Assessment of Density Functionals for π Systems: Energy Differences between Cumulenes and Poly-ynes; Proton Affinities, Bond Length Alternation, and Torsional Potentials of Conjugated Polyenes; and Proton Affinities of Conjugated Shiff Bases

Yan Zhao and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431

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Woodcock et al. [*J. Phys. Chem. A* **2002**, *106*, 11923] pointed out that no density functional was able to obtain the correct sign of the relative energies of the allene and propyne isomers of C_3H_4 and that density functional theory (DFT) predicts that poly-ynes are insufficiently stabilized over cumulenes for higher homologues. In the present work, we show that the recent M05 density functional predicts the correct ordering of allene and propyne and gives a mean unsigned error (MUE) of only 1.8 kcal/mol for the relative energies of the two isomers of C_3H_4, C_5H_4, and C_7H_4. Two other recent functionals, M05-2X and PWB6K, also give reasonably low MUEs, 2.7 and 3.0 kcal/mol, respectively, as compared to 6.2 kcal/mol for the popular B3LYP functional. Another challenging problem for density functionals has been a tendency to overpolarize conjugated π systems. We test this here by considering proton affinities of conjugated polyenes and conjugated Schiff bases. Again M05-2X performs quite well, with MUEs of 2.1 and 3.9 kcal/ mol, respectively, as compared to 5.8 and 5.9 kcal/mol for B3LYP. Averaged over the three problems, M05-2X has a MUE of 3.0 kcal/mol, the BMK functional of Boese et al. has an MUE of 3.2 kcal/mol, and M05 has an MUE of 5.1 kcal/mol. Twenty-two other tested functionals have MUEs of 5.2−8.1 kcal/mol averaged over the three test problems. Both M05 and M05-2X do quite well, compared to other density functionals, for torsion potentials in butadiene and styrene, and M05 does very well for bond length alternation in conjugated polyenes. Since the M05 functional has broad accuracy for main group and transition metal chemistry and M05-2X has broad accuracy for main group chemistry, we conclude that significant progress is being made in improving the performance of DFT across a wide range of problem types.

1. Introduction

There is increasing concern that Kohn−Sham density functional theory (DFT) is less accurate for π electrons than for σ electrons. This could perhaps be explained by the lower HOMO−LUMO gap in π systems, which means that molecules with π bonds (like ethylene) are less dominated by single configuration state functions than are σ-bonded molecules (like ethane). Since DFT is grounded in a single-configuration noninteracting-electron reference state, it might be less accurate for multi-configurational systems.[1−5] However, including near-degeneracy multi-configurational character in a wave function is known as static correlation, and it has been known for a long time that DFT exchange functionals include some static correlation.[6−8] Therefore it is of interest to make a more systematic examination of the ability of DFT to treat π electron systems.

We begin by summarizing some examples of problematic DFT performance for π electron systems. Choi et al.[9] showed that several density functionals overestimate the torsion barrier in butadiene but not 1-butene, suggesting that DFT overestimates the conjugation energy. Similar problems were studied by Sancho-Garcia and co-workers,[10−14] who related them to DFT self-interaction error. Fabiano and Sala[15] found that orbital-dependent self-exchange-free-exchange functionals, when combined with a correlation potential, give reasonably accurate torsion potentials for conjugated π systems. Champagne et al. calculated electronic response properties of conjugated polyacetylenes[16] and push−pull π-conjugated systems,[17] and they found that DFT overestimates the polarizabilities and hyperpolarizabilities with too steep dependence on chain length. They attributed this primarily to the exchange functional causing too much charge transfer, which might result from too small of a HOMO−LUMO gap. Inclusion of Hartree−Fock (HF) exchange seems to remedy the problem[18,19] and to make the band gap more accurate,[20] with the difficulty that the results are very sensitive to the details of the functional. Woodcock et al. studied the energetic errors in DFT calculations of cumulenes (e.g., penta-1,2,3,4-tetraene) and poly-ynes (e.g., penta-1,3-diyne). DFT was found to disfavor the former too weakly as compared to the latter, and all examined functionals favor allene over propyne, whereas experimentally the latter is more stable.[21,22] Jacquemin et al.[23−25] found that DFT underestimates bond-length alternation (BLA) in polymethineimine [(−CH=N−)$_n$] and in (=B=P=)$_n$, and they interpreted this as another manifestation of DFT overestimating the polarizability of the conjugated chains. Ciofini et al.[26] found that correcting for self-interaction errors greatly improves the predictions of BLA.

Although the self-interaction error of DFT functionals is often blamed for the inaccuracy of DFT, it has been shown that correcting this problem may give worse results by disrupting a delicate cancellation of error.[27] Thus it may be necessary to

* To whom correspondence should be addressed. E-mail: truhlar@umn.edu.

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TABLE 1: Tested DFT Methods[a]

method	year	refs	exchange $\rho,\nabla\rho$	X	τ	UEG	correlation $\rho,\nabla\rho$	τ	ScorF	UEG
SPWL[b]	1992	34, 30	Slater	0	no	yes	PW91-L	no	no	yes
B3LYP	1994	31, 32, 35, 81	B88	20	no	yes	LYP	no	yes	no
B1B95	1996	31, 37	B88	28	no	yes	B95	yes	yes	yes
PBE	1996	36	PBE	0	no	yes	PBE	no	no	yes
mPW1PW91[c]	1998	33, 38	mPW	25	no	yes	PW91	no	no	yes
B98	1998	40	B98	21.98	no	no	B98	no	no	no
B97-1	1998	39	B97-1	21	no	no	B97-1	no	no	no
PBEh[d]	1999	41	PBE	25	no	yes	PBE	no	no	yes
MPW1K	2000	42	mPW	42.8	no	yes	PW91	no	no	yes
B97-2	2001	39	B97-2	21	no	no	B97-2	no	no	no
O3LYP	2002	43	OPTX	11.6	no	no	LYP	no	no	no
τ-HCTHh	2002	45	τ-HCTHh	15	yes	no	τ-HCTHh	no	yes	no
TPSS	2003	46	TPSS	0	yes	yes	TPSS	yes	yes	yes
TPSSh	2003	47	TPSS	10	yes	yes	TPSS	yes	yes	yes
X3LYP	2004	32, 48	X	21.8	no	yes	LYP	no	yes	no
BB1K	2004	31, 37, 49	B88	42	no	yes	B95	yes	yes	yes
OHandHB95	2004	12, 31, 44	O	50	no	no	B95	yes	yes	yes
BMK	2004	51	BMK	42	yes	no	BMK	no	no	no
MPW1B95	2004	37, 38, 50	mPW	31	no	yes	B95	yes	yes	yes
MPWB1K	2004	37, 38, 50	mPW	44	no	yes	B95	yes	yes	yes
PW6B95	2005	52	PW6B95	28	no	yes	PW6B95	yes	yes	yes
PWB6K	2005	52	PWB6K	46	no	yes	PWB6K	yes	yes	yes
B97-3	2005	53	B97-2	26.93	no	no	B97-3	no	no	no
M05	2005	28	M05	28	yes	yes	M05	yes	yes	yes
M05-2X	2005	29	M05-2X	56	yes	yes	M05-2X	yes	yes	yes

[a] Column headings are explained in section 2. [b] The Slater−Perdew−Wang−Local (SPWL) functional is strictly local (depends on ρ, not ρ and $\nabla\rho$) and is sometimes called a local spin density approximation (LSDA). [c] Also called mPW0, mPW1PW, and MPW25. [d] Also called PBE0 or PBE1PBE.

develop better functional forms for density functionals that are not so sensitive to replacing local exchange approximations, with their favorable cancellation of error, by nonlocal HF exchange, which has no self-interaction energy. Recently progress has been achieved in this direction, resulting in the M05[28] and M05-2X[29] functionals.

In the present article, we will study the performance of these new functionals and 23 other functionals[12,28−53] for 5 problems involving π systems: (i) the cumulene vs poly-yne problem; (ii) proton affinities of conjugated polyenes; (iii) proton affinities of conjugated Schiff bases; (iv) BLA of butadiene and octatetraene; (v) the torsional potentials of butadiene and styrene, which are prototype conjugated π systems.

Proton affinities of Schiff bases are very important[54,55] for light-dependent biological functions, and the ability to calculate proton affinities of bases is also important for calculating the pK_a of their conjugate acid. The emphasis on proton affinities in the present work though is motivated by the fact that adding a proton to one end of a chain molecule is a very physical way to exert an electrostatic field on such a molecule. The proton affinity is increased in conjugated systems by charge delocalization along the conjugated chain.[54,55] Any deficiencies of theoretical models in describing the polarization of the system by the added charge are measured in chemical energy units, rather than units of polarizability or hyperpolarizability, so we can gauge the results in comparison to previous assessments[29,51,56] of DFT for thermochemistry. For this purpose the present article also reports new tests of the 25 density functionals for the calculations of proton affinities of eight small molecules, seven of which have only σ bonds. Comparing the errors for the small-molecule set to the errors for the conjugated molecules allows us to ascertain whether and to what extent conjugated π systems pose a special problem for DFT.

2. Data Sets and Computational Methods

The best estimates of the energy separations of the cumulenes and poly-ynes isomers are taken from the paper by Woodcock et al.[21] The best estimates of the proton affinities of the eight small molecules are zero-point-exclusive equilibrium proton affinities, which were obtained from experimental data and corrected for zero point energy and thermal vibrational−rotational contributions; these data were taken from the Supporting Information of a paper by Parthiban and Martin.[57]

The best estimates of proton affinities of the conjugated polyenes and Schiff bases are obtained as part of the present study by estimating the complete basis set (CBS) limit of coupled cluster theory with single and double excitations and a quasiperturbative treatment of triple excitations,[58] CCSD(T). We estimated the CCSD(T)/CBS limit of proton affinities via[59,60]

$$\Delta E[\mathrm{CCSD(T)/CBS}] = \Delta E[\mathrm{MP2/IB}] + (\Delta E[\mathrm{CCSD(T)/SB}] - \Delta E[\mathrm{MP2/SB}]) \quad (1)$$

where SB denotes small basis and IB denotes an infinite-basis-set calculation that involves the separate extrapolation of HF and correlation energies.[61,62] The HF energies are extrapolated by

$$E^{\mathrm{HF}}(n) = E^{\mathrm{HF}}_{\infty} + A^{\mathrm{HF}} n^{-\alpha} \quad (2)$$

and the MP2 correlation energies are extrapolated by

$$E^{\mathrm{cor}}(n) = E^{\mathrm{cor}}_{\infty} + A^{\mathrm{cor}} n^{-\beta} \quad (3)$$

where α and β are parameters, and n represents the highest angular momentum in an augmented correlation-consistent basis set; $n = 2$ for the aug-cc-pVDZ[63] basis, and $n = 3$ for the aug-cc-pVTZ[63] basis. The value used for α is 4.93, and that for β is 2.13 as determined in a previous paper.[62] We use the a VDZ basis set (which employs cc-pVDZ for the H atom and aug-cc-pVDZ for heavy atoms) for the ($\Delta E^{\mathrm{CCSD(T)}} - \Delta E^{\mathrm{MP2}}$) term in eq 1.

Torsion potentials for butadiene and styrene were calculated by fixing the torsion angle and optimizing all other degrees of freedom. In addition, full optimizations were carried out to find the transition state and the global minimum. The best estimates of the accurate results for these torsion potentials are taken from

TABLE 2: Energy Separation (kcal/mol) for the Cumulenes and Poly-ynes Isomers[a]

methods	E(**2**)−E(**1**)	E(**4**)−E(**3**)	E(**6**)−E(**5**)	MUE
best estimate	−1.40	−8.80	−14.30	
M05	−1.02	−6.98	−10.99	1.84
OHandHB95	0.77	−6.18	−11.30	2.60
HF	−0.67	−11.03	−19.35	2.67
M05-2X	1.01	−5.78	−10.77	2.99
PWB6K	1.04	−5.57	−10.41	3.19
MPWB1K	1.12	−5.32	−10.01	3.43
MPW1K	1.24	−5.18	−9.83	3.58
BB1K	1.16	−5.15	−9.71	3.60
BMK	1.35	−4.83	−9.34	3.89
MPW1B95	1.64	−3.79	−7.58	4.93
B1B95	1.72	−3.49	−7.08	5.22
PW6B95	1.78	−3.43	−7.02	5.27
B97-3	1.86	−3.32	−6.90	5.38
mPW1PW91	1.96	−3.07	−6.48	5.63
PBEh	1.96	−3.05	−6.45	5.65
B97-2	2.01	−2.76	−5.95	5.93
X3LYP	2.18	−2.61	−5.83	6.08
B3LYP	2.22	−2.44	−5.54	6.24
B98	2.30	−2.42	−5.60	6.26
B97-1	2.29	−2.36	−5.48	6.32
MP2	−4.61	−15.48	−23.57	6.39
τ-HCTHh	2.51	−1.68	−4.37	6.99
O3LYP	2.51	−1.47	−3.97	7.19
TPSSh	2.53	−1.46	−3.95	7.21
TPSS	2.98	−0.19	−1.97	8.44
PBE	3.10	0.16	−1.43	8.78
SPWL	3.44	0.66	−0.73	9.29

[a] The numbers in bold face are reference data from Woodcock et al.[21] and are used for the calculation of MUE. All other calculations employ the 6-311+G(2df,2p) basis set and the MP2/6-31+G(d,p) geometries (even the HF and MP2 calculations are at this smaller-basis MP2 geometries obtained with this smaller basis set). See Figure 1 for the structures of the compounds **1**−**6**.

CCSD(T)//CCD and CCSD(T)//MP2 calculations extrapolated to an infinite basis by Sancho-Garcia and Perez-Jimenez[10] and by Karpfen and Parasuk;[64] we denote these reference data as "CC/extrap.".

The best estimate of the BLA of a polyene (where BLA is defined more precisely in section 3.7) is

$$\text{BLA (best est.)} = \text{BLA[CCSD(T)/6-31-G(d)]} + \text{BLA[MP2/6-31+G(d,p)]} - \text{BLA[MP2/6-31G(d)]} \quad (4)$$

where the two MP2 calcualtions are from the work of Jacquemin et al.,[24] and the 6-31+G(d,p) calculation is from the present study.

All DFT calculations for isomerization energies, proton affinities, and torsional potentials employ the 6-311+G-(2df,2p) basis set,[65] whereas the 6-31+G(d,p) basis set is employed for BLA calculations. (Although we test only one basis set for each property, we note that the conclusions are expected to also apply to other reasonable basis sets.) The density functionals studied in this work are described in Table 1. In particular, Table 1 gives the following information about each of the functionals: year first published and reference, form used for the dependence on electron density (ρ) and its gradient ($\nabla\rho$) for exchange and correlation, the percentage X of HF exchange, whether kinetic energy density τ is used for exchange or correlation, whether the exchange and correlation functionals satisfy the uniform electron gas (UEG) limit, and whether the correlation functional is self-correlation free (SCorF).

All DFT calculations were carried out using a locally modified Gaussian03[66] program. The CCSD(T) calculations are performed with the MOLPRO program.[67]

3. Results and Discussion

3.1. Cumulenes and Poly-ynes. Table 2 gives the results for the cumulenes and poly-ynes, whose structures, **1**−**6**, are shown in Figure 1. In each case, we show the energy of the alkyne (**2**) or poly-yne (**4** or **6**) minus the energy of the isomeric cumulene (**1**, **3**, or **5**). All energies are zero-point-exclusive electronic energies including nuclear repulsion. The density functionals are listed in order of increasing mean unsigned error (MUE, also called mean absolute deviation) from the best estimate of Woodcock et al.[21] (which is taken from experiment for C_3 and from coupled-cluster calculations for C_5 and C_7).

In addition to showing results for the 25 density functionals of Table 1, Table 2 also shows results for HF[68] and Møller−Plesset second-order perturbation theory[69] (MP2), both with the 6-311+G(2df,2p) basis set. Table 2 shows that HF theory gives surprisingly accurate results, but this clearly arises from cancellation of errors since MP2 is much less accurate. Furthermore HF theory is not generally as accurate as DFT for thermochemistry when tested on broader sets of data, which is a consequence of the neglect of electron correlation in HF theory but not in DFT. Among the density functionals, the three most accurate are also three of the most recent functionals in Table 1, namely, M05, OHandHB95, and M05-2X. This is encouraging in showing the progress in functional development. Fur-

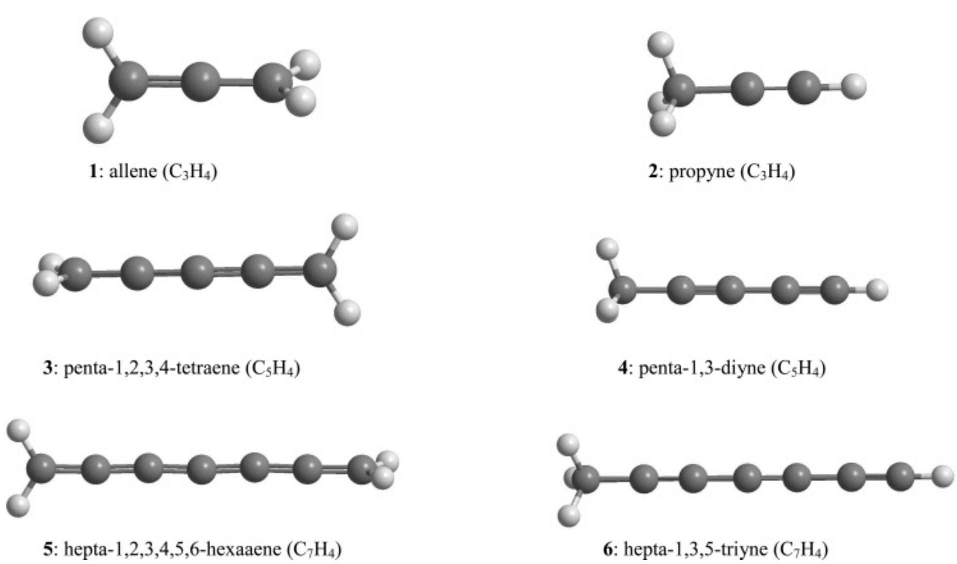

Figure 1. Structures of cumulenes and poly-ynes.

TABLE 3: Proton Affinities (kcal/mol) for Small Molecules

method	NH_3	H_2O	C_2H_2	SiH_4	PH_3	H_2S	HCl	H_2	MSE	MUE
best estimate[a]	211.9	171.8	156.6	156.5	193.1	173.7	137.1	105.9		
MP2/aVTZ[b]	210.5	170.0	155.5	157.0	193.0	172.8	136.8	105.7	−0.6	0.8
X3LYP	210.9	170.2	158.0	157.0	192.4	174.0	137.0	104.1	−0.4	0.9
MPW1B95	212.2	171.6	160.4	157.0	192.0	174.3	137.7	105.1	0.5	1.0
B3LYP	211.3	170.5	158.4	157.4	193.1	174.8	138.0	104.5	0.2	1.0
BMK	211.8	170.7	158.9	156.4	191.2	172.8	136.6	104.1	-0.5	1.1
MPWB1K	213.1	172.4	161.3	156.8	193.1	174.6	137.6	105.2	0.9	1.1
PW6B95	212.2	171.5	160.2	157.9	192.5	174.7	138.0	105.0	0.7	1.1
PWB6K	213.2	172.4	161.2	156.9	193.4	174.5	137.4	104.9	0.9	1.2
PBEH	213.0	172.2	160.7	156.6	192.8	175.0	138.8	106.3	1.1	1.2
B1B95	212.6	172.0	160.8	157.7	192.4	174.9	138.3	105.6	0.9	1.2
M05-2X	210.8	170.2	157.4	158.5	194.0	173.9	136.6	103.1	−0.3	1.2
PBE	210.9	170.4	158.9	157.0	190.3	174.3	138.9	106.0	0.0	1.4
BB1K	213.4	172.7	161.6	157.3	193.5	175.0	138.0	105.6	1.3	1.4
B98	213.3	172.4	160.4	158.2	193.6	175.4	138.7	105.9	1.4	1.4
B97-1	213.2	172.3	160.6	158.3	193.4	175.5	138.8	106.1	1.5	1.5
mPW1PW91	213.6	172.6	161.3	157.7	193.8	175.7	139.1	106.6	1.7	1.7
τ-HCTHh	213.4	172.5	161.1	158.9	193.8	175.8	139.4	106.5	1.9	1.9
M05	210.5	169.9	162.2	159.2	192.6	174.7	137.5	109.5	1.2	2.2
O3LYP	213.6	172.5	162.0	159.7	194.0	176.2	139.8	106.7	2.3	2.3
MPW1K	214.9	173.6	162.5	157.3	195.5	176.1	138.9	106.7	2.4	2.4
B97-3	214.2	172.9	161.3	158.8	195.4	177.0	140.3	107.0	2.5	2.5
TPSS	213.6	172.2	161.2	159.6	195.7	177.0	140.2	108.3	2.7	2.7
TPSSh	214.1	172.7	161.7	159.1	196.1	177.0	140.0	108.0	2.8	2.8
OHandHB95	215.7	174.6	164.6	158.1	195.1	176.2	139.2	106.9	3.0	3.0
B97-2	214.7	173.5	162.7	159.8	195.6	177.1	140.3	107.6	3.1	3.1
SPWL	206.7	167.6	153.4	149.2	183.3	168.5	134.1	102.9	-5.1	5.1

[a] The best estimates are zero-point-exclusive equilibrium proton affinities, which are calculated by using the experimental data, thermal contributions, and zero-point energies given in the Supporting Information of the paper by Parthiban and Martin.[57] All DFT calculations employ the 6-311+G(2df,2p) basis set and the MP2(full)/ 6-31G(2df,p) geometries; the geometries are taken from http://chemistry.anl.gov/compmat/g3theory.htm. [b] aVTZ denotes the aug-cc-pVTZ basis set.

TABLE 4: Proton Affinities (kcal/mol) for the Conjugated Polyenes[a]

method	P-2	P-4	P-6	P-8	P-10	MSE	MUE
best estimate[b]	167.8	193.4	209.7	219.7	225.9		
CCSD(T)/aVDZ[c]	167.8	194.1	210.2	220.0	226.8	0.3	0.3
MP2/aVTZ[c]	166.9	191.7	208.4	218.9	226.2	−1.0	1.0
M05-2X	168.1	195.2	211.9	222.5	229.9	2.1	2.1
SPWL	161.9	187.8	205.4	216.8	225.0	−4.1	4.1
PBE	167.9	196.4	214.3	225.7	234.0	4.2	4.2
BMK	168.7	197.2	214.4	225.3	233.0	4.3	4.3
MPW1B95	169.9	197.3	214.8	225.9	233.9	4.9	4.9
X3LYP	167.8	198.0	215.7	227.0	235.1	5.3	5.3
B1B95	170.3	197.8	215.4	226.5	234.5	5.5	5.5
PW6B95	169.8	198.0	215.6	226.8	234.8	5.6	5.6
MPWB1K	171.2	198.2	215.5	226.5	234.2	5.7	5.7
PBEH	170.4	198.2	215.7	226.8	234.8	5.7	5.7
B3LYP	168.2	198.5	216.3	227.6	235.7	5.8	5.8
PWB6K	171.1	198.6	216.0	226.9	234.6	6.0	6.0
BB1K	171.5	198.6	216.0	227.0	234.7	6.1	6.1
mPW1PW91	171.0	199.3	216.8	228.0	235.9	6.8	6.8
B97-1	170.4	199.9	217.5	228.7	236.7	7.2	7.2
B98	170.2	200.0	217.6	228.9	236.8	7.3	7.3
τ-HCTHh	170.7	200.1	217.8	229.1	237.1	7.5	7.5
B97-3	171.2	200.3	217.9	229.1	237.1	7.7	7.7
MPW1K	172.7	200.6	217.8	228.8	236.5	7.8	7.8
M05	172.2	201.2	218.1	228.8	236.4	7.9	7.9
OHandHB95	174.5	200.5	217.7	228.6	236.2	8.1	8.1
O3LYP	171.3	200.5	218.4	229.8	238.0	8.2	8.2
TPSS	171.1	200.7	218.7	230.3	238.6	8.4	8.4
TPSSh	171.8	200.9	218.8	230.2	238.4	8.6	8.6
B97-2	172.4	201.2	218.8	230.0	238.1	8.7	8.7
HF/aVTZ[c]	175.8	207.5	224.0	234.1	241.0	13.0	13.0

[a] See Figure 2 for the structures of the polyenes. MSE denotes mean signed error. [b] The best estimate are estimated CCSD(T)/CBS results obtained by eq 1. [c] aVDZ is a basis set which employs cc-pVDZ for the H atom and employs aug-cc-pVDZ for other heavier atoms. aVTZ denotes the aug-cc-pVTZ basis set.

TABLE 5: Proton Affinities (kcal/mol) for the Conjugated Schiff Bases[a]

method	SB-2	SB-4	SB-6	SB-8	SB-10	MSE	MUE
best estimate[b]	214.5	226.2	233.4	238.2	241.0		
MP2/aVTZ[c]	213.2	224.8	232.6	237.9	241.8	−0.7	0.8
CCSD(T)/aVDZ[c]	213.6	224.9	231.9	236.4	239.6	−1.4	1.4
SPWL	209.3	223.4	233.4	240.4	245.8	−0.3	2.9
M05-2X	215.7	228.8	237.5	243.4	247.7	3.9	3.9
PBE	213.7	228.2	238.3	245.3	250.7	4.5	4.8
BMK	216.5	229.8	238.7	244.8	249.3	5.1	5.1
X3LYP	215.3	229.6	239.3	246.0	251.1	5.5	5.5
M05	215.3	229.9	239.4	245.9	250.8	5.5	5.5
MPW1B95	216.1	230.2	239.6	246.1	250.9	5.8	5.8
B3LYP	215.6	230.0	239.7	246.5	251.5	5.9	5.9
PW6B95	216.2	230.4	239.9	246.5	251.4	6.1	6.1
B1B95	216.3	230.5	239.9	246.5	251.4	6.2	6.2
PBEH	216.7	230.8	240.3	246.8	251.8	6.5	6.5
MPWB1K	217.5	231.4	240.5	246.8	251.4	6.8	6.8
PWB6K	217.8	231.7	240.8	247.0	251.6	7.0	7.0
B97-1	217.0	231.2	240.8	247.5	252.5	7.1	7.1
BB1K	217.7	231.6	240.8	247.1	251.8	7.1	7.1
B98	217.2	231.5	241.0	247.7	252.7	7.3	7.3
TPSS	216.6	231.1	241.1	248.1	253.5	7.4	7.4
mPW1PW91	217.5	231.6	241.2	247.8	252.7	7.4	7.4
τ-HCTHh	217.1	231.5	241.2	248.0	253.1	7.4	7.4
TPSSh	217.4	231.8	241.5	248.4	253.6	7.8	7.8
B97-3	218.1	232.3	241.7	248.3	253.2	8.0	8.0
O3LYP	217.3	232.0	241.9	248.8	254.1	8.1	8.1
MPW1K	219.4	233.3	242.5	248.7	253.4	8.7	8.7
B97-2	218.6	232.9	242.5	249.2	254.2	8.7	8.7
OHandHB95	220.1	234.0	243.0	249.1	253.6	9.2	9.2
HF/aVTZ[c]	223.0	236.6	245.0	250.3	254.0	11.0	11.0

[a] See Figure 3 for the structures of the conjugated Schiff bases. MSE denotes mean signed error. [b] The best estimate are estimated CCSD(T)/CBS results obtained by eq 1. [c] aVDZ is a basis set which employs cc-pVDZ for H atom and employs aug-cc-pVDZ for other heavier atoms. aVTZ denotes the aug-cc-pVTZ basis set.

thermore the M05 functional, which does the best of any functional in the table, and which is the only functional to predict the correct sign for C_3H_4, has only 28% HF exchange, whereas Woodcock et al.[21] showed that hybrid functionals based on the B88 exchange functional[31] and the LYP correlation functional[32] require 53% HF exchange to get the sign correct and 77% HF exchange to get $\Delta E = -1.0$ kcal/mol. It is encouraging that M05 is the best functional since this functional was specifically

TABLE 6: Overall Performance of DFT Methods for Systematically Tested Energetic Quantities (kcal/mol)

method	πIE3[a] MUE	PA-P5[b] MUE	PA-SB5[c] MUE	SMPA8[d] MUE	MGAE109[e] MUEPB	IP13[f] MUE	MUE-π[g]	MUE-all[h]
M05-2X	2.99	2.07	3.90	1.23	0.48	3.54	2.98	2.37
BMK	3.89	4.29	5.08	1.07	0.47	4.21	4.42	3.17
MPW1B95	4.93	4.93	5.85	1.00	0.62	2.14	5.23	3.24
MPWB1K	3.43	5.67	6.79	1.11	0.98	2.05	5.30	3.34
B1B95	5.22	5.45	6.19	1.20	0.55	2.18	5.62	3.46
M05	1.84	7.92	5.54	2.16	0.53	2.87	5.10	3.48
PWB6K	3.19	6.00	7.04	1.16	1.43	2.28	5.41	3.52
BB1K	3.60	6.10	7.08	1.39	1.34	2.09	5.59	3.60
PW6B95	5.27	5.58	6.14	1.13	0.40	3.24	5.66	3.63
PBEh	5.65	5.73	6.53	1.19	0.91	3.23	5.97	3.87
X3LYP	6.08	5.28	5.50	0.95	1.42	4.73	5.62	3.99
B3LYP	6.24	5.79	5.90	1.02	0.91	4.72	5.98	4.10
B97-1	6.32	7.21	7.06	1.48	0.75	2.84	6.86	4.28
PBE	8.78	4.21	4.81	1.35	3.03	3.58	5.93	4.29
B98	6.26	7.25	7.29	1.44	0.64	3.21	6.93	4.35
mPW1PW91	5.63	6.77	7.42	1.74	0.88	3.72	6.61	4.36
OHandHB95	2.60	8.08	9.20	2.99	1.73	3.04	6.63	4.61
B97-3	5.38	7.67	8.00	2.54	0.59	3.51	7.02	4.62
MPW1K	3.58	7.82	8.73	2.37	2.34	3.53	6.71	4.73
τ-HCTHh	6.99	7.50	7.44	1.87	0.75	4.03	7.31	4.76
O3LYP	7.19	8.18	8.08	2.26	0.76	2.54	7.82	4.84
B97-2	5.93	8.67	8.75	3.10	0.65	2.21	7.78	4.88
TPSSh	7.21	8.57	7.82	2.78	0.98	3.17	7.87	5.09
TPSS	8.44	8.44	7.36	2.67	1.03	3.11	8.08	5.17
SPWL[i]	9.29	4.06	2.94	5.11	16.89	5.18	5.43	7.25

[a] πIE3 denotes the three π isomeric energy differences in Table 2. [b] PA-CP5 denotes the database of the proton affinities of the five conjugated polyenes in Table 4. [c] PA-SB5 denotes the database of the proton affinities of the five conjugated Schiff bases in Table 5. [d] SMPA8 denotes the database of the proton affinities of the eight small molecules in Table 2. [e] MGAE109 denotes a database of 109 atomization energies for main group compounds.[29,70,71] In this case the error is expressed on a per bond (PB) basis. [f] IP13 denotes a database of 13 ionization potentials.[29,72,73] [g] MUE-π is the average of MUEs of the ES3, PA-P5, and PA-SB5 columns. [h] MUE-π is the average of MUEs of all previous columns. [i] This is the SPWL version of the LSDA.

TABLE 7: Torsional Energetics (kcal/mol) of Various Conformation of 1,3-Butadiene Relative to the Global s-trans Minimum

method	basis	ref	s-cis	gauche	TS	MUE
CCSD(T)	extrap.	64	3.47	2.90	6.10	0.00
M05	6-311+G(2df,2p)	this work	3.76	3.26	6.53	0.36
M05-2X	6-311+G(2df,2p)	this work	3.88	3.04	6.65	0.37
BB1K	6-311++G(2df,2p)	13	3.92	3.03	6.82	0.43
OHandHB95	cc-pVTZ	12	4.04	3.34	6.70	0.54
MPW1K	6-311++G(2df,2p)	13	4.06	3.38	6.81	0.59
TPSSHH	cc-pVTZ	14	4.06	3.39	6.89	0.62
BHandHLYP	cc-pVTZ	12	4.10	3.65	6.84	0.71
B97-1	cc-pVTZ	12	3.94	3.49	7.17	0.71
B98	cc-pVTZ	12	3.96	3.51	7.15	0.72
B97-2	cc-pVTZ	12	4.02	3.55	7.12	0.74
B3LYP	6-311+G(2df,2p)	this work	4.05	3.61	7.16	0.78
PBEh	cc-pVTZ	12	4.02	3.48	7.48	0.84
TPSSh	cc-pVTZ	14	4.00	3.62	7.50	0.88
PBE	cc-pVTZ	12	4.04	3.66	7.61	0.95
TPSS	cc-pVTZ	14	4.01	3.70	7.72	0.99

developed[28,29] to perform well for multireference systems such as transition-metal compounds. The M05-2X functional has the wrong sign for ΔE for C_3H_4 but still has an error of only 2.4 kcal/mol for C_3H_4 and an MUE of 3.0 kcal/mol for C_3-C_7. This is relatively very good because we note that the Woodcock et al. challenge to DFT was published in 2002, but only one functional, namely, MPW1K, published prior to 2004 has an MUE below 5.2 kcal/mol. In fact, eight of the nine best performing functionals in Table 1 were published in 2004 or later, again illustrating excellent progress in functional development.

3.2. Proton Affinities of Small Molecules. Before considering proton affinities of conjugated π systems, it is useful to examine proton affinities for a set of small molecules to develop a baseline for judging the quality of proton affinities. Such a study is presented in Table 3, which contains acetylene and seven σ-bonded small molecules. The mean MUE for all 25 density functionals in Table is 1.8 kcal/mol, and if we delete acetylene, this drops to 1.5 kcal/mol. Thus, if the studies of conjugated π systems show typical errors larger than this, it will confirm the troublesome nature of π systems for DFT. It is interesting to notice, though, that the MUE of all 25

TABLE 8: Torsional Energetics (kcal/mol) of the Planar (ΔE^0) and Perpendicular (ΔE^{90}) Conformation of Styrene with Respect to the Global Minimum; Torsional Angle for the Global Minimum (Φ_{min}) Is Also Reported

method	basis	ref	Φ_{min} (°)	ΔE^0	ΔE^{90}	MUE[a]	MMUE[b]	AMUE[c]
CCSD(T)	extrap.	10	13	0.01	3.00	0.00	0.00	d
M05	6-311+G(2df,2p)	this work	0.00	0.00	3.58	0.30	0.33	3.90
M05-2X	6-311+G(2df,2p)	this work	9.89	0.01	3.65	0.33	0.35	2.33
OHandHB95	cc-pVTZ	12	0.00	0.00	3.71	0.36	0.45	5.08
BB1K	6-311++G(2df,2p)	13	0.00	0.00	4.01	0.51	0.47	4.31
MPW1K	6-311++G(2df,2p)	13	0.00	0.00	3.82	0.42	0.50	5.16
BHandHLYP	cc-pVTZ	12	0.00	0.00	3.85	0.43	0.57	n. c.
TPSSHH	cc-pVTZ	14	0.00	0.00	3.93	0.47	0.55	n. c.
B3LYP	6-311+G(2df,2p)	this work	0.00	0.00	4.08	0.55	0.66	4.65
PBEh	cc-pVTZ	12	0.00	0.00	4.10	0.56	0.70	4.65
TPSSh	cc-pVTZ	14	0.00	0.00	4.43	0.72	0.80	6.10
PBE	cc-pVTZ	12	0.00	0.00	4.47	0.74	0.84	4.66
TPSS	cc-pVTZ	14	0.00	0.00	4.59	0.80	0.89	6.28

[a] MUE of previous columns. [b] Mean of MUE in Table 7 and MUE in this table. [c] Average of MUE in Tables 2, 4, and 5 and MMUE in this table. [d] Not calculated.

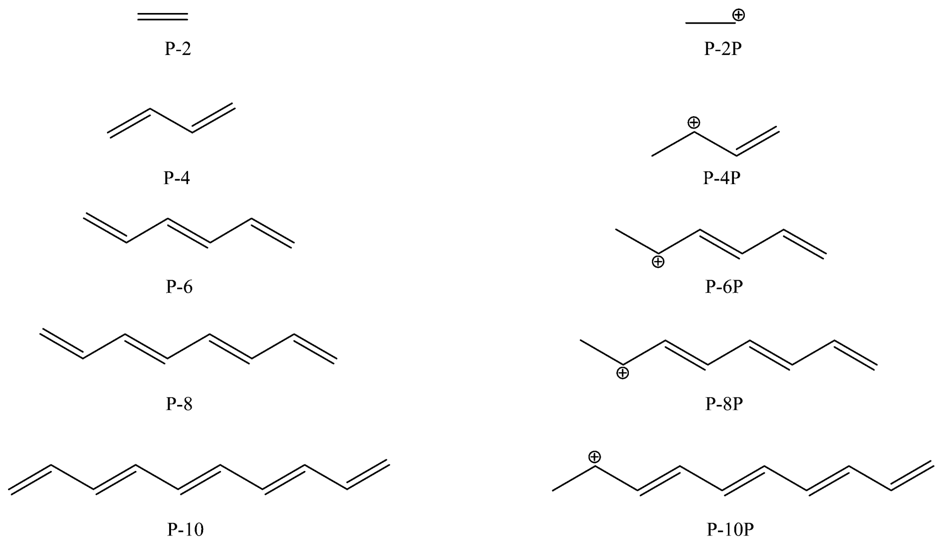

Figure 2. Structures of conjugated polyenes and protonated polyenes.

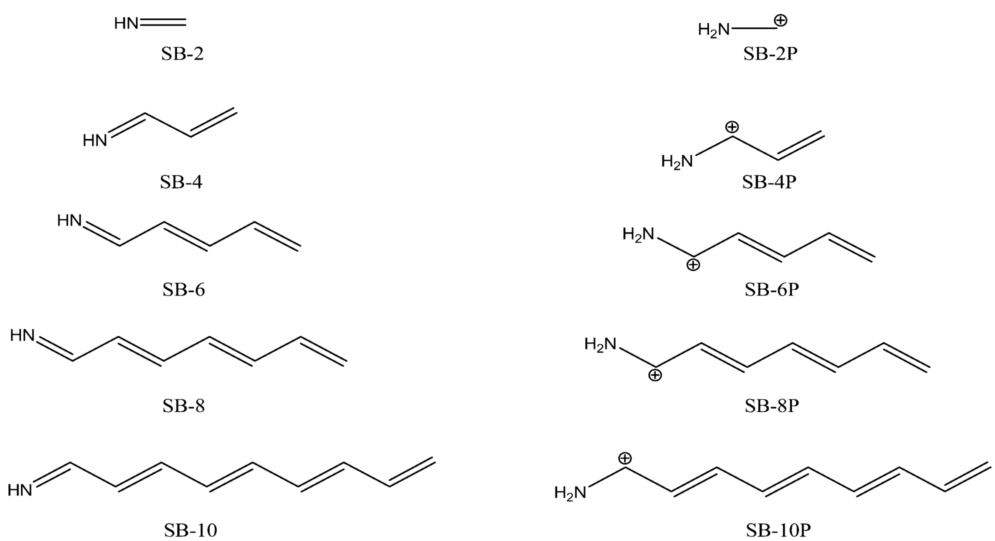

Figure 3. Structures of conjugated Schiff bases and protonated conjugated Schiff bases.

functionals for acetylene is 4.0 kcal/mol. The reader may find it interesting to compare this to the MUE for conjugated π systems.

3.3. Proton Affinities of Conjugated Polyenes. Table 4 shows that the typical errors in proton affinities for conjugated polyene are much larger than those in Table 3. In fact the average MUE for the 25 density functionals in Table 4 is 2.8 kcal/mol for ethylene and 7.7 kcal/mol for the C_4-C_{10} polyenes. These values are considerably larger than average MUE of 1.5 kcal/mol for the seven σ-bonded molecules. However M05-2X has an MUE in Table 4 of only 2.1 kcal/mol, which is comparable to the typical performance (1.8 kcal/mol) of functionals in Table 3 and is only 1.75 times larger than the MUE of M05-2X for proton affinities of small molecules. In fact M05-2X outperforms all other density functionals by a large margin in Table 4.

3.4. Proton Affinities of Conjugated Schiff Bases. The proton affinities of conjugated Schiff bases are 15−44 kcal/mol larger than those for conjugated hydrocarbons with the same chain length, and they show a milder dependence on chain length. M05-2X is again quite accurate followed by an $X = 0$ functional, PBE, and a high-X functional BMK. Since the HF result is itself very bad; it seems that merely including a high percentage of HF exchange is not the key to success. The inclusion of HF exchange in M05-2X and BMK must help in a more subtle way. We conclude that a high percentage of HF exchange is useful only when it is combined with a density functional that is optimized consistently with high HF exchange.

3.5. Combined Assessment for Isomerization and Proton Affinities of π Systems. Table 6 is an attempt to provide a more global assessment of energetic quantities. The first three columns are for the three π-system databases considered above, and the MUE π column is the unweighted average of these three columns. M05-2X is a clear winner (with an MUE π value of 3.0 kcal/mol, as compared to an average MUE π value of 6.1 kcal/mol for all 25 functionals); it is encouraging that eight of the nine best performing functionals for MUE π were published in 2004 or later.

Because of its good performance on metal bonding problems with large near-degeneracy correlation effects, one might have expected M05 to perform better here than M05-2X, and indeed it does for the cumulene vs poly-yne problem. M05 also performs very well in an overall capacity. Its MUE π value of 5.10 kcal/mol is the third best in Table 6, trailing only M05-2X and BMK. We note that the π systems studied here have modest, not large, near-degeneracy correlation effects. Further-

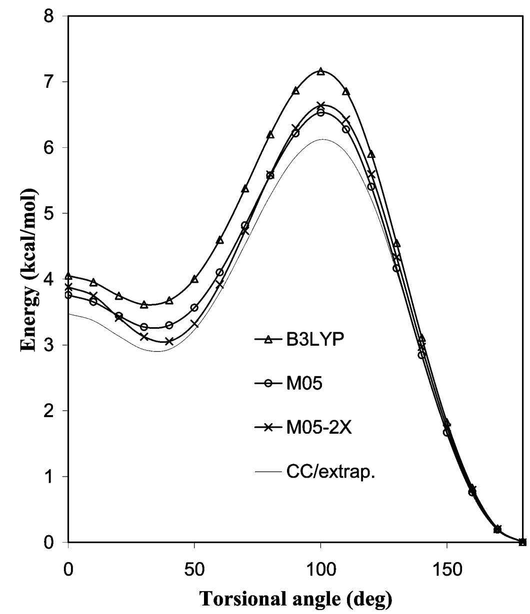

Figure 4. Torsional potential of 1,3-butadiene by B3LYP, M05, and M05-2X.

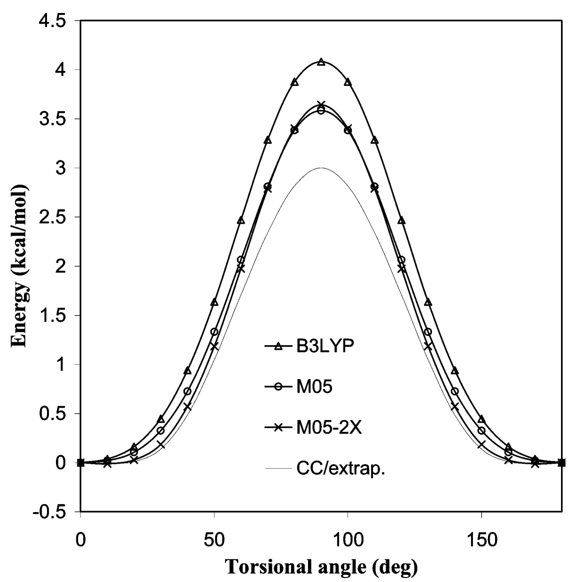

Figure 5. Torsional potential of styrene by B3LYP, M05, and M05-2X.

more success on the proton affinity problem seems to be related more to eliminating spurious self-exchange than to including static correlation, whereas the opposite is true for the cumulene/poly-yne problem.

Table 6 also include the results for the small-molecule proton affinity test set (SMPA8, see Table 3), a test set of main group atomization energies (MGAE109 from previous work[29,70,71]), and a test set of ionization potentials (IP13 from previous work[72,73]). Averaging errors over all six test sets gives MUE-all. By adding diversity to the data, we test whether the functionals that perform well for π systems are also broadly applicable, and we find that they are. By the criterion of the last column of Table 6, M05-2X is the best functional, and MPW1B95 is the best functional with $X \leq 31$. The 10-year-old functional B1B95 also does quite well, as does BMK.

3.6. Torsion Potentials. We calculated the torsion potentials of butadiene and styrene with the M05, M05-2X, and B3LYP functionals, and we compare these to best estimates and several

TABLE 9: BLA (Å) for Butadiene and Octatetraene

method	basis set	ref	$N = 2$	$N = 4^a$	MUE
CCSD(T)	best estimate[b]	this work	0.1126	0.0916	0.0000
MP4	6-31G(d)	24	0.1146	0.0906	0.0015
CCSD(T)	6-31G(d)	24	0.1154	0.0941	0.0027
MP2	6-31G(d)	24	0.1138	0.0864	0.0032
M05	6-31+G(d,p)	this work	0.1140	0.0859	0.0035
MP2	6-31+G(d,p)	this work	0.1110	0.0839	0.0046
PBEh	6-31G(d)	24	0.1157	0.0852	0.0048
mPW1PW91	6-31G(d)	24	0.1164	0.0859	0.0048
B3LYP	6-31+G(d,p)	this work	0.1151	0.0843	0.0049
X3LYP	6-31G(d)	24	0.1173	0.0861	0.0051
B97-2	6-31G(d)	24	0.1158	0.0843	0.0053
B98	6-31G(d)	24	0.1182	0.0867	0.0053
B97-1	6-31G(d)	24	0.1174	0.0856	0.0054
TPSSh	6-31G(d)	24	0.1130	0.0789	0.0066
O3LYP	6-31G(d)	24	0.1089	0.0753	0.0100
M05-2X	6-31+G(d,p)	this work	0.1247	0.1008	0.0107
CCSD	6-31+G(d,p)	this work	0.1213	0.1045	0.0108
TPSS	6-31G(d)	24	0.1090	0.0718	0.0117
CCSD	6-31G(d)	24	0.1233	0.1061	0.0126
PBE	6-31G(d)	24	0.1052	0.0678	0.0156

[a] N is the half of the number of carbon atoms; so $N = 2$ denotes butadiene, and $N = 4$ denotes octatetraene. This is the notation used by Jacquemin et al.[24] [b] See eq 4 for the definition of the best estimate of BLA.

calculations from the literature in Tables 7 and 8 and Figures 4 and 5. The M05 and M05-2X functionals both perform quite well, with errors only about half as large as those for B3LYP and most previously tested functionals. The M05-2X functional is the only one that correctly predicts that the global minimum geometry of styrene is twisted.

3.7. BLA in Polyenes. Table 9 gives results for the alternation of bond lengths in butadiene and octatetraene, a problem studied preveiously by Jacquemin et al.[24] In both cases the central C−C bond is nominally a single bond, and it is flanked by equivalent double bonds. The BLA is defined as the length of the central C−C bond minus the length of either of these flanking bonds. Table 9 shows that the M05 functional is by far the best functional for BLA, and M05-2X has below average performance. Clearly, though, the perception in the literature that this is a peculiar failure of DFT is an oversimplified generalization, since the highly regarded[74,75] ab initio CCSD wave function method, which is usually very good for geometries, is one of the worst performers in Table 9.

4. Conclusions

As anticipated from previous work,[9,12−14,16−23,25,26] this study shows that DFT is less accurate for π-bonded systems than for systems with only σ bonds. However the new M05-2X functional retains its accuracy much better than the other 24 functionals tested here for the energetics of π systems. Furthermore, when the test set is expanded to include proton affinities, atomization energies, and ionization potentials of σ-bonded systems, M05-2X continues to outperform other functionals by a large margin, and it also does quite well for torsion potentials in π-conjugated systems. Moreover, we have shown in other work[29,76−78] that M05-2X gives the best accuracy of existing functionals for noncovalent interactions including dispersion-dominated interactions, dipolar interactions, hydrogen bonding, charge-transfer complexes, and $\pi-\pi$ stacking. We have also shown that M05-2X gives very good accuracy for barrier heights of hydrogen-atom transfer reactions.[29] Thus M05-2X has excellent performance (relative to other existing density functionals) across a broad range of thermochemistry, thermochemical kinetics, and noncovalent interactions for main group chemistry, including both π- and σ-bonded organic systems. Unfortunately the M05-2X is less accurate than MP2 and several other density functionals for bond length alternation in polyenes, although it is still more accurate than CCSD.

The M05 functional is also quite good for energetics, at least when compared to all functionals except M05-2X. In addition it has excellent performance for BLA in polyenes.

One area where M05-2X does not perform well is bond dissociation energies of bonds to transition-metal atoms.[29] The M05 functional provides the best across-the-board performance for simultaneous good accuracy on such systems and on main-group thermochemistry, thermochemical kinetics, and noncovalent interactions.[28,29] In the present study we find that M05 is the best functional for BLA in polyenes, but it has an average MUE of 5.1 kcal/mol for the three energetic π-system databases as compared to 3.0 kcal/mol for M05-2X. Of the 23 other functionals tested, only one, BMK, has a smaller MUE-π than M05, namely, 4.4 kcal/mol. However BMK is not accurate for bond energies of transition-metal atoms.[29] Thus we continue to recommend M05 as a functional with broad accuracy for organometallic chemistry. Three other functionals developed in our group, namely, MPW1B95,[50] MPWB1K,[50] and PWB6K,[52,62,79,80] have MUE-π of 5.2−5.42 kcal/mol, only slightly better than the local spin density approximation value of 5.43 kcal/mol. The other 19 functionals tested have an MUE-π value of 5.6−8.1 kcal/mol, which is worse than the local spin density approximation. Although the local spin density approximation has poor performance for main-group atomization energies (see Table 6) and is not recommended for modern applications of DFT, it does provide a baseline for further functional development. Thus, in developing improved density functionals, we recommend that developers check the MUE-π values to make sure that one does not degrade the accuracy below that of the local spin density approximation.

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