The Performance of the Handy/Cohen Functionals, OLYP and O3LYP, for the Computation of Hydrocarbon Pericyclic Reaction Activation Barriers[†]

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The performance of two local exchange functionals, OLYP and O3LYP, developed by Handy and Cohen (*Mol. Phys.* **2001**, *99*, 403), has been assessed for predicting activation barriers and reaction energies for a set of eleven pericyclic reactions for which experimental data are well established. The results are compared to B3LYP and CBS-QB3 results previously reported (Guner et al. *J. Phys. Chem. A* **2003**, *107*, 11445).

Introduction

The performance and reliability of computational methods has often been evaluated through the use of thermodynamic data sets such as G1, G2, and G3, which include atomization energies, ionization energies, electron affinities, and proton affinities.[1] Data sets for activation enthalpies have been developed for only limited types of reactions.[2]

We have recently provided a data set for 11 pericyclic reactions of unsaturated hydrocarbons.[2] This data set includes the electrocyclic reactions, sigmatropic shifts, and cycloadditions and reversions shown in Figure 1. We previously evaluated the performance of ab initio, density functional, CASSCF, CASPT2, and CBS-QB3 methods in terms of activation enthalpies, reaction energies, and transition-structure geometries. For activation enthalpies, CBS-QB3 and CASPT2 proved to be the most accurate methods. The hybrid density-functional method B3LYP provides reasonably accurate results as well. Interestingly, B3LYP gives good results for hydrocarbon reactions with the relatively small 6-31G(d) basis set, and increasing the size of the basis set results in a small degradation of the quality of the results for those hydrocarbon pericyclic reactions.

The previous publication also provides tables with all relevant experimental data and provides critical evaluations of the accuracies of the data for each of the reactions. In that paper, we compared computational data to the most reliable experimental data.[2]

Handy and Cohen have developed a new local exchange functional OPTX, which is based on the inherent nonseparability of exchange and left−right correlation.[3] We have now evaluated the performance of these Handy/Cohen functionals for the computation of activation enthalpies and reaction enthalpies.

Left−right correlation denotes "static" or "nondynamical" correlation that rectifies the incorrect dissociation limits computed by the Hartree−Fock wave function. The latter can be interpreted as due to the unphysical delocalization of the exchange hole in covalent bond breaking.[4,5] Local approximations for the exchange energy do not have this deficiency and can thus describe bond dissociation better.

The functional form of the Handy−Cohen exchange is derived from Becke's exchange functional.[6] However, its gradient correction term is different, and it gains additional flexibility by abandoning the condition that the functional should reproduce the uniform electron gas limit. The authors argue that the latter condition is not important for molecules. The gradient correction term of the Handy−Cohen exchange functional reproduces the Hartree−Fock energies of isolated atoms better than other functionals.[3] In a later paper,[7] the authors combine their exchange functional with the Lee−Yang−Parr[8] correlation functional, to give the OLYP functional, and also define a hybrid functional, O3LYP, which contains exact (Hartree−Fock) exchange.

Hoe, Cohen, and Handy evaluated the performance of this new functional.[9] According to their study, the hybrid functional O3LYP performs better than the popular B3LYP for 93 systems in predicting molecular geometries,[10] and OLYP performs better than BLYP in predicting thermochemistry and molecular geometries.

Baker and Pulay studied the performance of OPTX for predicting geometries, heats of reaction, and activation parameters for 12 organic reactions, comparing the results with the BLYP and B3LYP.[11] They found that OLYP and O3LYP are among the best functionals but are not significantly better than B3LYP. For heats of reaction, OLYP is favored over BLYP and O3LYP over B3LYP. With the larger basis set, 6-311G(2df,2pd), the average error is smaller for OLYP than B3LYP. Two of the reactions studied here were included in that earlier study.[11]

More recently, Pulay and Baker reported an evaluation of OLYP and O3LYP density functionals for predicting atomic excitation energies, ionization potentials, bond dissociation energies, geometries, and vibrational frequencies for first-row transition metals.[12] They found that OLYP performs better than BLYP but O3LYP and B3LYP are the same in quality for molecular calculations. For atomic excitation and ionization energies, OLYP and O3LYP give quite inferior results as compared to BLYP and B3LYP.

Magyarfalvi and Pulay investigated several methods including OLYP for NMR shieldings.[13] The OLYP functional provides better results for magnetic shieldings than either BLYP or

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TSP Data Set
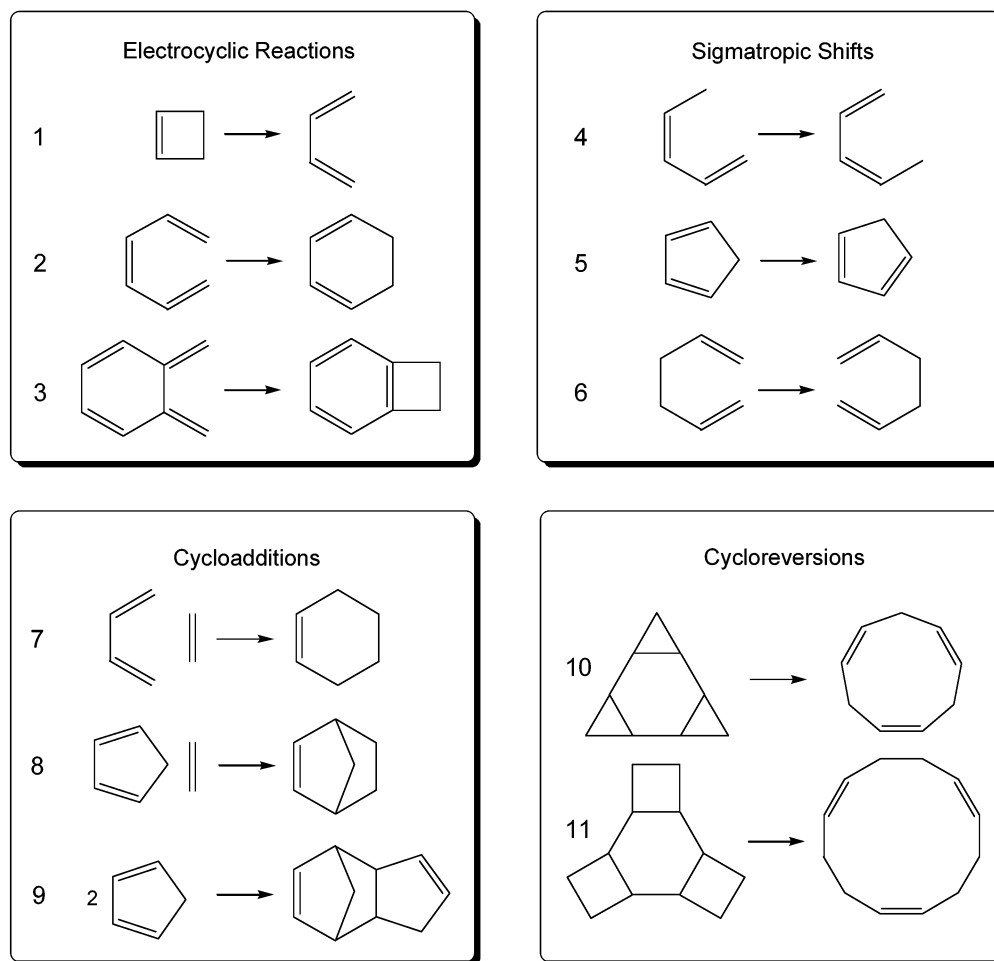
Figure 1. Eleven pericyclic reactions of hydrocarbons used for benchmarking.

B3LYP, but for ^{13}C shieldings, Hartree−Fock is still a good method.

We have assessed of the performance of newly developed OLYP and O3LYP in predicting activation enthalpies and reaction enthalpies for the test set of 11 pericyclic reactions studied previously.[2]

Computational Methods

B3LYP calculations were performed with Gaussian 98.[14] OLYP and O3LYP calculations were performed with the PQS ab initio program developed by Parallel Quantum Solutions.[15]

B3LYP, OLYP, and O3LYP were each paired with three basis sets, 6-31G(d),[16] 6-311+G(2d,p), and 6-311G(2df,2pd). Geometries were optimized using OLYP with three basis sets and with B3LYP/6-31G(d). O3LYP energies are single-point calculations on the OLYP-optimized geometries for each basis set. B3LYP with 6-311G+G(2d,p) and 6-311G(2df,2pd) are single-point calculations on OLYP-optimized geometries with the corresponding basis set. Energies include zero-point energy corrections, using frequencies computed at the B3LYP/6-31G(d) level, scaled by 0.9804. Since the geometries are all very close, the use of single-point calculations should introduce very small errors.

Frequency calculations were used to characterize reactants and products as minima and saddle points as first-order transition structures. Reported activation enthalpies ($\Delta H^{\ddagger}_{0K}$) cor-

respond to 0 K and include a zero-point energy (ZPE) correction.

B3LYP, the most popular density functional, is a combination of the Dirac−Slater exchange term,[17] Becke's 1988 nonlocal exchange functional (B88),[18] Vosko, Wilk, and Nusair's local correlation functional (VWN),[19] Lee, Yang, and Parr's nonlocal correlation functional (LYP),[20] and 20% of exact Hartree−Fock exchange.[21] It is defined as

$$B3LYP = 0.2XHF + 0.8XS + 0.72XB88 + 0.19VWN + 0.81LYP$$

The O3LYP functional replaces B88 with the OPTX functional using a different mixing coefficient (0.81 instead of 0.72), and it replaces the local correlation function VWN with VWN5.[9] Additionally, the amount of exact Hartree−Fock exchange is reduced from 20 to 12%. O3LYP is defined as

$$O3LYP = 0.1161XHF + 0.9262XS + 0.8133OPTX + 0.19VWN5 + 0.81LYP$$

OLYP is a nonhybrid method that does not include an exact exchange. In principle, such methods should be much faster for large systems than hybrid density functional methods, including exact exchange.

Results

Table 1 lists both the computed and experimental activation enthalpies and heats of reaction. Evaluation of the experimental

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TABLE 1: Computed and Experimental Enthalpies of Activation ($\Delta H^{\ddagger}_{0K}$)* and Energies of Reaction (ΔH_{rxn0K}) for 11 Pericyclic Reactions of Hydrocarbons, from the Literature or Reported Here

method		reactions 1	2	3	4	5	6	7	8	9	10	11
OLYP/6-31G(d)	$\Delta H^{\ddagger}$	33.8 33.8[a]	28.9	23.6	33.5	23.4	30.8	26.7 25.2[a]	23.9	24.1	21.2	48.7
	ΔH_{rxn}	−9.7 −9.7[a]	−11.4	−17.2	0.0	0.0	0.0	−33.4 −35.2[a]	−16.3	−7.4	−11.3	−7.0
OLYP/6-311+G(2d,p)	$\Delta H^{\ddagger}$	31.7	29.3	23.4	33.2	21.9	33.1	30.1	27.7	28.0	18.7	45.1
	ΔH_{rxn}	−11.9	−9.3	−14.8	0.0	0.0	0.0	−26.4	−9.5	0.8	−15.8	−13.0
OLYP/6-311G(2df,2pd)	$\Delta H^{\ddagger}$	32.3 32.4[a]	29.4	23.5	33.2	21.8	32.6	29.2 27.7[a]	26.5	26.8	20.3	45.7
	ΔH_{rxn}	−11.5 −11.5[a]	−9.4	−15.3	0.0	0.0	0.0	−27.6 −29.4[a]	−11.0	−2.0	−12.9	−11.9
O3LYP/6-31G(d)// OLYP/6-31G(d)	$\Delta H^{\ddagger}$	35.6 35.6[a]	29.7	24.9	35.2	24.4	33.0	26.8 25.4[a]	23.9	24.1	24.5	53.4
	ΔH_{rxn}	−9.1 −9.1[a]	−13.6	−18.4	0.0	0.0	0.0	−37.3 −39.1[a]	−19.7	−11.4	−10.2	−5.0
O3LYP/6-311+G(2d,p)// OLYP/6-311+G(2d,p)	$\Delta H^{\ddagger}$	33.4	30.3	24.8	34.9	22.8	35.1	30.1	27.5	27.7	21.7	49.6
	ΔH_{rxn}	−11.6	−11.2	−15.7	0.0	0.0	0.0	−30.3	−12.9	−3.3	−15.2	−11.5
O3LYP/6-311G(2df,2pd)// OLYP/6-311G(2df,2pd)	$\Delta H^{\ddagger}$	34.0 34.1[a]	30.4	24.9	34.9	22.6	34.6	29.3 27.9[a]	26.5	26.8	23.4	50.1
	ΔH_{rxn}	−11.5 −11.1[a]	−9.4	−15.3	0.0	0.0	0.0	−27.6 −33.1[a]	−11.0	−2.0	−12.9	−11.9
B3LYP/6-31G(d)	$\Delta H^{\ddagger}$	33.9	30.1	27.3	36.6	26.6	34.1	24.9	22.2	21.1	22.0	50.4
	ΔH_{rxn}	−12.7	−12.5	−14.1	0.0	0.0	0.0	−36.6	−18.6	−11.1	−20.8	−13.9
B3LYP/6-311+G(2d,p)// O3LYP/6-311+G(2d,p)	$\Delta H^{\ddagger}$	31.5	30.8	27.5	36.6	25.4	35.2	28.0	25.9	24.8	19.2	46.0
	ΔH_{rxn}	−15.9	−9.7	−10.7	0.0	0.0	0.0	−29.1	−11.1	−3.5	−26.4	−22.4
B3LYP/6-311G(2df,2pd)// OLYP/6-311G(2df,2pd)	$\Delta H^{\ddagger}$	32.0	31.2	27.8	36.9	25.3	35.2	27.6	25.2	24.4	20.5	46.2
	ΔH_{rxn}	−15.8	−9.5	−11.0	0.0	0.0	0.0	−29.6	−11.8	−5.3	−24.1	−21.9
CBS-QB3	$\Delta H^{\ddagger}$	32.0	28.8	25.2	36.8	25.8	33.0	22.9	17.3	11.6	21.5	
	ΔH_{rxn}	−12.6	−14.8	−12.8	0.0	0.0	0.0	−38.3	−24.6	−22.2	−19.8	
Experimental	$\Delta H^{\ddagger\ b}$	31.9	30.2	29.2	36.7	23.7	34.5	23.3	21.6	15.1	24.4	46.5
	ΔH_{rxn}	−10.7	−15.3	−10.5	0.0	0.0	0.0	−39.6	−23.2	−19.7		

[a] Data are taken from ref 11. Energies include zero-point energy corrections, using frequencies computed at the Hartree−Fock level (HF/6-31G*), scaled by 0.89. [b] $\Delta H^{\ddagger}_{0K}$ are reported in ref 2.

TABLE 2: Mean Deviations (MDs), Mean Absolute Deviations (MADs), Standard Deviations (SDs), and Maximum Negative and Positive Errors of Predicted $\Delta H^{\ddagger}_{0K}$ Relative to Experimental Values for Reactions 1−9 (kcal/mol)

| method	MD	MAD	SD	max error negative	max error positive
B3LYP/6-31G(d)	+1.1	1.7	1.9	1.9[a]	6.0[d]
CBS-QB3	−1.4	1.9	1.6	4.3[c]	2.1[d]
B3LYP/6-311G(2df,2pd)// OLYP/6-311G(2df,2pd)	+2.2	2.5	2.9	1.4[a]	9.3[d]
B3LYP/6-311+G(2d,p)// OLYP/6-311+G(2d,p)	+2.2	2.7	3.1	1.7[a]	9.7[d]
O3LYP/6-31G(d)// OLYP/6-31G(d)	+1.3	3.0	2.6	4.3[a]	9.0[d]
OLYP/6-31G(d)	+0.3	3.4	2.6	5.6[a]	9.0[d]
O3LYP/6-311G(2df,2pd)// OLYP/6-311G(2df,2pd)	+2.0	3.6	3.7	4.3[a]	11.7[d]
OLYP/6-311G(2df,2pd)	+2.3	3.8	4.1	4.4[a]	12.6[d]
O3LYP/6-311+G(2d,p)// OLYP/6-311+G(2d,p)	+1.0	4.1	3.5	5.7[a]	9.8[d]
OLYP/6-311+G(2d,p)	+1.4	4.4	4.0	5.8[a]	13.0[d]

[a] Reaction 3: ring closing of *o*-xylylene to benzocyclobutene. [b] Reaction 5: 1,5-H shift of cyclopentadiene. [c] Reaction 8: Diels−Alder reaction between cyclopentadiene and ethylene. [d] Reaction 9: dimerization of cyclopentadiene.

data was explained in our previous paper.[2] Experimental activation enthalpies have been corrected to 0 K for direct comparison to computed values.

Table 2 includes the mean deviation (MD), mean absolute deviation (MAD), standard deviation (SD) of the MAD, and the largest positive and negative errors for the computed 0 K activation enthalpies from the experimental values for the reduced set of nine reactions for which accurate activation energies are believed to be available. We include reactions 10 and 11 for individual comparisons, but as described earlier,[2] the experimental errors in the activation energies of these reactions are too large for inclusion in our benchmarks.

Deviations of calculated activation enthalpies from experimental values by each method are shown graphically in Figure 2. The MAD indicates the types of errors that are typical, the SD (error bars) shows the spread of the error, and the gray box gives the worst absolute errors. Table 2 and Figure 2 also include high-accuracy calculations, CBS-QB3, in addition to the new OLYP and O3LYP results. CBS-QB3 is believed to be relatively accurate but requires much more computer time than the DFT methods.[2]

The differences in performance among all methods are small, but it is clear that B3LYP with a small basis set is more accurate than the other functionals while also requiring modest computer time due to the small basis set. B3LYP/6-31G(d) has the lowest MAD and SD values, which are 1.7 and 1.9 kcal/mol, respectively. As shown in Figure 2, O3LYP, with a given basis set, performs better than the corresponding OLYP calculation, although the differences are small. All of the DFT methods show the largest positive error for reaction 9, the dimerization of
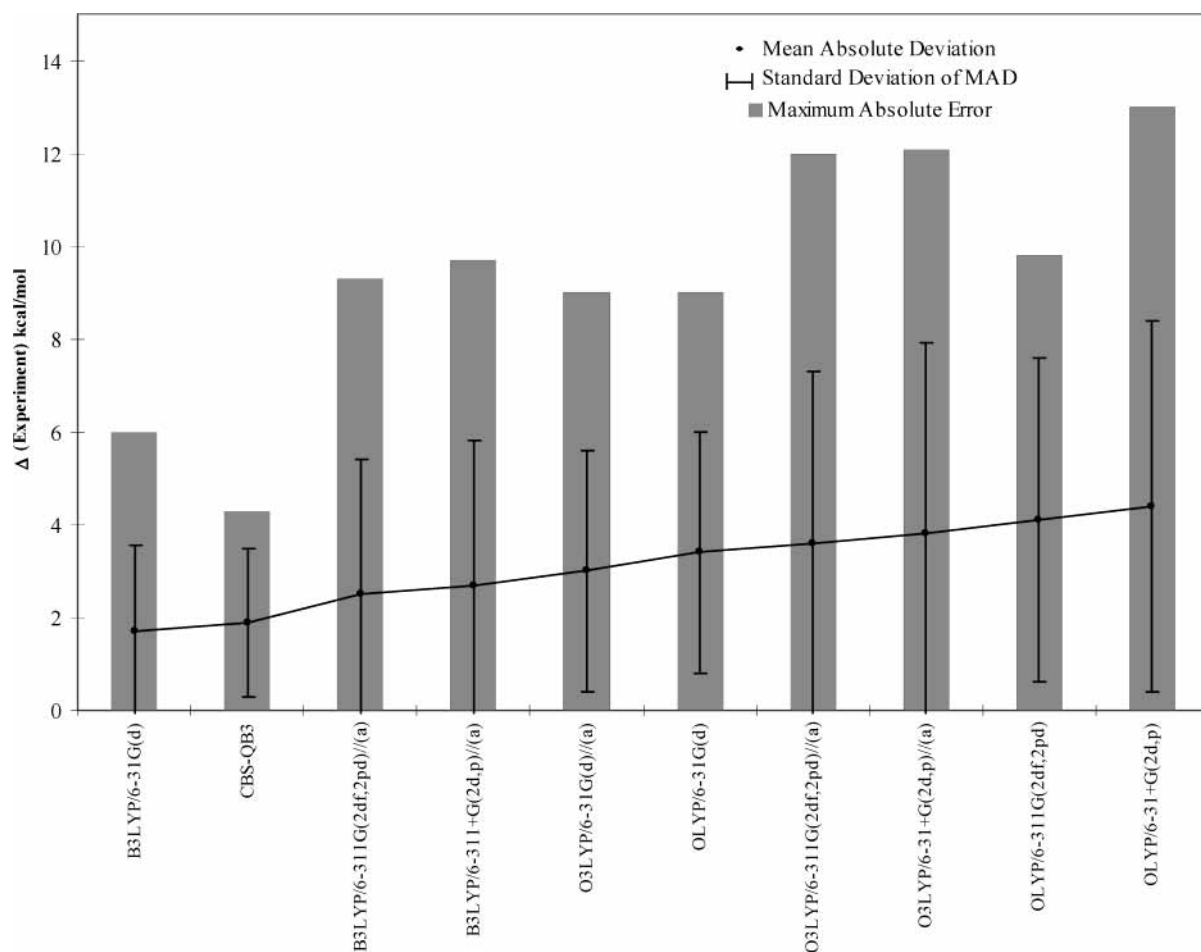
Figure 2. Statistical assessment of performance of different methods for the prediction of $\Delta H^{\ddagger}_{0K}$ for pericyclic reactions 1−9. (a) OLYP with the corresponding basis set.
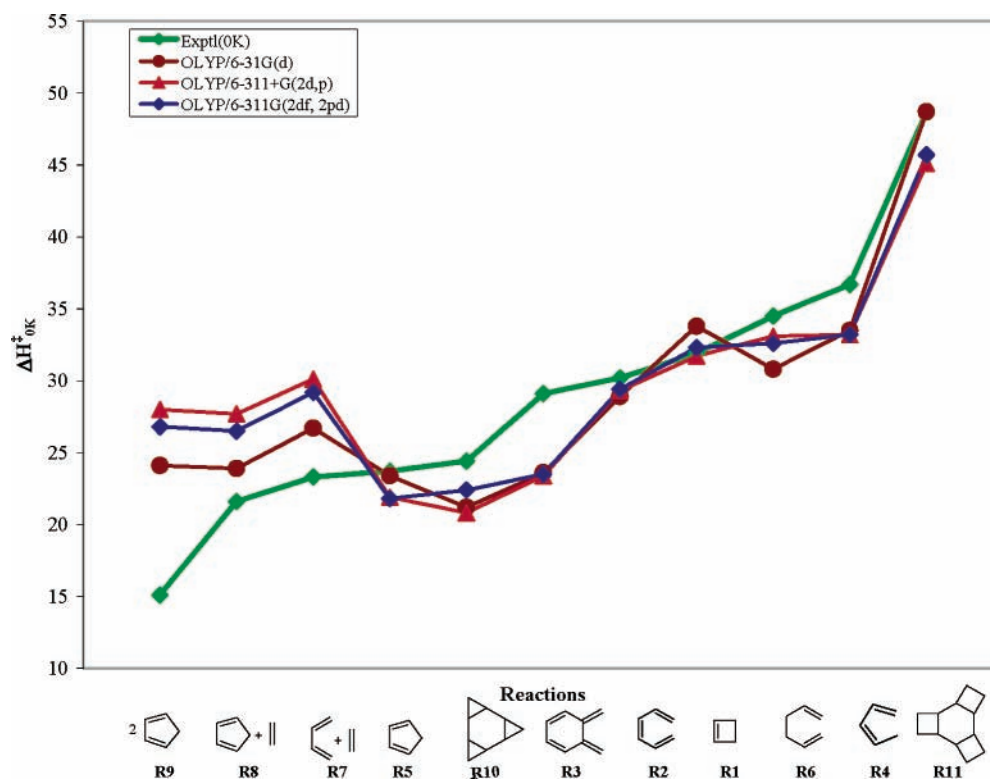
Figure 3. Comparison of experimental activation enthalpies for 11 pericyclic reactions to predictions by OLYP methods with three different basis sets. The data are arranged in order of increasing experimental activation enthalpy.

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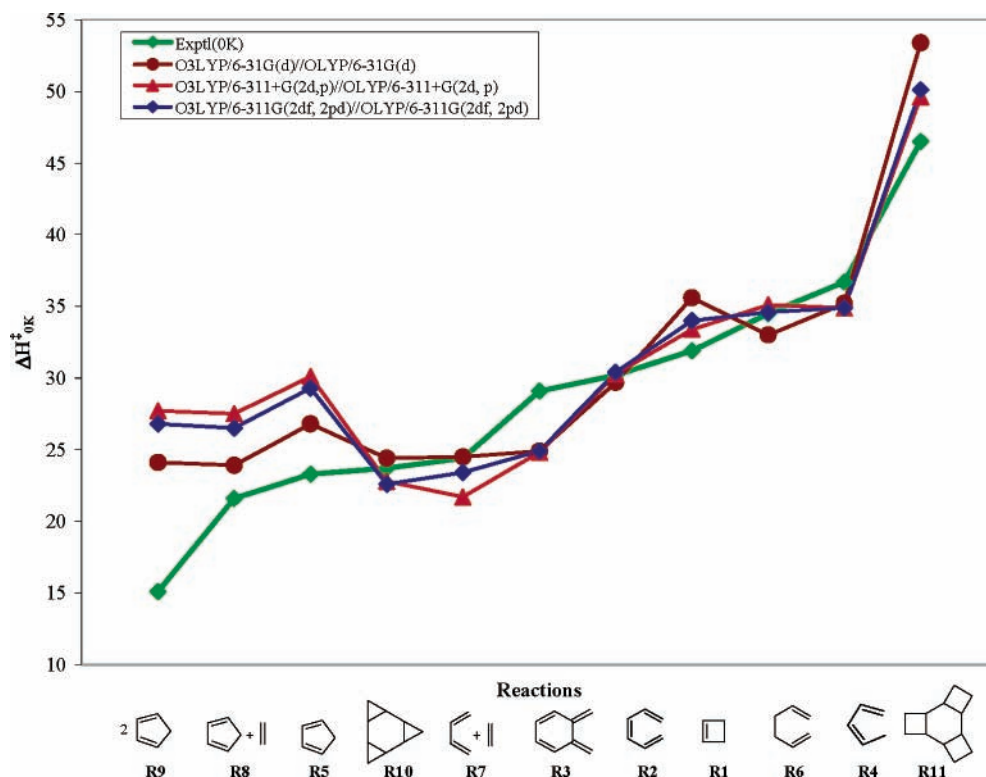
Figure 4. Comparison of experimental activation enthalpies for 11 pericyclic reactions to predictions by O3LYP methods with three basis sets. The data are arranged in order of increasing experimental activation enthalpy.
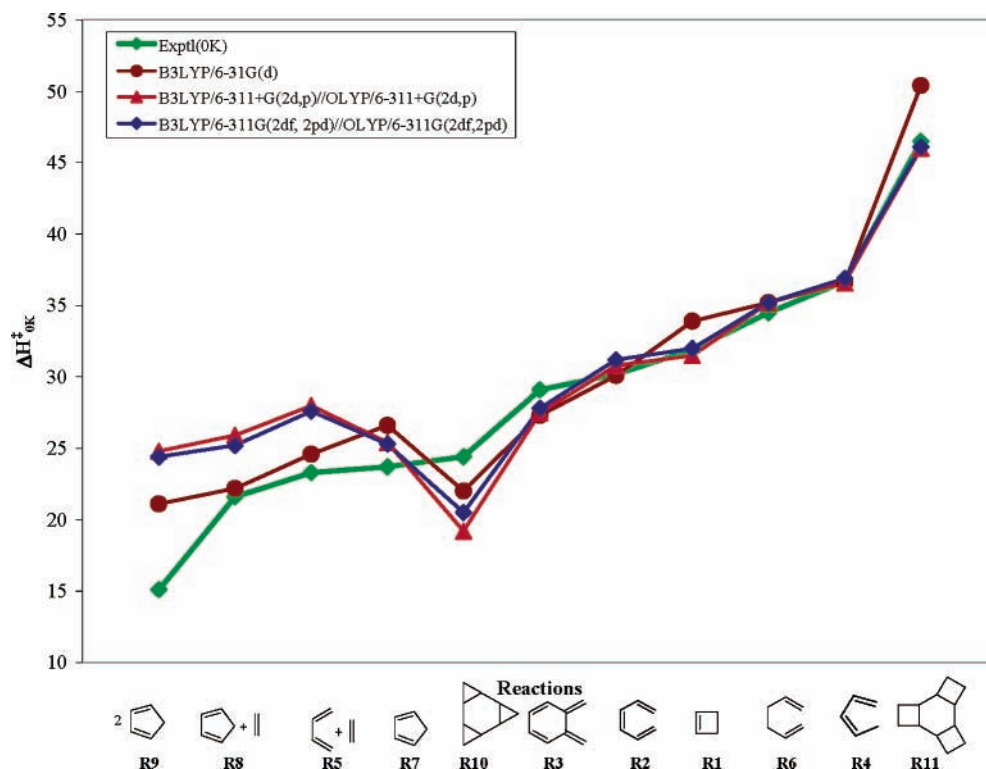

Figure 5. Comparison of experimental activation enthalpies for 11 pericyclic reactions to predictions by B3LYP methods with three basis sets. The data are arranged in order of increasing experimental activation enthalpy.

cyclopentadiene. A majority of the DFT methods show the largest negative error for reaction 3, the ring-closing reaction of *o*-xylylene to benzocyclobutene.

Basis-set effects are shown in Figures 3, 4, and 5 for OLYP, O3LYP, and B3LYP methods. For all methods, OLYP, O3LYP,

and B3LYP, the small basis set, 6-31G(d), provides the best results. This unusual effect was noted earlier,[2] and applies only to these hydrocarbon pericyclic reactions.

Table 3 and Figure 6 compare the ability of the computational methods to predict heats of reactions. Among the DFT methods
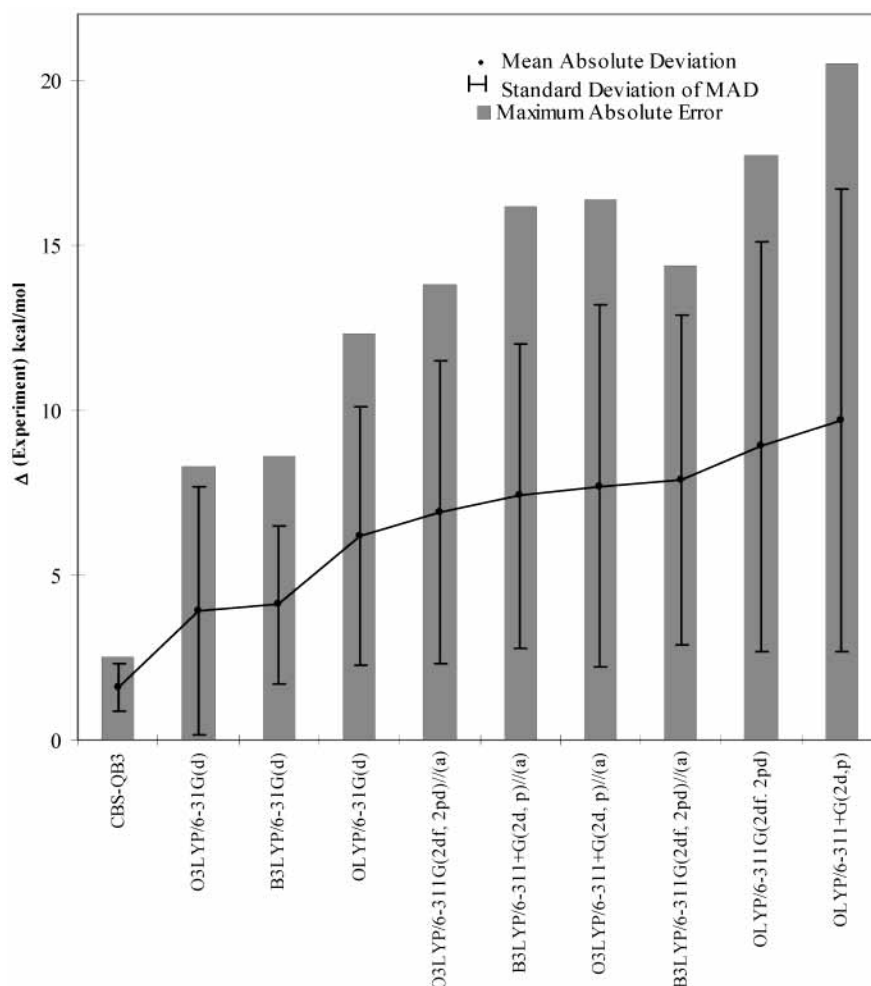
Figure 6. Statistical assessment of performance of different methods for the prediction of ΔH_{rxn} for six pericyclic reactions. Differences are given in kcal/mol, with the computed values subtracted from the experimental values.

TABLE 3: MDs, MADs, SDs, and Maximum Negative and Positive Errors Relative to Experiment for Six Calculated Energies of Reaction (kcal/mol)

	MD	MAD	SD	max error negative	positive
CBS-QB3	−1.0	1.6	0.7	2.5[d]	1.3[c]
O3LYP/6-31G(d)	+1.6	3.9	3.8	7.9[b]	8.3[d]
B3LYP/6-31G(d)	+2.2	4.1	2.4	3.6[b]	8.6[d]
OLYP/6-31G(d)	+3.9	6.2	3.9	6.3[b]	12.9[d]
O3LYP/6-311G(2df,2pd)// OLYP/6-311G(2df,2pd)	+4.8	6.9	4.6	5.7[b]	13.8[d]
B3LYP/6-311+G(2d,p)// OLYP/6-311+G(2d,p)	+6.5	7.4	4.6	5.2[a]	16.2[d]
O3LYP/6-311+G(2d,p)// OLYP/6-311+G(2d,p)	+5.7	7.7	5.5	5.2[b]	16.4[d]
B3LYP/6-311G(2df,2pd)// OLYP/6-311G(2df,2pd)	+6.0	7.9	5.0	5.1[a]	14.4[d]
OLYP/6-311G(2df,2pd)	+7.0	8.9	6.2	4.8[b]	17.7[d]
OLYP/6-311+G(2d,p)	+8.0	9.8	7.2	4.3[b]	20.5[d]

[a] Reaction 1: ring opening of cyclobutene to butadiene. [b] Reaction 3: ring closing of *o*-xylylene to benzocyclobutane. [c] Reaction 7: Diels–Alder reaction between butadiene and ethylene. [d] Reaction 9: dimerization of cyclopentadiene.

studied here, O3LYP with the 6-31G(d) basis set has the lowest MAD value of 3.9 kcal/mol. As for the prediction of activation enthalpies, O3LYP is more reliable than OLYP. B3LYP with the smaller 6-31G(d) basis set provides better results than B3LYP with larger basis sets.

Conclusion

We have investigated the performance of the OLYP and O3LYP density functionals of Handy and co-workers with three basis sets, making comparisons to B3LYP with three basis sets and to CBS-QB3. The reliabilities of these methods were evaluated based on their ability to reproduce experimental values for activation enthalpies and heats of reaction, using nine pericyclic reactions for which accurate experimental values are available.

The new density functional methods, OLYP and O3LYP, give results comparable to B3LYP calculations. B3LYP with a small basis set provides the best activation barrier for this test set of reactions, so this provides a practical method for the exploration of hydrocarbon pericyclic reactions.

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