2X/6-3g(d)			
	E_o	H_{corr}	G_{corr}	ZPE
2,2-Dimethylpentane	−276.239366	0.230120	0.186120	0.219693
4,4-Dimethylpent-1-ene	−275.010862	0.205633	0.163043	0.195795
Cycloheptane	−275.035841	0.209838	0.171462	0.201976
Cyclohepta-1,3,5-triene	−271.377165	0.136474	0.100791	0.129851
Cyclohepta-1,3-diene	−272.592107	0.161000	0.123047	0.153676
Cycloheptene	−273.812872	0.185183	0.147448	0.177646

Table 2.
Calculated total electronic energy (E_o), H_{corr}, G_{corr}, and the zero-point vibrational energies (ZPE) at the M06-2X/6-31g(d) level (in hartree).

Compounds	E_D[a]	E_T[b]	E_∞[c]
H_2	−1.1723118	−1.1737775	−1.17439464
Ethane	−79.582513	−79.674425	−79.713125
Ethyne	−77.109286	−77.187516	−77.220455
Ethene	−78.354614	−78.438673	−78.474067
Propane	−118.780810	−118.914036	−118.970132
Propadiene	−116.314867	−116.433424	−116.483343
Prop-1-yne	−116.315794	−116.435339	−116.485674
Prop-1-ene	−117.556774	−117.682351	−117.735225
Cis- butane	−157.978111	−158.152797	−158.226349
But-2-yne	−155.521138	−155.681776	−155.749412
Isobutene	−157.981505	−158.156035	−158.229521
Isobutane	−156.760003	−156.927219	−156.997626
Trans -butane	−157.979256	−158.153758	−158.227233
(2E)-but-2-ene	−156.758622	−156.925479	−156.995734
(2Z)-but-2-ene	−156.756385	−156.923701	−156.994150
Pentane	−197.176630	−197.392504	−197.483398
(2E)-pent-2-ene	−195.956786	−196.164955	−196.252605
(2Z)-pent-2-ene	−195.954467	−196.163063	−196.250893
2-Methylbutane	−197.177674	−197.393756	−197.484738
2-Methylbut-1-ene	−195.957367	−196.165990	−196.253832
2-Methylbut-2-ene	−195.959195	−196.167943	−196.255837
3-Methylbut-1-ene	−195.954457	−196.163021	−196.250837
Cyclopentane	−195.977809	−196.185015	−196.272260
Cyclopenta-1,3-diene	−193.544249	−193.735901	−193.816596
Hexane	−236.376059	−236.633206	−236.741478
1,5-Hexdiene	−233.926959	−234.168762	−234.270574
Hex-1-ene	−235.151737	−235.401337	−235.506432
2,3-Dimethylbutane	−236.377394	−236.635041	−236.743524

Compounds	E_D[a]	E_T[b]	E_∞[c]
2,3-Dimethylbuta-1,3-diene	−233.940431	−234.183237	−234.285471
2,3-Dimethylbuta-1-ene	−235.156478	−235.406736	−235.512108
2,3-Dimethylbuta-2-ene	−235.157255	−235.407711	−235.513167
2,2-Dimethylbutane	−236.380072	−236.637444	−236.745811
3,3-Dimethylbuta-1-ene	−235.156438	−235.406113	−235.511240
Cyclohexane	−235.187080	−235.434840	−235.539160
Benzene	−231.580490	−231.805751	−231.900598
Cyclohexa-1,3-diene	−232.746205	−232.978902	−233.076879
Cyclohexene	−233.965459	−234.205764	−234.306946
Heptane	−275.574466	−275.872952	−275.998630
Hept-1-ene	−274.350163	−274.641090	−274.763585
2,2-Dimethylpentane	−275.578608	−275.877182	−276.002897
4,4-Dimethylpent-1-ene	−274.355543	−274.646391	−274.768853
Cycloheptane	−274.375461	−274.664943	−274.786830
Cyclohepta-1,3,5-triene	−270.731145	−270.997511	−271.109665
Cyclohepta-1,3-diene	−271.941636	−272.215680	−272.331066
Cycloheptene	−273.157974	−273.439442	−273.557955

Limit energies were obtained using the web page http://sf.anu.edu.au/ ~vvv900/cbs/#ref_3 [36].
[a]M06-2X/cc-pVDZ//M06-2X/6-31g(d) level.
[b]M06-2X/cc-pVTZ//M06-2X/6-31g(d) level.
[c]cc-pV(TD)Z extrapolated level.

Table 3.
Computed CCSD(T)/ccpVXZ energies at the M06-2X/6-31g(d) geometries, where X = D, T, as well as extrapolated values by the Eq. (2) (in hartree).

(T)/cc-pVXZ energies computed at the M06-2X/6-31g(d) geometries, where X = D, T. **Table 3** also shows extrapolated values by the Eq. (2) (denoted E_∞).

It is noted from **Table 3** that the cc-pV(DT)Z extrapolated level yield electronic energies for all reactants and products less than CCSD(T)/cc-pVDZ and CCSD (T)/cc-pVTZ levels, and it is expected that the calculations of the hydrogenation enthalpies by cc-pV(DT)Z extrapolated level are compatible with the experimental values.

3.2.2 Enthalpies of hydrogenation at 298.15 K in gas phase

The usual way to calculate enthalpies of reaction is to calculate heats of formation, and take the appropriate sums and difference (Eq. (3)).

$$\Delta_{\text{hyd}}H^{\circ}(298) \sum_{\text{products}} \Delta_f H^{\circ}(298) - \sum_{\text{reactans}} \Delta_f H^{\circ}(298) \tag{3}$$

However, since Gaussian program provides the sum of electronic and thermal enthalpies, there is a short cut: namely, to simply take the difference of the sums of these values for the reactants and the products. This works since the number of atoms of each element is the same on both sides of the reaction, therefore all the atomic information cancels out, and you need only the molecular data. For example,

using the information in **Table 2** (or **Table 3** for energies), the enthalpy of reaction can be calculated simply by Eq. (4):

$$\Delta_{\text{hyd}}H^0_{298} = \sum (E_0 + H_{corr})_{\text{porducts}} - \sum (E_0 + H_{corr})_{\text{reactants}} \quad (4)$$

E_0 can represent either E_{DZ}, E_{TZ}, E_{QZ} or E_∞ keeping the calculated H_{corr} value at M06-2X/6-31g(d) level is fixed. The calculated enthalpies of hydrogenation are

	CCSD(T)/cc-pVXZ//M06-2X/6–13(d)			
Reactions	**X = D[a]**	**X = T[b]**	**E_∞[c]**	**$\Delta_{hyd}H^o$(exp.)[d]**
Ethyne +2 H_2 → ethane	16.0	4.4	−0.5	−312.0 ± 0.63
Ethene + H_2 → ethane	5.1	2.0	0.7	−136.3 ± 0.3
Propadiene +2 H_2 → propane	11.4	4.1	−1.3	−295.1 ± 0.1
Prop-1-yne + 2 H_2 → propane	16.0	6.1	−0.5	−289.6 ± 0.63
Prop-1-ene + H_2 → propane	4.9	2.0	−0.4	−125.0 ± 0.42
But-2-yne + 2 H_2 → butane	15.2	4.1	−0.6	−272.4 ± 1.3
Isobutene + H_2 isobutane	7.6	3.0	1.1	−117.8 ± 0.42
(2E)-but-2-ene + H_2 → butane	6.1	1.7	−0.2	−118.5 ± 0.42
(2Z)-but-2-ene + H_2 → butane	7.6	3.9	2.4	−114.6 ± 0.42
(2E)-pent-2-ene + H_2 → pentane	5.8	2.3	0.8	−113.8 ± 0.8
(2Z)-pent-2-ene + H_2 → pentane	−1.7	−5.3	−6.7	−117.7 ± 0.8
2-Methylbut-1-ene + H_2 → 2-methylbutane	2.9	−1.3	−3.1	−118.2 ± 0.42
2-Methylbut-2-ene + H_2 → 2-methylbutane	4.7	0.2	−1.7	−111.6 ± 0.3
3-Methylbut-1-ene + H_2 → 2-methylbutane	2.6	−1.4	−3.1	−126.3 ± 0.3
Cyclopenta-1,3-diene +2 H_2 → cyclopentane	11.1	4.4	1.6	−210.8 ± 0.84
Hex-1,5-diene +2 H_2 → hexane	13.1	5.8	2.8	−251.2 ± 0.42
Hex-1-ene + H_2 → hexane	5.6	1.6	0.0	−126.0 ± 2.0
2,3-Dimethylbuta-1,3-diene +2 H_2 → 2,3-dimethylbutane	11.3	2.7	−0.9	−223.4 ± 0.63
2,3-Dimethylbuta-1-ene + H_2 → 2,3-dimethylbutane	7.2	2.9	1.0	−116.1 ± 0.4
2,3-Dimethylbuta-2-ene + H_2 → 2,3-dimethylbutane	10.1	2.7	−0.9	−110.4 ± 0.42
3,3-Dimethylbuta-1-ene + H_2 → 2,2-dimethylbutane	4.5	0.9	−0.6	−125.9 ± 0.63
Benzene +3 H_2 → cyclohexane	18.6	6.4	1.3	−205.3 ± 0.6
Cyclohexa-1,3-diene +2 H_2 → cyclohexane	13.1	5.1	1.8	−229.6 ± 0.42
Cyclohexene + H_2 → cyclohexane	6.0	1.8	0.0	−118.6 ± 0.42
Hept-1-ene + H_2 → heptane	6.4	2.4	0.8	−125.1 ± 0.3
4,4-Dimethylpent-1-ene + H_2 → 2,2-dimethylpentane	5.9	2.5	1.0	−122.5 ± 0.42
Cyclohepta-1,3,5-triene +3 H_2 → cycloheptane	18.6	8.0	3.5	−301.7 ± 1.3
Cyclohepta-1,3-diene +2 H_2 → cycloheptane	12.5	5.6	2.6	−212.4 ± 0.63
Cycloheptene + H_2 → cycloheptane	4.5	1.7	0.6	−108.9 ± 0.63

[a] *CCSD(T)/cc-pVDZ//M06-2X/6-31g(d) level.*
[b] *CCSD(T)/cc-pVTZ//M06-2X/6-31g(d) level.*
[c] *cc-pV(TD)Z extrapolated level.*
[d] *NIST-JANAF thermo-chemical tables.*

Table 4.
Difference between experimental and calculation values of standard enthalpies of hydrogenation of some unsaturated hydrocarbons in the gas phase at 298.15 K (in kJ Mol^{-1}).

Level	MAD	RMS	Error%	SD	R^2
CCSD(T)/cc-pVDZ//M06-2X/6-31g(d)	8.8	10.0	5.0%	2.78	0.9987
CCSD(T)//cc-pVTZ//M06-2X/6-31g(d)	3.4	3.9	2.0%	2.11	0.9992
cc-pV(DT)Z extrapolated level	1.5	2.1	1.0%	2.12	0.9992

Table 5.
Statistical parameters for all used methods to calculate hydrogenation enthalpies. (in kJ Mol^{-1}).

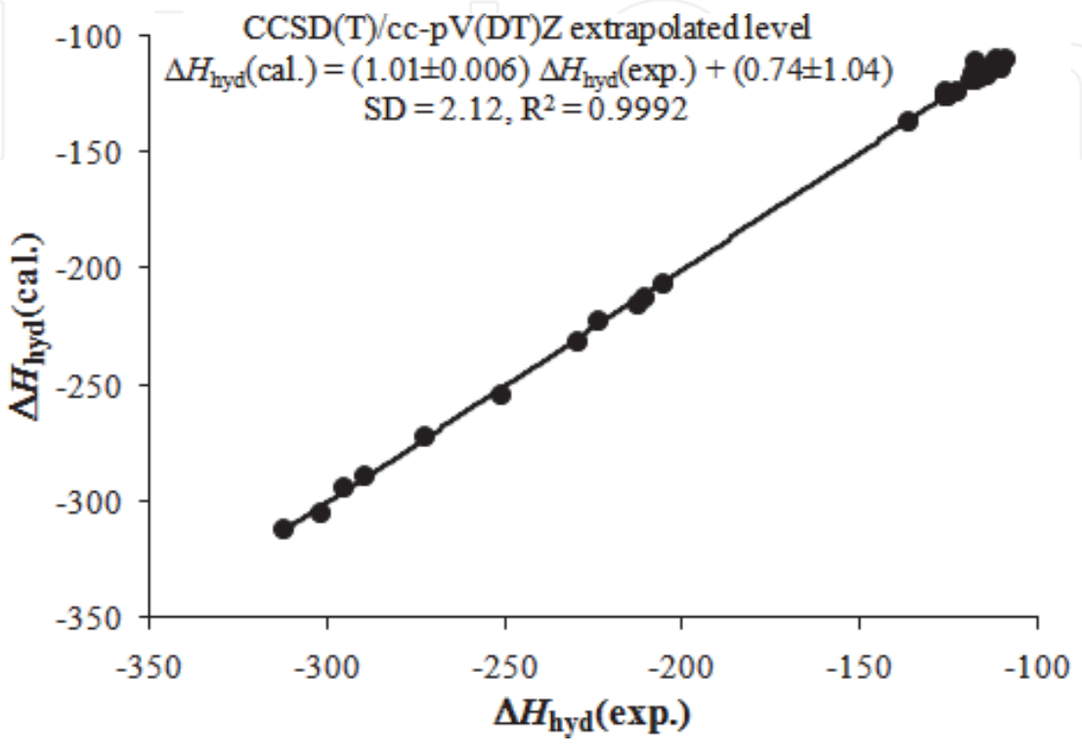

Figure 1.
Calculated versus experimental hydrogenation enthalpy $\left[\Delta H^{\circ}_{\mathrm{hyd}}(298,15\,K), kJ\,mol^{-1}\right]$ *of 29 hydrocarbons.*

reported in **Table 4**, along with the experimental values. **Table 5** shows statistical parameters for all used computational methods. **Figure 1** shows a linear analysis of the best calculated results in terms of experimental results.

Our best theoretical estimates of the enthalpies of hydrogenation are based on basis set limit extrapolation calculations, when the pair cc-pVDZ and cc-pVTZ are used, and the mean absolute deviation (MAD) between experimental and calculated values is 1.5 kJ mol^{-1} (**Table 5**). The enthalpies of hydrogenation of some alkenes (12 compounds) have been calculated at the HF, B3LYP, M06, MP2, G3, G4, CBS-QB3, CBS-APNO, and W1BD levels and, in the case of the first four methods, using a variety of basis sets up to aug-ccpVTZ [37], and it is found that the MAD decreases gradually from the first to the last method (18.4–4.2 kJ mol^{-1}). Moreover, Rogers et al. [38–40] calculated the hydrogenation enthalpy at 298.15 K for reactions involving cyclic and acyclic C4 (20 reactions), cyclic C5 (23 reactions) and C6 (24 reactions) hydrocarbons using the G2 and G2(MP2) ab initio methods, and it is found that the MAD is about 3.3, 3.7 and 5.0 kJ $^{-1}$, respectively.

4. Conclusion

Enthalpies of hydrogenation are relatively easy to calculate with CCSD(T)/cc-pVXZ/M06-31g(d)/6-31g(d) level, where X = D, T, giving fairly good agreement

with experiment, especially when cc-pVTZ basis set are used, and basis set extrapolation techniques by Eq. (2) seem to represent an easy-to-use alternative, especially when the pair cc-pVDZ and cc-pVTZ are used.

Appendix: supporting information (All computed molecule Cartesian coordinates (XYZ)) were optimized at the M06-2X/6-31g(d) level

1			
Hydrogen (H2)			
H	0.000000000	0.000000000	0.368263000
H	0.000000000	0.000000000	-0.368263000
2			
Ethane (C2H6)			
C	0.000000000	0.000000000	0.762978000
C	0.000000000	0.000000000	-0.762978000
H	0.000000000	1.019590000	1.159421000
H	-0.882991000	-0.509795000	1.159421000
H	0.882991000	-0.509795000	1.159421000
H	0.000000000	-1.019590000	-1.159421000
H	-0.882991000	0.509795000	-1.159421000
H	0.882991000	0.509795000	-1.159421000
3			
Ethene (C2H4)			
C	0.000000000	0.000000000	0.663573000
C	0.000000000	0.000000000	-0.663573000
H	0.000000000	0.923826000	1.234547000
H	0.000000000	-0.923826000	1.234547000
H	0.000000000	-0.923826000	-1.234547000
H	0.000000000	0.923826000	-1.234547000
4			
Ethyne (C2H2)			
C	0.000000000	0.000000000	0.600962000
H	0.000000000	0.000000000	1.668037000
C	0.000000000	0.000000000	-0.600962000
H	0.000000000	0.000000000	-1.668037000
5			
Propadiene			
C	0.000000000	0.000000000	0.000000000
C	0.000000000	0.000000000	1.304952000
C	0.000000000	0.000000000	-1.304952000
H	0.000000000	0.928749000	1.868109000
H	0.000000000	-0.928749000	1.868109000

H	0.928749000	0.000000000	-1.868109000
H	-0.928749000	0.000000000	-1.868109000
6			
Propane			
C	0.000000000	1.266248000	-0.260978000
C	0.000000000	0.000000000	0.591962000
H	0.000000000	2.169798000	0.355701000
H	0.883659000	1.299469000	-0.907461000
H	-0.883659000	1.299469000	-0.907461000
C	0.000000000	-1.266248000	-0.260978000
H	0.877466000	0.000000000	1.249203000
H	-0.877466000	0.000000000	1.249203000
H	0.000000000	-2.169798000	0.355701000
H	-0.883659000	-1.299469000	-0.907461000
H	0.883659000	-1.299469000	-0.907461000
7			
Propene			
C	-1.286905000	0.145875000	0.000000000
C	0.000000000	0.478432000	0.000000000
H	-1.601612000	-0.895181000	0.000000000
H	-2.072231000	0.895120000	0.000000000
H	0.274287000	1.533078000	0.000000000
C	1.134779000	-0.502407000	0.000000000
H	1.773172000	-0.366223000	0.880442000
H	0.765971000	-1.531971000	0.000000000
H	1.773172000	-0.366223000	-0.880442000
8			
Propyne			
C	0.000000000	0.000000000	1.423679000
C	0.000000000	0.000000000	0.219688000
H	0.000000000	0.000000000	2.490285000
C	0.000000000	0.000000000	-1.242799000
H	0.000000000	1.022382000	-1.631230000
H	0.885409000	-0.511191000	-1.631230000
H	-0.885409000	-0.511191000	-1.631230000
9			
But-2-yne			
C	0.000000000	0.000000000	2.066654000
H	0.000000000	1.021413000	2.458673000
H	0.884570000	-0.510706000	2.458673000
H	-0.884570000	-0.510706000	2.458673000

C	0.000000000	0.000000000	0.602950000
C	0.000000000	0.000000000	-2.066654000
H	0.000000000	1.021413000	-2.458673000
H	0.884570000	-0.510706000	-2.458673000
H	-0.884570000	-0.510706000	-2.458673000
C	0.000000000	0.000000000	-0.602950000
10			
(Z)-but-2-ane			
C	0.583174000	1.434814000	-0.567859000
C	0.583174000	0.495360000	0.636830000
C	-0.583174000	-0.495360000	0.636830000
C	-0.583174000	-1.434814000	-0.567859000
H	-0.372885000	1.964655000	-0.647990000
H	0.741015000	0.890494000	-1.503781000
H	1.375535000	2.184468000	-0.485094000
H	0.547339000	1.089204000	1.557738000
H	1.528690000	-0.062264000	0.665299000
H	-1.528690000	0.062264000	0.665299000
H	-0.547339000	-1.089204000	1.557738000
H	-1.375535000	-2.184468000	-0.485094000
H	0.372885000	-1.964655000	-0.647990000
H	-0.741015000	-0.890494000	-1.503781000
11			
(Z)-but-2-ene			
C	0.000000000	0.666919000	0.667097000
C	0.000000000	-0.666919000	0.667097000
H	0.000000000	1.168257000	1.634362000
H	0.000000000	-1.168257000	1.634362000
C	0.000000000	1.580592000	-0.524061000
C	0.000000000	-1.580592000	-0.524061000
H	-0.880001000	-2.233321000	-0.510523000
H	0.000000000	-1.037863000	-1.471533000
H	0.880001000	-2.233321000	-0.510523000
H	0.000000000	1.037863000	-1.471533000
H	-0.880001000	2.233321000	-0.510523000
H	0.880001000	2.233321000	-0.510523000
12			
Isobutene2-methylprop-1-ene			
C	0.000000000	0.000000000	0.124902000
C	0.000000000	0.000000000	1.456866000
C	0.000000000	1.272771000	-0.678500000

C	0.000000000	-1.272771000	-0.678500000
H	0.000000000	-0.925843000	2.025187000
H	0.000000000	0.925843000	2.025187000
H	-0.880053000	1.319051000	-1.331393000
H	0.880053000	1.319051000	-1.331393000
H	0.000000000	2.157033000	-0.036707000
H	-0.880053000	-1.319051000	-1.331393000
H	0.000000000	-2.157033000	-0.036707000
H	0.880053000	-1.319051000	-1.331393000
13			
Methylrpopane			
C	-0.878102000	1.160442000	0.000000000
C	0.318200000	0.209420000	0.000000000
C	0.318200000	-0.659704000	1.256954000
C	0.318200000	-0.659704000	-1.256954000
H	-1.816717000	0.592600000	0.000000000
H	-0.876505000	1.803417000	0.886375000
H	-0.876505000	1.803417000	-0.886375000
H	1.236570000	0.812776000	0.000000000
H	-0.585386000	-1.280771000	1.290810000
H	1.184708000	-1.328777000	1.278998000
H	0.337765000	-0.047918000	2.164877000
H	-0.585386000	-1.280771000	-1.290810000
H	0.337765000	-0.047918000	-2.164877000
H	1.184708000	-1.328777000	-1.278998000
14			
(E)-but-2-ane			
C	0.704814000	1.820298000	0.000000000
C	0.704814000	0.294113000	0.000000000
C	-0.704814000	-0.294113000	0.000000000
C	-0.704814000	-1.820298000	0.000000000
H	0.188158000	2.209779000	0.883837000
H	0.188158000	2.209779000	-0.883837000
H	1.721212000	2.224575000	0.000000000
H	1.249565000	-0.076964000	0.878126000
H	1.249565000	-0.076964000	-0.878126000
H	-1.249565000	0.076964000	-0.878126000
H	-1.249565000	0.076964000	0.878126000
H	-1.721212000	-2.224575000	0.000000000
H	-0.188158000	-2.209779000	0.883837000
H	-0.188158000	-2.209779000	-0.883837000

15			
(E)-but-2-ene			
C	-0.326383000	0.580069000	0.000000000
C	0.326383000	-0.580069000	0.000000000
H	-1.417413000	0.566444000	0.000000000
H	1.417413000	-0.566444000	0.000000000
C	0.326383000	1.930669000	0.000000000
C	-0.326383000	-1.930669000	0.000000000
H	-0.032478000	-2.513587000	0.880427000
H	-1.416586000	-1.840628000	0.000000000
H	-0.032478000	-2.513587000	-0.880427000
H	1.416586000	1.840628000	0.000000000
H	0.032478000	2.513587000	-0.880427000
H	0.032478000	2.513587000	0.880427000
16			
(2E)-pent-2-ene			
C	2.314095000	-0.475261000	0.268047000
C	1.301568000	0.569988000	-0.210535000
C	-0.062964000	-0.022508000	-0.417562000
C	-1.160170000	0.335620000	0.246048000
C	-2.517862000	-0.272036000	0.051547000
H	-0.132949000	-0.822240000	-1.158725000
H	-1.084442000	1.130940000	0.989387000
H	2.000934000	-0.903693000	1.224639000
H	2.397884000	-1.295127000	-0.453050000
H	3.308026000	-0.036515000	0.395398000
H	1.236711000	1.388220000	0.516039000
H	1.659489000	1.009665000	-1.150825000
H	-3.247227000	0.481088000	-0.268021000
H	-2.490794000	-1.061858000	-0.704665000
H	-2.895632000	-0.705300000	0.984558000
17			
(2E)-pentane			
C	-2.087737000	-0.686201000	0.167473000
C	-1.397858000	0.612858000	-0.246114000
H	-1.623234000	-1.556933000	-0.305129000
H	-2.032398000	-0.827405000	1.252942000
H	-3.144187000	-0.681110000	-0.116273000
H	-1.418421000	0.705421000	-1.339990000
H	-1.966593000	1.464569000	0.145544000
C	0.049630000	0.716811000	0.239083000

H	0.067617000	0.686754000	1.338032000
H	0.456416000	1.695525000	-0.048477000
C	0.968945000	-0.377016000	-0.304259000
H	0.891736000	-0.401137000	-1.399776000
H	0.629781000	-1.357571000	0.050730000
C	2.424147000	-0.166949000	0.106336000
H	2.802766000	0.788870000	-0.271303000
H	2.522458000	-0.153609000	1.197253000
H	3.071296000	-0.960391000	-0.278665000
18			
(2Z)-pent-2-ene			
C	-2.157668000	-0.306501000	-0.421749000
C	-1.015663000	-0.162833000	0.590132000
C	0.010326000	0.832747000	0.126525000
C	1.294369000	0.612662000	-0.160571000
C	2.043151000	-0.685516000	-0.070879000
H	-0.369285000	1.846982000	-0.004792000
H	1.886162000	1.462897000	-0.498228000
H	-1.779911000	-0.681064000	-1.377533000
H	-2.924349000	-0.997521000	-0.059313000
H	-2.635896000	0.660617000	-0.608730000
H	-1.429497000	0.172242000	1.550224000
H	-0.560025000	-1.140190000	0.773568000
H	2.868553000	-0.607338000	0.645958000
H	1.409139000	-1.519046000	0.237378000
H	2.488018000	-0.940929000	-1.039284000
19			
(2Z)-pentane			
C	-1.818548000	0.753538000	0.174327000
C	-1.147340000	-0.470732000	-0.450177000
H	-1.113210000	1.577154000	0.316941000
H	-2.639982000	1.118341000	-0.450018000
H	-2.232022000	0.501813000	1.156923000
H	-1.903976000	-1.254866000	-0.566214000
H	-0.805475000	-0.230539000	-1.466300000
C	0.036454000	-1.015801000	0.368373000
H	-0.115502000	-0.771139000	1.429186000
H	0.051833000	-2.110186000	0.308069000
C	1.407278000	-0.498829000	-0.079387000
H	2.180294000	-0.956901000	0.549432000
H	1.597958000	-0.846640000	-1.103214000

C	1.555115000	1.020482000	-0.032216000
H	2.574480000	1.324615000	-0.288218000
H	0.878078000	1.509222000	-0.740322000
H	1.329769000	1.407174000	0.968220000
20			
1,2 Di metgyl cyclo propane			
C	-0.983015000	0.923486000	0.000000000
C	0.245532000	0.490166000	0.753182000
C	0.245532000	0.490166000	-0.753182000
H	-1.826999000	0.237791000	0.000000000
H	-1.259771000	1.972523000	0.000000000
H	0.818353000	1.295146000	1.208149000
H	0.818353000	1.295146000	-1.208149000
C	0.245532000	-0.790236000	-1.556100000
C	0.245532000	-0.790236000	1.556100000
H	-0.406160000	-1.546084000	-1.108730000
H	-0.117937000	-0.607772000	-2.572546000
H	1.251787000	-1.216486000	-1.629081000
H	1.251787000	-1.216486000	1.629081000
H	-0.117937000	-0.607772000	2.572546000
H	-0.406160000	-1.546084000	1.108730000
21			
1,2 Di metgyl cyclo propene			
C	0.000000000	0.000000000	1.391105000
C	0.000000000	0.647537000	0.034858000
C	0.000000000	-0.647537000	0.034858000
C	0.000000000	-1.958662000	-0.652173000
C	0.000000000	1.958662000	-0.652173000
H	0.912511000	0.000000000	1.995747000
H	-0.912511000	0.000000000	1.995747000
H	-0.881068000	-2.541300000	-0.363244000
H	0.000000000	-1.840975000	-1.738686000
H	0.881068000	-2.541300000	-0.363244000
H	-0.881068000	2.541300000	-0.363244000
H	0.881068000	2.541300000	-0.363244000
H	0.000000000	1.840975000	-1.738686000
22			
1,3-Pentadiene(Z)			
C	2.386185000	0.144512000	0.000000000
C	1.101237000	-0.219798000	0.000000000
C	0.000000000	0.740650000	0.000000000

C	-1.309264000	0.457570000	0.000000000
C	-1.947457000	-0.899208000	0.000000000
H	2.674974000	1.192770000	0.000000000
H	3.188346000	-0.585678000	0.000000000
H	0.854201000	-1.278983000	0.000000000
H	0.299494000	1.788083000	0.000000000
H	-2.003506000	1.296454000	0.000000000
H	-1.218572000	-1.711476000	0.000000000
H	-2.589570000	-1.021763000	0.879756000
H	-2.589570000	-1.021763000	-0.879756000
23			
2-Methylbut-1-ene			
C	-1.897352000	0.069688000	-0.379011000
C	-0.803183000	-0.497117000	0.532182000
C	0.590454000	-0.115154000	0.094446000
C	0.898099000	1.358700000	0.048952000
C	1.496741000	-1.033911000	-0.237691000
H	-1.913284000	1.163502000	-0.353795000
H	-1.735338000	-0.242153000	-1.415566000
H	-2.884222000	-0.282783000	-0.066139000
H	-0.969559000	-0.131539000	1.555187000
H	-0.883921000	-1.588740000	0.568655000
H	0.309642000	1.863055000	-0.726222000
H	0.646334000	1.839248000	1.002285000
H	1.955247000	1.539160000	-0.160321000
H	2.500315000	-0.757627000	-0.549409000
H	1.266234000	-2.095358000	-0.207945000
24			
2-Methylbut-2-ene			
C	-1.739392000	-0.815690000	0.000068000
C	-0.445666000	-0.042781000	-0.000004000
C	0.731454000	-0.676023000	0.000031000
C	2.107037000	-0.076409000	-0.000012000
C	-0.622934000	1.452321000	-0.000085000
H	-2.344490000	-0.563945000	-0.879881000
H	-1.567257000	-1.895111000	0.000185000
H	-2.344512000	-0.563761000	0.879948000
H	0.707982000	-1.766396000	0.000117000
H	2.672750000	-0.405010000	-0.879551000
H	2.095891000	1.015122000	-0.000370000
H	2.672570000	-0.404435000	0.879859000

H	-1.198192000	1.767121000	-0.879475000
H	-1.197796000	1.767263000	0.879516000
H	0.320061000	2.000645000	-0.000338000
25			
2-Methylbutane			
C	1.780516000	-0.000029000	-0.519793000
C	0.912273000	-0.000063000	0.738834000
C	-0.603203000	0.000003000	0.481637000
C	-1.060235000	1.257557000	-0.259637000
H	2.841975000	0.000039000	-0.255438000
H	1.595066000	-0.884813000	-1.136689000
H	1.595016000	0.884859000	-1.136563000
H	1.163734000	-0.878612000	1.346829000
H	1.163751000	0.878509000	1.346795000
H	-0.724263000	2.166339000	0.251626000
H	-0.665606000	1.280184000	-1.281506000
H	-2.152272000	1.293270000	-0.330286000
H	-1.089018000	0.000004000	1.467320000
C	-1.060336000	-1.257501000	-0.259674000
H	-0.665592000	-1.280203000	-1.281495000
H	-0.724520000	-2.166308000	0.251651000
H	-2.152364000	-1.293073000	-0.330443000
26			
3-Methylbut-1-ene			
C	1.517055000	-0.862537000	0.318229000
C	0.477587000	-0.019857000	-0.432825000
C	-0.887587000	-0.639452000	-0.271180000
C	-1.965772000	-0.056795000	0.245400000
C	0.538897000	1.437769000	0.013736000
H	1.307767000	-0.848847000	1.393325000
H	1.502760000	-1.905424000	-0.014449000
H	2.526055000	-0.468418000	0.160305000
H	0.729278000	-0.062673000	-1.503161000
H	-0.960847000	-1.676811000	-0.601961000
H	-2.905847000	-0.591711000	0.336269000
H	-1.956820000	0.971942000	0.593763000
H	0.312097000	1.523918000	1.082556000
H	1.540556000	1.846234000	-0.150203000
H	-0.176082000	2.057026000	-0.536608000
27			
Cyclopenta			

C	0.000000000	1.237205000	0.367436000
C	0.340648000	0.685452000	-1.023943000
C	-0.340648000	-0.685452000	-1.023943000
C	0.000000000	-1.237205000	0.367436000
C	0.000000000	0.000000000	1.301698000
H	0.693538000	2.015338000	0.697761000
H	-0.999214000	1.686189000	0.341522000
H	1.425719000	0.553833000	-1.123100000
H	0.009942000	1.338647000	-1.836720000
H	-1.425719000	-0.553833000	-1.123100000
H	-0.009942000	-1.338647000	-1.836720000
H	-0.693538000	-2.015338000	0.697761000
H	0.999214000	-1.686189000	0.341522000
H	-0.877412000	0.005682000	1.954484000
H	0.877412000	-0.005682000	1.954484000
28			
Cyclopenta-1,3-diene			
C	-1.177268000	-0.280759000	-0.000082000
C	-0.735260000	0.988357000	0.000143000
C	0.735254000	0.988361000	-0.000114000
C	1.177270000	-0.280752000	0.000041000
H	-2.209216000	-0.610008000	-0.000131000
H	-1.348626000	1.882297000	0.000233000
H	1.348614000	1.882306000	-0.000183000
H	2.209219000	-0.609995000	0.000059000
C	0.000004000	-1.214780000	0.000009000
H	0.000033000	-1.873598000	-0.879427000
H	-0.000021000	-1.873571000	0.879466000
29			
Pentane			
C	1.275667000	-0.527113000	0.000000000
C	0.000000000	0.312488000	0.000000000
H	1.274183000	-1.185569000	0.878212000
H	1.274183000	-1.185569000	-0.878212000
C	-1.275794000	-0.527541000	0.000000000
H	-0.000235000	0.973329000	0.878523000
H	-0.000235000	0.973329000	-0.878523000
C	-2.540546000	0.327170000	0.000000000
H	-1.273566000	-1.186150000	-0.878131000
H	-1.273566000	-1.186150000	0.878131000
H	-3.444413000	-0.288920000	0.000000000

H	-2.573779000	0.973295000	0.883728000
H	-2.573779000	0.973295000	-0.883728000
C	2.540652000	0.328153000	0.000000000
H	3.444340000	-0.288153000	0.000000000
H	2.573497000	0.974161000	-0.883830000
H	2.573497000	0.974161000	0.883830000
30			
Hexane			
C	0.429918000	1.910882000	0.000000000
C	-0.416794000	0.639666000	0.000000000
H	1.088648000	1.905049000	0.878012000
H	1.088648000	1.905049000	-0.878012000
C	0.416794000	-0.639666000	0.000000000
H	-1.077316000	0.643829000	0.878621000
H	-1.077316000	0.643829000	-0.878621000
C	-0.429918000	-1.910882000	0.000000000
H	1.077316000	-0.643829000	-0.878621000
H	1.077316000	-0.643829000	0.878621000
H	-1.088648000	-1.905049000	0.878012000
H	-1.088648000	-1.905049000	-0.878012000
C	0.416794000	-3.181079000	0.000000000
C	-0.416794000	3.181079000	0.000000000
H	1.062641000	-3.219144000	0.883682000
H	-0.205277000	-4.080748000	0.000000000
H	1.062641000	-3.219144000	-0.883682000
H	-1.062641000	3.219144000	0.883682000
H	0.205277000	4.080748000	0.000000000
H	-1.062641000	3.219144000	-0.883682000
31			
Hex1-ene			
C	3.059992000	-0.191825000	0.443719000
C	2.031872000	-0.193363000	-0.399121000
C	0.770381000	0.599545000	-0.216038000
C	-0.469432000	-0.294413000	-0.100878000
C	-1.763936000	0.502583000	0.045414000
C	-2.993402000	-0.394630000	0.161583000
H	3.053025000	0.421594000	1.341658000
H	3.944231000	-0.796826000	0.270109000
H	2.072945000	-0.824722000	-1.287818000
H	0.634999000	1.279548000	-1.069067000
H	0.857556000	1.227717000	0.679261000

H	-0.348838000	-0.965753000	0.759219000
H	-0.537335000	-0.939318000	-0.988075000
H	-1.874101000	1.172797000	-0.816907000
H	-1.691686000	1.148473000	0.929906000
H	-2.913980000	-1.053717000	1.032463000
H	-3.098725000	-1.028497000	-0.725217000
H	-3.910937000	0.191320000	0.266394000
32			
1,5-Hexadiene			
C	0.758365000	1.082281000	0.132388000
C	-0.758365000	1.082282000	-0.132388000
C	1.443512000	-0.106603000	-0.476858000
C	-1.443512000	-0.106603000	0.476857000
C	2.164328000	-0.995960000	0.198166000
C	-2.164328000	-0.995960000	-0.198166000
H	1.184567000	2.006667000	-0.278514000
H	0.944888000	1.097748000	1.213365000
H	-0.944891000	1.097752000	-1.213365000
H	-1.184567000	2.006667000	0.278517000
H	1.309651000	-0.233049000	-1.552214000
H	-1.309647000	-0.233051000	1.552213000
H	2.634034000	-1.842946000	-0.291621000
H	2.310076000	-0.906735000	1.272141000
H	-2.634031000	-1.842948000	0.291621000
H	-2.310079000	-0.906734000	-1.272140000
33			
Cyclohexane			
C	1.262524000	0.728918000	0.234036000
C	0.000000000	1.457837000	-0.234036000
C	1.262524000	-0.728918000	-0.234036000
C	-1.262524000	0.728918000	0.234036000
C	0.000000000	-1.457837000	0.234036000
C	-1.262524000	-0.728918000	-0.234036000
H	2.158102000	1.246032000	-0.127892000
H	1.303908000	0.752778000	1.332235000
H	-0.000044000	2.491987000	0.127892000
H	0.000029000	1.505607000	-1.332235000
H	1.303879000	-0.752829000	-1.332235000
H	2.158146000	-1.245955000	0.127892000
H	-1.303879000	0.752829000	1.332235000
H	-2.158146000	1.245955000	-0.127892000

H	0.000044000	-2.491987000	-0.127892000
H	-0.000029000	-1.505607000	1.332235000
H	-2.158102000	-1.246032000	0.127892000
H	-1.303908000	-0.752778000	-1.332235000
34			
Cyclohexene			
C	1.493515000	0.041995000	0.112710000
C	0.663935000	1.299645000	0.060049000
C	0.689634000	-1.182733000	-0.330220000
C	-0.663940000	1.299643000	-0.060038000
C	-0.689633000	-1.182730000	0.330228000
C	-1.493513000	0.041991000	-0.112723000
H	2.383076000	0.161360000	-0.517404000
H	1.868656000	-0.105470000	1.135883000
H	1.195274000	2.247684000	0.118372000
H	0.563006000	-1.155757000	-1.420384000
H	1.236070000	-2.101254000	-0.092430000
H	-1.195279000	2.247680000	-0.118380000
H	-1.236069000	-2.101254000	0.092447000
H	-0.563007000	-1.155740000	1.420392000
H	-2.383086000	0.161354000	0.517372000
H	-1.868631000	-0.105478000	-1.135904000
35			
1,3-Cyclohexadiene			
C	0.053086000	1.420006000	0.110022000
C	-0.053086000	0.732806000	1.253379000
C	0.317632000	0.696571000	-1.188121000
C	0.053086000	-0.732806000	1.253379000
C	-0.317632000	-0.696571000	-1.188121000
C	-0.053086000	-1.420006000	0.110022000
H	0.009378000	2.505852000	0.107322000
H	-0.199118000	1.245544000	2.199955000
H	-0.048864000	1.277555000	-2.039930000
H	1.407129000	0.603229000	-1.319023000
H	0.199118000	-1.245544000	2.199955000
H	-1.407129000	-0.603229000	-1.319023000
H	0.048864000	-1.277555000	-2.039930000
H	-0.009378000	-2.505852000	0.107322000
36			
Benzene			
C	0.000000000	1.392899000	0.000000000

C	-1.206286000	0.696449000	0.000000000
C	-1.206286000	-0.696449000	0.000000000
C	0.000000000	-1.392899000	0.000000000
C	1.206286000	-0.696449000	0.000000000
C	1.206286000	0.696449000	0.000000000
H	0.000000000	2.478737000	0.000000000
H	-2.146649000	1.239368000	0.000000000
H	-2.146649000	-1.239368000	0.000000000
H	0.000000000	-2.478737000	0.000000000
H	2.146649000	-1.239368000	0.000000000
H	2.146649000	1.239368000	0.000000000
37			
2,2-Dimethylbutane			
C	-0.891138000	-0.493307000	1.251301000
C	-0.370919000	0.222873000	0.000000000
C	1.169743000	0.270629000	0.000000000
C	1.881540000	-1.081438000	0.000000000
C	-0.891138000	-0.493307000	-1.251301000
C	-0.891138000	1.664786000	0.000000000
H	-0.501945000	-0.023609000	2.162317000
H	-0.601978000	-1.549129000	1.262973000
H	-1.985360000	-0.450049000	1.291227000
H	1.493610000	0.845543000	0.878474000
H	1.493610000	0.845543000	-0.878474000
H	2.966509000	-0.941691000	0.000000000
H	1.627577000	-1.672866000	-0.884945000
H	1.627577000	-1.672866000	0.884945000
H	-0.501945000	-0.023609000	-2.162317000
H	-1.985360000	-0.450049000	-1.291227000
H	-0.601978000	-1.549129000	-1.262973000
H	-0.542658000	2.207179000	0.886401000
H	-1.986701000	1.686130000	0.000000000
H	-0.542658000	2.207179000	-0.886401000
38			
2,3-Dimethylbut-1-ene			
C	0.659232000	-0.195091000	-0.376320000
C	-0.758257000	0.238013000	-0.048663000
C	1.076755000	-1.393536000	0.489668000
C	-1.068744000	1.449914000	0.412114000
C	-1.827608000	-0.802948000	-0.270301000
C	1.691496000	0.922771000	-0.254484000

H	0.649873000	-0.535486000	-1.423394000
H	1.040697000	-1.122393000	1.550654000
H	2.099986000	-1.700065000	0.250914000
H	0.425460000	-2.258481000	0.336733000
H	-2.098779000	1.715751000	0.632887000
H	-0.322860000	2.217576000	0.588034000
H	-1.756161000	-1.611912000	0.465518000
H	-1.728065000	-1.263127000	-1.260728000
H	-2.826508000	-0.367173000	-0.192154000
H	1.774495000	1.264263000	0.783396000
H	1.428232000	1.782970000	-0.876827000
H	2.676389000	0.563342000	-0.567120000
39			
2,3-Dimethylbut-2-ene			
C	0.000000000	0.000000000	0.671173000
C	0.000000000	0.000000000	-0.671173000
C	-0.023373000	1.248611000	1.520147000
C	-0.023373000	-1.248611000	-1.520147000
C	0.023373000	1.248611000	-1.520147000
C	0.023373000	-1.248611000	1.520147000
H	0.927460000	1.370741000	2.054393000
H	-0.801416000	1.159365000	2.288220000
H	-0.218303000	2.163384000	0.961223000
H	0.927460000	-1.370741000	-2.054393000
H	-0.801416000	-1.159365000	-2.288220000
H	-0.218303000	-2.163384000	-0.961223000
H	0.218303000	2.163384000	-0.961223000
H	-0.927460000	1.370741000	-2.054393000
H	0.801416000	1.159365000	-2.288220000
H	0.218303000	-2.163384000	0.961223000
H	-0.927460000	-1.370741000	2.054393000
H	0.801416000	-1.159365000	2.288220000
40			
2,3-Dimethylbuta-1,3-diene			
C	-0.048431000	0.739804000	0.000000000
C	0.048431000	-0.739804000	0.000000000
C	1.232834000	-1.362556000	0.000000000
C	-1.232834000	1.362556000	0.000000000
C	-1.232834000	-1.534469000	0.000000000
C	1.232834000	1.534469000	0.000000000
H	1.292502000	-2.446623000	0.000000000

H	2.175776000	-0.826780000	0.000000000
H	-1.292502000	2.446623000	0.000000000
H	-2.175776000	0.826780000	0.000000000
H	-1.840021000	-1.303373000	0.881915000
H	-1.840021000	-1.303373000	-0.881915000
H	-1.023657000	-2.606232000	0.000000000
H	1.840021000	1.303373000	0.881915000
H	1.840021000	1.303373000	-0.881915000
H	1.023657000	2.606232000	0.000000000
41			
2,3-Dimethylbutane			
C	-0.234895000	0.734238000	0.000000000
C	0.234895000	-0.734238000	0.000000000
H	-1.336373000	0.723893000	0.000000000
H	1.336373000	-0.723893000	0.000000000
C	0.234895000	1.483701000	1.249947000
C	0.234895000	1.483701000	-1.249947000
C	-0.234895000	-1.483701000	1.249947000
C	-0.234895000	-1.483701000	-1.249947000
H	1.327318000	1.431574000	1.339772000
H	1.327318000	1.431574000	-1.339772000
H	-1.327318000	-1.431574000	1.339772000
H	-1.327318000	-1.431574000	-1.339772000
H	-0.043497000	2.540861000	1.194199000
H	-0.199022000	1.076299000	2.166612000
H	-0.043497000	2.540861000	-1.194199000
H	-0.199022000	1.076299000	-2.166612000
H	0.043497000	-2.540861000	1.194199000
H	0.199022000	-1.076299000	2.166612000
H	0.043497000	-2.540861000	-1.194199000
H	0.199022000	-1.076299000	-2.166612000
42			
3,3-Dimethylbut-1-ene			
C	0.353190000	0.000609000	-0.000026000
C	-0.999465000	-0.675214000	-0.000105000
C	-2.191693000	-0.086344000	-0.000016000
C	1.119964000	-0.454409000	-1.251863000
C	1.120240000	-0.455428000	1.251347000
C	0.236688000	1.524864000	0.000626000
H	-0.954618000	-1.766596000	-0.000166000
H	-3.106208000	-0.670982000	0.000021000

H	-2.305984000	0.993632000	-0.000028000
H	1.218068000	-1.545397000	-1.277328000
H	2.127783000	-0.024058000	-1.261702000
H	0.600398000	-0.138891000	-2.162255000
H	1.219797000	-1.546319000	1.275015000
H	0.600027000	-0.142057000	2.162145000
H	2.127460000	-0.023762000	1.262103000
H	-0.296827000	1.880611000	0.888408000
H	-0.297058000	1.881397000	-0.886724000
H	1.233616000	1.977959000	0.000725000
43			
Heptane			
C	0.000000000	3.816380000	-0.355934000
C	0.000000000	2.550538000	0.497249000
C	0.000000000	1.275049000	-0.343162000
C	0.000000000	0.000000000	0.497153000
C	0.000000000	-1.275049000	-0.343162000
C	0.000000000	-2.550538000	0.497249000
C	0.000000000	-3.816380000	-0.355934000
H	0.883668000	3.851044000	-1.001985000
H	-0.883668000	3.851044000	-1.001985000
H	0.000000000	4.719247000	0.261473000
H	0.877995000	2.547991000	1.156034000
H	-0.877995000	2.547991000	1.156034000
H	-0.878586000	1.275903000	-1.003697000
H	0.878586000	1.275903000	-1.003697000
H	0.878658000	0.000000000	1.157453000
H	-0.878658000	0.000000000	1.157453000
H	-0.878586000	-1.275903000	-1.003697000
H	0.878586000	-1.275903000	-1.003697000
H	0.877995000	-2.547991000	1.156034000
H	-0.877995000	-2.547991000	1.156034000
H	0.883668000	-3.851044000	-1.001985000
H	0.000000000	-4.719247000	0.261473000
H	-0.883668000	-3.851044000	-1.001985000
44			
Hept-1-ene			
C	3.692297000	0.028549000	0.511847000
C	2.690421000	0.199001000	-0.345267000
C	1.389176000	-0.548470000	-0.304483000
C	0.188884000	0.381040000	-0.091386000

C	-1.143889000	-0.363761000	-0.086599000
C	-2.344382000	0.555634000	0.129274000
C	-3.670073000	-0.201302000	0.131988000
H	3.631048000	-0.703658000	1.313598000
H	4.608215000	0.607152000	0.445302000
H	2.786275000	0.945692000	-1.134834000
H	1.247545000	-1.094471000	-1.247969000
H	1.421289000	-1.299699000	0.494489000
H	0.316660000	0.918774000	0.856942000
H	0.176568000	1.145757000	-0.880365000
H	-1.264338000	-0.901542000	-1.037704000
H	-1.129179000	-1.131904000	0.699428000
H	-2.221584000	1.091322000	1.079300000
H	-2.357131000	1.322114000	-0.656300000
H	-3.687483000	-0.954244000	0.927060000
H	-4.518051000	0.471536000	0.288407000
H	-3.824438000	-0.720975000	-0.819598000
45			
Cycloheptane			
C	1.540218000	-0.757590000	0.103863000
C	1.539673000	0.758424000	-0.103985000
C	0.303129000	-1.503353000	-0.411665000
C	0.302232000	1.503480000	0.411742000
C	-0.956989000	-1.229545000	0.422263000
C	-1.774812000	-0.000626000	-0.000180000
C	-0.957879000	1.229151000	-0.421999000
H	2.436806000	-1.169628000	-0.374998000
H	1.640684000	-0.971628000	1.177230000
H	2.436076000	1.171097000	0.374675000
H	1.639780000	0.972488000	-1.177384000
H	0.123246000	-1.256849000	-1.467568000
H	0.520383000	-2.577146000	-0.382375000
H	0.122666000	1.256978000	1.467695000
H	0.518925000	2.577387000	0.382331000
H	-1.617911000	-2.103210000	0.393286000
H	-0.651897000	-1.123453000	1.471726000
H	-2.434456000	-0.274800000	-0.832574000
H	-2.435441000	0.272841000	0.831661000
H	-1.619386000	2.102348000	-0.392348000
H	-0.652910000	1.123927000	-1.471587000
46			

Cycloheptene			
C	0.939356000	-1.298189000	-0.289022000
C	-0.427770000	-1.524953000	0.375058000
C	1.639039000	-0.002500000	0.128026000
C	-1.537559000	-0.664007000	-0.178750000
C	0.943343000	1.295358000	-0.289111000
C	-0.423032000	1.526208000	0.375150000
C	-1.535477000	0.668765000	-0.178758000
H	1.595075000	-2.138227000	-0.030196000
H	0.816195000	-1.317336000	-1.379279000
H	-0.705382000	-2.578162000	0.268292000
H	-0.324350000	-1.344353000	1.455986000
H	1.756342000	-0.002621000	1.221614000
H	2.653598000	-0.004169000	-0.288485000
H	-2.393544000	-1.180120000	-0.609202000
H	1.601747000	2.133339000	-0.030454000
H	0.820180000	1.314701000	-1.379352000
H	-0.320020000	1.344939000	1.455997000
H	-0.697460000	2.580291000	0.268765000
H	-2.389773000	1.187633000	-0.609248000
47			
Cyclohepta-1,3-diene			
C	0.626434000	-1.333437000	-0.444722000
C	-0.687971000	-1.403822000	0.344298000
C	1.630982000	-0.320385000	0.096587000
C	-1.648946000	-0.291034000	0.029113000
C	1.200146000	1.118461000	0.116506000
C	-0.025181000	1.648909000	-0.008730000
C	-1.334932000	0.999430000	-0.140935000
H	1.102963000	-2.320040000	-0.433508000
H	0.400314000	-1.100786000	-1.491392000
H	-1.180706000	-2.359727000	0.138085000
H	-0.464456000	-1.405737000	1.421161000
H	1.933505000	-0.610052000	1.113718000
H	2.548954000	-0.385960000	-0.502840000
H	-2.694995000	-0.570273000	-0.079947000
H	2.019096000	1.825928000	0.241881000
H	-0.075849000	2.736268000	0.007137000
H	-2.152030000	1.681646000	-0.367001000
48			
Cyclohepta-1,3,5-triene			

C	0.964691000	1.217230000	-0.203092000
C	1.433199000	0.000827000	0.549650000
C	-0.341603000	1.525117000	-0.283706000
C	0.966111000	-1.216127000	-0.203079000
C	-1.419861000	0.678036000	0.190554000
C	-1.419069000	-0.679659000	0.190528000
C	-0.339831000	-1.525505000	-0.283710000
H	1.702040000	1.858591000	-0.679737000
H	2.518483000	0.001460000	0.668971000
H	0.977725000	0.000561000	1.549688000
H	-0.633152000	2.462759000	-0.752945000
H	1.704202000	-1.856672000	-0.679679000
H	-2.351095000	1.176801000	0.451907000
H	-2.349726000	-1.179516000	0.451856000
H	-0.630301000	-2.463496000	-0.752921000
49			
2,2-Dimethylpentane			
C	-2.154402000	-0.685199000	0.000000000
C	-0.621362000	-0.698299000	0.000000000
C	-0.131793000	0.762807000	0.000000000
C	1.381503000	0.980454000	0.000000000
C	1.737571000	2.466132000	0.000000000
C	-0.131793000	-1.435877000	1.251552000
C	-0.131793000	-1.435877000	-1.251552000
H	-2.541975000	-0.170102000	0.886403000
H	-2.541975000	-0.170102000	-0.886403000
H	-2.554471000	-1.705369000	0.000000000
H	-0.557966000	1.269257000	-0.878932000
H	-0.557966000	1.269257000	0.878932000
H	1.829251000	0.501703000	0.879010000
H	1.829251000	0.501703000	-0.879010000
H	1.326566000	2.965874000	0.883635000
H	2.820398000	2.620465000	0.000000000
H	1.326566000	2.965874000	-0.883635000
H	-0.433818000	-0.905544000	2.162348000
H	-0.557085000	-2.444993000	1.292827000
H	0.958268000	-1.536168000	1.262279000
H	-0.557085000	-2.444993000	-1.292827000
H	-0.433818000	-0.905544000	-2.162348000
H	0.958268000	-1.536168000	-1.262279000
50			

4,4-Dimethylpent-1-ene			
C	-1.066700000	1.348704000	0.637920000
C	-0.793507000	-0.024821000	0.015959000
C	0.454353000	0.031139000	-0.897384000
C	1.710994000	0.497945000	-0.219693000
C	2.755100000	-0.281174000	0.049890000
C	-0.580273000	-1.058089000	1.125718000
C	-1.994208000	-0.437624000	-0.840752000
H	-0.263309000	1.646746000	1.319598000
H	-1.163915000	2.120188000	-0.135275000
H	-1.999296000	1.329605000	1.212801000
H	0.621989000	-0.968812000	-1.319260000
H	0.229350000	0.699988000	-1.740856000
H	1.749439000	1.549144000	0.066591000
H	3.642689000	0.098991000	0.546189000
H	2.757930000	-1.334164000	-0.223691000
H	0.284819000	-0.799812000	1.744369000
H	-1.462190000	-1.114986000	1.773679000
H	-0.406820000	-2.054409000	0.701931000
H	-2.900236000	-0.514094000	-0.229161000
H	-2.182008000	0.296370000	-1.632836000
H	-1.822997000	-1.411237000	-1.314032000

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