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Benchmarking semiempirical, Hartree-Fock, DFT, and MP2 methods against the ionization energies and electron affinities of short- through long-chain [n]acenes and [n]phenacenes

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2 **Benchmarking semiempirical, Hartree-Fock, DFT, and MP2 methods against the ionization**
3 **energies and electron affinities of short- through long-chain [n]acenes and [n]phenacenes**

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12

Draft

Abstract

14

Vertical and adiabatic ionization energies (IEs) and electron affinities (EAs) were calculated for the $n=1-10$ [n]acenes using a wide range of semiempirical, Hartree-Fock, density functional, and second order Moller-Plesset perturbation theory model chemistries. None of the model chemistries examined was able to accurately predict the IEs or EAs for both short through long [n]acenes, as well as for extrapolations to the polymeric limit, when compared to available experimental and benchmark theoretical data. Except for 6-31G(d), the choice of the basis set does not affect B3LYP results significantly. Analogous calculations using a suite of eight modern and/or popular density functionals for the $n=1-10$ n[phenacenes] revealed similar problems in estimating the IEs and EAs of these compounds, with the sole exception of the M062X functional for AIEs and potentially the APFD, B3LYP, and MN12SX functionals for AEAs. The poor IE/EA prediction performance for the parent [n]acenes and [n]phenacenes may extend to their substituted derivatives and heteroatom substituted analogs. Consequently, caution should be exercised in the application of non-high level calculations for estimating the IE/EA of these important classes of materials.

28

Keywords: [n]acenes; [n]phenacenes; Ionization energies; Electron affinities; Benchmarking; Organic electronics

31

32 Introduction

33

34 The [n]acenes and their derivatives offer potential in the field of organic electronics.¹⁻³ Consequently,
35 the molecular properties of these compounds are of interest, both in terms of experimental
36 measurements as well as the development and application of suitable theoretical methods. Unique
37 challenges exist for computational approaches in dealing with these molecules, as evidenced by the
38 various predictions for the multiplicities and open/closed shell natures of their ground states.⁴⁻¹⁸
39 Notable high-level work by Deleuze and co-workers may have resolved controversies arising from the
40 prior application of lower-level theory, and their results indicate these molecules should be ground state
41 closed shell singlets¹⁹⁻²¹ with positive singlet-triplet gaps that converge on a vanishingly small
42 energetic transition between these multiplicities at the polymer limit (i.e., as $n \rightarrow \infty$). In concert with
43 these efforts, it was recently shown that among the generally available semiempirical, Hartree-Fock
44 (HF), density functional theory (DFT), and second order Moller-Plesset perturbation (MP2) methods,
45 only the B2PLYP and mPW2PLYP functionals (which combine exact HF exchange with an MP2-like
46 correlation to the DFT calculation) appear to accurately describe the singlet-triplet gaps of both the
47 short- through long-chain [n]acenes (e.g., benzene through decacene) as well as extrapolations to the
48 polymeric limit.^{22,23}

49

50 In the current study, we turn our attention to an examination of how well a broad range of
51 semiempirical, HF, DFT, and MP2 methods perform for predicting the ionization energies (IEs) and
52 electron affinities (EAs) of the [n]acenes as well as their "zig-zag" relatives, the [n]phenacenes. In
53 particular, we give special regard as to whether the theoretical approaches meet a required criteria of
54 accurate IE/EA prediction for both short and long homologs. This criteria seems a basic standard to
55 apply for theoretical studies into the use of these types of compounds for organic electronic and related

56 applications. Within this context, the goal of any reasonable theoretical method is to reproduce
57 molecular energies and energy transitions within the bounds of experimental accuracy (generally taken
58 to be ~ 1 kcal/mol = 4.2 kJ/mol). For IEs and EAs, which are commonly reported in units of electron
59 volts (eV; 1 eV = 96.5 kJ/mol), this accuracy requirement means a required absolute error for the
60 computational approach of < 0.04 eV.

61
62 While high-level composite methods and similarly expensive theoretical approaches can achieve
63 thermochemical accuracy for IEs and EAs,²⁴⁻³¹ lower level methods generally have average errors in
64 the range of tens of kJ/mol.³²⁻³⁴ However, high-level methods are presently computationally impractical
65 for mid- through longer-chain [n]acenes, necessitating a move to lower levels of theory to study these
66 compounds. In addition, because of synthetic difficulties, experimental IE data are only available for
67 the n=1-6 [n]acenes and [n]phenacenes and EA data for the n=1-5 [n]acenes and [n]phenacenes.
68 Additional experimental challenges resulted in relatively large uncertainties for some of the IE/EA
69 measurements, which led to the need for subsequent benchmark theoretical investigations^{35,36} that
70 helped better constrain the actual IE/EA values. Thus, in the present work we provide comparisons of
71 model chemistry and basis set dependent IE/EA estimates for the n=1-10 [n]acenes and [n]phenacenes
72 with both the available experimental and benchmark theoretical datasets, and the findings herein should
73 help guide the future development of theoretical methods better suited to model this important class of
74 compounds.

76 **Computational details**

77
78 Geometry optimizations, frequency calculations, and single point energy (SPE) calculations employed
79 Gaussian 09 (G09)³⁷ with various combinations of the following semiempirical, HF, DFT, and MP2

80 model chemistries and basis sets: model chemistries, AM1,³⁸⁻⁴⁰ B1B95,⁴¹ B1LYP,⁴¹⁻⁴³ B2PLYPD,^{44,45}
 81 B3LYP,^{42,43,46} B3P86,^{46,47} B3PW91,^{46,48-50} B97D,⁵¹ B98,^{52,53} BHandH,^{42,43,54-57} BHandHLYP,^{42,43,54-56,58}
 82 BLYP,^{42,43,58} BMK,⁵⁹ CAM-B3LYP,⁶⁰ HCTH/147,⁶¹⁻⁶³ HCTH/407,⁶¹⁻⁶³ HF,⁶⁴⁻⁶⁶ HFB,⁵⁸ HFS,⁵⁴⁻⁵⁶
 83 HSE06,⁶⁷⁻⁷³ LC-wPBE,⁷⁴⁻⁷⁷ M05,⁷⁸ M052X,⁷⁹ M06,⁸⁰ M062X,⁸⁰ M06HF,⁸¹ M06L,⁸⁰ MP2,⁸²⁻⁸⁶
 84 mPW1LYP,^{42,43,87} mPW1PBE,⁸⁷⁻⁸⁹ mPW2PLYPD,^{45,90} mPW3PBE,⁸⁷⁻⁸⁹ O3LYP,^{42,43,91} OPBE,^{88,89,92,93}
 85 OTPSS,⁹²⁻⁹⁴ PBE0,^{88,89,95} PDDG,⁹⁶⁻¹⁰⁰ PM3,^{101,102} PM6,¹⁰³ tHCTH,¹⁰⁴ tHCTHhyb,¹⁰⁴ TPSSh,⁹⁴
 86 VSXC,¹⁰⁵ wB97,¹⁰⁶ wB97X,¹⁰⁶ wB97XD,¹⁰⁷ X3LYP,¹⁰⁸ XAlpha,⁵⁴⁻⁵⁶ APFD and APFD,¹⁰⁹
 87 B2PLYPD3,^{44,45,110} MN12SX,¹¹¹ B97D3,^{51,110} HISSbPBE,¹¹² M11L,¹¹³ MN12L,¹¹⁴ and SOGGA11X;¹¹⁵
 88 basis sets, 6-31G(d),¹¹⁶⁻¹²¹ 6-311++G(d,p),^{122,123} 6-311++G(2d,2p),^{122,123} SVP,^{124,125} TZV,^{124,125}
 89 TZVP,^{124,125} cc-pVDZ,¹²⁶⁻¹²⁹ and cc-pVTZ.¹²⁶⁻¹²⁹

90

91 Structures were confirmed as true minima absent imaginary frequencies. No symmetry constraints were
 92 employed for calculations, and with the exception of the benzene neutral/anion pair for electron affinity
 93 estimates (where an ultrafine grid was used for geometry optimizations and frequency calculations at
 94 the B3LYP/6-31G(d) level), all calculations used the default fine grid. B3LYP calculations on the
 95 [n]acene cation using the 6-31G(d), 6-311++G(d,p), and TZVP basis sets failed to converge; therefore,
 96 this compound was omitted from adiabatic ionization energy (AIE) calculations. Geometry
 97 visualizations were conducted with Gabedit 2.2.12.¹³⁰ KyPlot v.2.b.15¹³¹ was employed for all
 98 statistical analyses.

99

100 Results and discussion

101

102 Geometry optimizations and frequency calculations were conducted on the neutral, cationic, and
 103 anionic forms of the n=1-10 [n]acenes (i.e., from benzene through decacene; Figure 1) at the B3LYP/6-

31G(d) level of theory. Using the B3LYP/6-31G(d) optimized geometries for the neutral form of each compound, vertical ionization energies (VIEs) were calculated for the $n=1-10$ [n]acenes across a broad range of model chemistries (semiempirical, HF, DFT, and MP2 methods) at the x/TZVP//B3LYP/6-31G(d) level of theory (Supplementary Materials Table S1; semiempirical calculations are at the x//B3LYP/6-31G(d) level). Experimental VIEs are available for benzene through hexacene, and range from 9.2 to 9.25 eV (benzene), 8.09 to 8.31 ± 0.03 eV (naphthalene), 7.40 to 7.44 ± 0.03 eV (anthracene), 6.97 ± 0.02 to 7.01 eV (tetracene), 6.61 ± 0.02 eV (pentacene), and 6.36 ± 0.02 eV (hexacene).

Deleuze et al.³⁵ have completed a suite of benchmark quality VIE calculations on these compounds using a focal point analysis (FPA) extrapolated to the CCSD(T)/cc-pV ∞ Z level and obtained the following values which are in good agreement with the experimental dataset: 9.45 eV (benzene), 8.24 eV (naphthalene), 7.47 eV (anthracene), 6.95 eV (tetracene), 6.57 eV (pentacene), and 6.43 eV (hexacene). Using a single exponential decay function regression having a y-axis offset of the general form $y = ae^{-bx} + c$ ($x=n$, $y(x)=\text{VIE}$ in eV; $c=\text{VIE}$ at the polymeric limit), we obtained VIE as $n \rightarrow \infty$ for the [n]acenes at 5.86 and 6.00 eV, respectively, using the experimental and benchmark theoretical datasets. Despite the high qualities of fit ($r > 0.9999$) we found using this statistical model for the ionization energies and electron affinities of [n]acenes, we note that caution needs to be exercised when extrapolating from a relatively limited suite of chain lengths.

In comparison, extrapolated VIE at the [n]acene polymeric limit using the semiempirical, HF, DFT, and MP2 methods at the x/TZVP//B3LYP/6-31G(d) level of theory (semiempirical calculations are at the x//B3LYP/6-31G(d) level) range from 3.50 eV (HF) to 6.46 eV (MP2), with the DFT and semiempirical methods having VIE as $n \rightarrow \infty$ lying between these two end members (Table 1). The AM1 (5.88 eV) and PM3 (6.04 eV) semiempirical methods have the best projected VIE agreement at the

polymer limit when compared with the experimental and benchmark theoretical data. However, both the AM1 and PM3 methods have poor agreement with the benchmark theoretical data for benzene through hexacene (mean signed deviations [MSD], mean absolute deviations [MAD], and root mean squared deviations [RMSD] of 0.11/0.27, 0.18/0.28, and 0.19/0.31 eV, respectively). Consequently, while these methods may provide reasonable extrapolated VIEs at the polymeric limit for the [n]acenes, they have unsatisfactory prediction performance for the chain lengths considered herein.

An analogous problem is observed when one uses the criteria of the lowest MSD/MAD/RMSD against the benzene through hexacene benchmark theoretical dataset for assessing the quality of a VIE prediction method. The LC-wPBE and M062X functionals have the best error metrics for the n=1-6 [n]acenes (equivalent MSD/MAD/RMSD of -0.06/0.06/0.09 eV for both methods), but the projected VIEs at the polymeric limits (5.38 and 5.41 eV, respectively) are well below the experimental and benchmark theoretical estimates. With the exception of the four semiempirical methods (AM1, PM3, PM6, and PDDG) and the MP2 approach, all model chemistries underestimate the projected VIE at the polymer limit based on comparisons with the experimental data and benchmark theoretical calculations. As well, the MP2 method shows signs of beginning an upward VIE trend between n=8-10, thereby forming a parabolic VIE versus acene length relationship. Overall, no single semiempirical, HF, DFT, or MP2 method is able to adequately estimate the VIEs of short- through long-chain acenes. These deficiencies are illustrated in Figure 2, which shows trends and extrapolations for the benchmark theoretical estimates and those obtained at the M062X/TZVP//B3LYP/6-31G(d), PM3//B3LYP/6-31G(d), and B2PLYPD/TZVP//B3LYP/6-31G(d) levels of theory.

For the semiempirical, HF, DFT, and MP2 VIEs, regression analyses were also conducted using the n=1-6 homologs and compared to the n=1-10 polymeric limit extrapolations in order to investigate the

152 sensitivity of the $n=7-10$ datapoint inclusions on projected VIEs as $n \rightarrow \infty$. The $n=1-6$ projected
153 polymeric limit VIEs are generally about 0.2 to 0.3 eV higher than the corresponding $n=1-10$ projected
154 polymeric limit VIEs. However, even with the reduced regression dataset (making the analysis directly
155 comparable to that conducted on the available experimental and benchmark theoretical datasets, where
156 only the $n=1-6$ data is available), none of the model chemistries examined meets the criteria of reliably
157 reproducing $[n]$ acene VIEs for both short and long homologs. The basis set dependence of estimated
158 VIEs was also considered at the B3LYP/y//B3LYP/6-31G(d) level with representative Pople, Ahlrichs,
159 and Dunning type basis sets (Table 2). With the exception of the 6-31G(d) basis set, the basis set effects
160 on calculated and extrapolated VIEs are not significant. Thus, model chemistry effects on extrapolated
161 VIEs for the $[n]$ acenes dominate any reasonable basis set size influences.

162
163 Frequency calculations were completed at the B3LYP/6-31G(d) level on the neutral and cationic forms
164 of benzene through nonacene in order to obtain the following zero-point vibrational energy (ZPVE)
165 plus thermal (T) corrections (values in eV): benzene, -0.05; naphthalene, 0.00; anthracene, +0.02;
166 tetracene, +0.02; pentacene, +0.03; and hexacene through nonacene, +0.04. These values are in
167 excellent agreement with the B3LYP/cc-pVDZ ZPVE corrections reported by Deleuze et al.³⁵
168 benzene, -0.07; naphthalene, -0.01; anthracene, +0.01; tetracene, +0.02; pentacene, +0.03; and
169 hexacene, +0.03. As with the VIE calculations, we find no HF, semiempirical, DFT, or MP2 model
170 chemistry that meets the criteria of accurate AIE estimation for both short and long $[n]$ acenes (Table 3
171 and Supplementary Materials Table S2), although the M062X functional is close to the requisite error
172 boundaries (MSD=-0.05, MAD=0.06, and RMSD=0.09 eV). For comparison, projected AIEs at the
173 polymeric limits using the experimental and benchmark values are 5.99 and 5.97 eV, respectively.

174
175 The equivalent set of calculations with the same suite of model chemistries were conducted in order to

estimate vertical electron affinities (VEAs). None of the methods considered were able to achieve thermochemical accuracy as compared to the benchmark theoretical³⁶ values for the $n=1-6$ [n]acenes (Table 4 and Supplementary Materials Table S3). The benchmark theoretical extrapolation to the polymeric limit ($VEA_{n \rightarrow \infty}$) is 2.16 eV. With the exception of the MP2 (1.12 eV), HFB (1.72 eV), HFS (1.77 eV), and XAlpha (2.11 eV) model chemistries, all other methods exhibited gross overestimations of $VEA_{n \rightarrow \infty}$ ranging from 2.28 eV (HF) up to 3.54 eV (PM6). While the XAlpha functional offers a $VEA_{n \rightarrow \infty}$ that is in modest agreement with expectations, it displayed poor predictive performance (MSD=-0.42, MAD=0.42, and RMSD=0.44 eV) compared to the benchmark theoretical values for the 1-6 [n]acenes. For the Ahlrichs and Dunning type basis sets, there is a relative absence of basis set effects (Supplementary Materials Table S4), but for the Pople type basis sets there are substantially higher VEAs with the 6-311++G(d,p) and 6-311++G(2d,2p) basis sets than with the 6-31G(d) basis set. The 6-311++G(d,p) and 6-311++G(2d,2p) basis also yield anomalously high VEAs for the $n=1-10$ [n]acenes, as well as $VEA_{n \rightarrow \infty}$ values, when compared to the Ahlrichs and Dunning type basis sets.

ZPVE+T corrections were calculated at the B3LYP/6-31G(d) level, resulting in the following values: benzene, 0.24 eV; naphthalene, 0.16 eV; anthracene, 0.13 eV; tetracene, 0.11 eV; and pentacene through decacene, 0.10 eV. These values are in excellent agreement with those calculated by Deleuze et al.³⁶ at the B3LYP/cc-pVTZ level: benzene, 0.27 eV; naphthalene, 0.16 eV; anthracene, 0.14 eV; tetracene, 0.13 eV; pentacene, 0.12 eV; and hexacene, 0.11 eV. The experimental adiabatic electron affinity (AEA) database (see Supplementary Materials Table S5 for individual experimental and all theoretical AEA values) has too much scatter to allow any meaningful assessment of a consensus AEA for any of the $n=1-5$ [n]acenes for which data is available, as well as for any application of regression analysis to estimate a polymeric limit AEA ($AEA_{n \rightarrow \infty}$). The benchmark theoretical values for the $n=1-6$ [n]acenes are amenable to regression analysis, giving a projected $AEA_{n \rightarrow \infty}$ of 2.38 eV. Through

fortuitous error cancellation, the HF method comes closest to the benchmark theoretical $AEA_{n \rightarrow \infty}$ (2.41), but its error metrics for the $n=1-10$ [n]acenes are very poor (Table 5). Overall, none of the methods examined is able to adequately estimate the AEAs for these compounds.

VIE, AIE, VEA, and AEA calculations were also undertaken on the $n=3-10$ [n]phenacenes using a set of some of the most modern and/or popular density functionals (APFD, B2PLYPD3, B3LYP, LC-wPBE, M062X, MN12SX, mPW2PLYPD, wB97XD). Experimental VIEs are available for the $n=3-5$ [n]phenacenes. With phenanthrene ($n=3$), chrysene ($n=4$), and picene ($n=5$), the experimental values appear to be well-constrained with minimal scatter and centered at about 7.88, 7.60, and 7.52 eV, respectively. The single VIE report for benzo[6]picene ($n=6$) at 7.20 eV appears to be too low based on both the $n=3-5$ experimental trend as well as the declining $n=3-10$ trends from the theoretical data. When compared against these experimental values, the DFT estimates are -- as with the [n]acenes -- in poor agreement (Supplementary Materials Table S6). NIST evaluated AIEs are available for the $n=3-5$ [n]phenacenes (7.891 ± 0.001 , 7.60 ± 0.01 , and 7.51 ± 0.02 eV, respectively), and a single datapoint (7.36 ± 0.02) for benzo[6]picene. The M062X functional provides excellent agreement against all of these experimental values (Supplementary Materials Table S7), having deviations of no greater than 0.02 eV. All other functionals displayed poor AIE estimation capacity. Based on $n=3-6$ performance with the M062X functional, the $n=7-9$ [n]phenacene AIEs predicted by this method (7.32, 7.26, and 7.24 eV) should be taken as likely at thermochemical accuracy.

Neither experimental nor benchmark VEAs are available for the $n=3-10$ [n]phenacenes. AEAs, calculated using ZPVE+T corrections (0.15 eV for $n=3-5$, 0.16 eV for $n=6-10$) at the B3LYP/6-31G(d) level, increase in inverse exponential decay form and range from -0.22 to +0.08 eV for phenanthrene up to +0.67 to +1.08 eV for [10]phenacene (Supplementary Materials Table S8). The values obtained

with the APFD, B3LYP, and MN12SX functionals are within the corresponding experimental ranges for the $n=3-5$ [n]phenacenes (-0.01 to $+0.31$, $+0.32$ to $+0.40$, and 0.54 eV, respectively).

Based on previous discussions in the literature regarding the difficulty of calculating EAs using DFT methods -- notably due to the self-interaction error and the incorrect asymptotic shape of the approximate potential for the anion,^{132,133} it was expected that EAs may be more unreliably predicted than IEs for the [n]acenes and [n]phenacenes. On the other hand, across all methods examined, the VEA calculations had average smaller MSD (0.13 vs. -0.33 eV), MAD (0.30 vs. 0.39 eV), and RMSD (0.32 vs. 0.41 eV) compared to the corresponding benchmark theoretical data than did the VIE estimates. Similarly, the average MSD (0.08 vs. -0.32 eV), MAD (0.29 vs. 0.38 eV), and RMSD (0.31 vs. 0.40 eV) for the AEA calculations compared to the corresponding benchmark theoretical data was lower than the AIE estimates. Hartree-Fock method errors were substantially higher for the VIE/AIE pair versus the VEA/AEA pair, whereas the reverse pattern was observed at the MP2 level. Among the 57 model chemistries considered, 46 had lower MAD for VEA and AEA than they did for the respective VIE and AIE estimates.

Conclusions

Vertical and adiabatic ionization energies (IEs) and electron affinities (AEs) were calculated for the $n=1-10$ [n]acenes and [n]phenacenes using a wide range of semiempirical, Hartree-Fock, density functional, and second order Moller-Plesset perturbation theory model chemistries. In comparison to available experimental and benchmark theoretical values, none of the model chemistries considered met all the required criteria of accurate IE and EA prediction for both short- through longer chain members of these compound classes, as well as for extrapolations to the polymeric limit. Basis set

248 influences of IE/EA predictive capacity were minimal compared to the effects of changing model
249 chemistry. The poor IE/EA prediction performance of these theoretical methods on the parent [n]acenes
250 and [n]phenacenes may extend to their substituted derivatives and heteroatom substituted analogs,
251 thereby warranting caution in their employment for such property prediction efforts on these important
252 classes of materials.

253

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259 improved the quality of the manuscript.

260

261 **Figure Captions**

262

263 **Figure 1.** General structure of the polyacenes (**1**) and the individual members from benzene (**2**; n=1)
264 through decacene (**11**; n=10).

265

266 **Figure 2.** Trends in calculated VIEs for benzene through decacene at the x//B3LYP/6-31G(d) level of
267 theory (x=M062X/TZVP, PM3, and B2PLYPD/TZVP) along with benchmark theoretical calculations
268 from ref. ³⁵ and corresponding associated extrapolations to the polymeric limit using a single
269 exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$. Regression estimated
270 VIEs at the polymeric limit are provided along the right y-axis.

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272 **Figures**

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276 Figure 1.

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281 Figure 2.

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283 **Table 1.** Summary n=1-6 [n]acene vertical ionization energy (VIE) error statistics compared to the
 284 corresponding benchmark dataset ³⁵ and n=1-10 [n]acene extrapolated VIEs at the polymeric limit
 285 ($VIE_{n \rightarrow \infty}$) for various model chemistries at the x/TZVP//B3LYP/6-31G(d) level of theory. Note that
 286 semiempirical method VIEs are at the x//B3LYP/6-31G(d) level of theory. Values are in eV.
 287

Model chemistry	MSD ^a	MAD ^b	RMSD ^c	$VIE_{n \rightarrow \infty}$	Model chemistry	MSD	MAD	RMSD	$VIE_{n \rightarrow \infty}$
AM1	0.11	0.18	0.19	5.88	M062X	-0.06	0.06	0.09	5.41
APF	-0.30	0.30	0.31	5.18	M06HF	0.24	0.24	0.25	5.65
APFD	-0.30	0.30	0.31	5.18	M06L	-0.46	0.46	0.47	4.99
B1B95	-0.35	0.35	0.37	5.13	M11L	-0.23	0.23	0.24	5.28
B1LYP	-0.50	0.50	0.51	4.97	MN12L	-0.49	0.49	0.50	4.92
B2PLYPD	-0.32	0.32	0.33	5.23	MN12SX	-0.23	0.23	0.25	5.19
B2PLYPD3	-0.32	0.32	0.33	5.23	MP2	0.14	0.14	0.15	6.46
B3LYP	-0.34	0.34	0.35	5.14	mPW1LYP	-0.47	0.47	0.48	4.99
B3P86	0.28	0.28	0.29	5.76	mPW1PBE	-0.31	0.31	0.32	5.17
B3PW91	-0.29	0.29	0.30	5.20	mPW2PLYPD	-0.31	0.31	0.32	5.22
B97D	-0.50	0.50	0.51	4.98	mPW3PBE	-0.27	0.27	0.29	5.21
B97D3	-0.50	0.50	0.51	4.98	O3LYP	-0.45	0.45	0.46	5.02
B98	-0.37	0.37	0.38	5.11	OPBE	-0.39	0.39	0.41	5.08
BHandH	-0.42	0.42	0.43	5.01	OTPSS	-0.38	0.38	0.39	5.10
BHandHLYP	-0.46	0.46	0.47	4.95	PBE0	-0.30	0.30	0.31	5.18

BLYP	-0.57	0.57	0.58	4.76	PDDG	0.30	0.31	0.34	6.10
BMK	-0.27	0.27	0.28	5.19	PM3	0.27	0.28	0.31	6.04
CAM-B3LYP	-0.22	0.22	0.23	5.27	PM6	0.28	0.33	0.36	6.12
HCTH/147	-0.32	0.32	0.34	5.16	SOGGA11X	-0.25	0.25	0.27	5.19
HCTH/407	-0.27	0.27	0.29	5.21	tHCTH	-0.32	0.32	0.33	5.17
HF	-1.45	1.45	1.45	3.50	tHCTHhyb	-0.29	0.29	0.30	5.19
HFB	-1.46	1.46	1.46	4.02	TPSSh	-0.43	0.43	0.44	5.04
HFS	-1.42	1.42	1.42	3.95	VSXC	-0.48	0.48	0.49	5.00
HISSbPBE	-0.27	0.27	0.29	5.08	wB97	-0.18	0.18	0.19	5.27
HSE06	-0.32	0.32	0.34	5.11	wB97X	-0.19	0.19	0.20	5.32
LC-wPBE	-0.06	0.06	0.09	5.38	wB97XD	-0.23	0.23	0.24	5.34
M05	-0.46	0.46	0.47	5.06	X3LYP	-0.37	0.37	0.39	5.10
M052X	-0.11	0.11	0.13	5.36	XAlpha	-1.06	1.06	1.06	4.44
M06	-0.33	0.33	0.34	5.18					

^a Mean signed deviation. ^b Mean absolute deviation. ^c Root mean squared deviation.

Table 2. Estimated basis set effects on calculated vertical ionization energies (VIEs) for the $n=1-10$ [n]acenes and the extrapolated VIEs at the polymeric limit ($\text{VIE}_{n \rightarrow \infty}$) using the B3LYP/y//B3LYP/6-31G(d) level of theory. Values are in eV.

basis set	[n]acene										$\text{VIE}_{n \rightarrow \infty}$
	1	2	3	4	5	6	7	8	9	10	
6-31G(d)	9.01	7.69	6.87	6.33	5.94	5.64	5.42	5.24	5.10	4.98	4.86
6-311++G(d,p)	9.27	7.96	7.16	6.62	6.23	5.94	5.71	5.54	5.39	5.27	5.16
6-311++G(2d,2p)	9.25	7.94	7.14	6.60	6.21	5.92	5.70	5.52	5.37	5.26	5.13
SVP	9.25	7.92	7.11	6.56	6.17	5.88	5.66	5.48	5.33	5.22	5.10
TZV	9.31	7.97	7.15	6.60	6.21	5.91	5.69	5.51	5.36	5.25	5.11
TZVP	9.26	7.95	7.14	6.60	6.21	5.92	5.70	5.52	5.38	5.26	5.14
cc-pVDZ	9.16	7.85	7.04	6.49	6.10	5.81	5.59	5.41	5.27	5.15	5.03
cc-pVTZ	9.23	7.92	7.11	6.57	6.18	5.89	5.66	5.48	5.34	5.22	5.09

295 **Table 3.** Summary n=1-6 [n]acene adiabatic ionization energy (AIE) error statistics compared to the
296 corresponding benchmark dataset ³⁵ and n=1-9 [n]acene extrapolated AIEs at the polymeric limit
297 (AIE_{n→∞}) for various model chemistries at the x/TZVP//B3LYP/6-31G(d) level of theory. Note that
298 semiempirical method AIEs are at the x//B3LYP/6-31G(d) level of theory. Values are in eV.
299

Model chemistry	MSD ^a	MAD ^b	RMSD ^c	AIE _{n→∞}	Model chemistry	MSD	MAD	RMSD	AIE _{n→∞}
AM1	0.09	0.14	0.16	5.95	M062X	-0.05	0.06	0.09	5.42
APF	-0.29	0.29	0.30	5.22	M06HF	0.24	0.24	0.25	5.68
APFD	-0.29	0.29	0.30	5.22	M06L	-0.44	0.44	0.46	5.03
B1B95	-0.34	0.34	0.36	5.15	M11L	-0.21	0.21	0.23	5.30
B1LYP	-0.48	0.48	0.50	5.02	MN12L	-0.47	0.47	0.49	4.96
B2PLYPD	-0.31	0.31	0.32	5.27	MN12SX	-0.21	0.21	0.24	5.23
B2PLYPD3	-0.31	0.31	0.32	5.26	MP2	0.14	0.14	0.15	6.41
B3LYP	-0.32	0.32	0.34	5.19	mPW1LYP	-0.46	0.46	0.47	5.04
B3P86	0.29	0.29	0.31	5.80	mPW1PBE	-0.30	0.30	0.31	5.21
B3PW91	-0.28	0.28	0.29	5.24	mPW2PLYPD	-0.30	0.30	0.31	5.26
B97D	-0.50	0.50	0.51	5.04	mPW3PBE	-0.26	0.26	0.28	5.25
B97D3	-0.49	0.49	0.51	5.04	O3LYP	-0.43	0.43	0.45	5.08
B98	-0.36	0.36	0.37	5.16	OPBE	-0.39	0.39	0.40	5.13
BHandH	-0.40	0.40	0.42	5.01	OTPSS	-0.37	0.37	0.39	5.15
BHandHLYP	-0.45	0.45	0.46	4.99	PBE0	-0.29	0.29	0.31	5.20

BLYP	-0.55	0.55	0.57	4.98	PDDG	0.28	0.28	0.30	6.11
BMK	-0.26	0.26	0.27	5.23	PM3	0.25	0.25	0.28	6.08
CAM-B3LYP	-0.21	0.21	0.22	5.35	PM6	0.28	0.33	0.36	6.23
HCTH/147	-0.31	0.31	0.33	5.22	SOGGA11X	-0.24	0.24	0.26	5.24
HCTH/407	-0.26	0.26	0.28	5.26	tHCTH	-0.31	0.31	0.33	5.22
HF	-1.43	1.43	1.44	3.58	tHCTHhyb	-0.28	0.28	0.30	5.24
HFB	-1.46	1.46	1.46	4.14	TPSSh	-0.43	0.43	0.44	5.08
HFS	-1.39	1.39	1.39	4.17	VSXC	-0.47	0.47	0.49	5.05
HISSbPBE	-0.26	0.26	0.28	5.11	wB97	-0.17	0.17	0.18	5.33
HSE06	-0.31	0.31	0.33	5.21	wB97X	-0.17	0.17	0.19	5.36
LC-wPBE	-0.04	0.05	0.08	5.42	wB97XD	-0.22	0.22	0.23	5.37
M05	-0.45	0.45	0.46	5.10	X3LYP	-0.36	0.36	0.38	5.15
M052X	-0.11	0.11	0.13	5.39	XAlpha	-1.04	1.04	1.04	4.48
M06	-0.31	0.31	0.33	5.21					

300 ^a Mean signed deviation. ^b Mean absolute deviation. ^c Root mean squared deviation.

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Table 4. Summary n=1-6 [n]acene vertical electron affinity (VEA) error statistics compared to the corresponding benchmark dataset ³⁶ and n=1-10 [n]acene extrapolated VEAs at the polymeric limit (VEA_{n→∞}) for various model chemistries at the x/TZVP//B3LYP/6-31G(d) level of theory. Note that semiempirical method VEAs are at the x//B3LYP/6-31G(d) level of theory. Values are in eV.

Model chemistry	MSD ^a	MAD ^b	RMSD ^c	VEA _{n→∞}	Model chemistry	MSD	MAD	RMSD	VEA _{n→∞}
AM1	1.13	1.13	1.14	3.35	M062X	0.13	0.18	0.20	2.73
APF	0.17	0.20	0.22	2.72	M06HF	0.16	0.20	0.23	2.88
APFD	0.17	0.20	0.22	2.72	M06L	0.10	0.16	0.18	2.63
B1B95	0.03	0.13	0.15	2.59	M11L	0.39	0.39	0.42	2.96
B1LYP	-0.03	0.09	0.12	2.50	MN12L	-0.01	0.15	0.18	2.67
B2PLYPD	-0.11	0.12	0.16	2.36	MN12SX	0.18	0.22	0.24	2.81
B2PLYPD3	-0.11	0.12	0.16	2.36	MP2	-0.58	0.58	0.58	1.12
B3LYP	0.13	0.16	0.17	2.68	mPW1LYP	0.00	0.10	0.12	2.53
B3P86	0.76	0.76	0.77	3.31	mPW1PBE	0.16	0.19	0.21	2.72
B3PW91	0.19	0.22	0.24	2.74	mPW2PLYPD	-0.10	0.11	0.15	2.39
B97D	0.10	0.15	0.17	2.64	mPW3PBE	0.21	0.23	0.25	2.76
B97D3	0.10	0.15	0.17	2.64	O3LYP	0.04	0.12	0.14	2.56
B98	0.08	0.14	0.16	2.63	OPBE	0.15	0.20	0.21	2.71
BHandH	-0.07	0.12	0.16	2.57	OTPSS	0.16	0.21	0.22	2.69
BHandHLYP	-0.06	0.11	0.14	2.56	PBE0	0.16	0.19	0.21	2.72

BLYP	0.02	0.10	0.12	2.55	PDDG	1.21	1.21	1.22	3.41
BMK	0.01	0.12	0.15	2.60	PM3	1.20	1.20	1.20	3.36
CAM-B3LYP	0.11	0.14	0.15	2.62	PM6	1.30	1.30	1.31	3.54
HCTH/147	0.27	0.27	0.30	2.79	SOGGA11X	0.08	0.14	0.16	2.67
HCTH/407	0.32	0.32	0.35	2.86	tHCTH	0.31	0.31	0.34	2.82
HF	-0.80	0.80	0.81	2.28	tHCTHhyb	0.21	0.23	0.25	2.75
HFB	-0.76	0.76	0.77	1.72	TPSSh	0.10	0.16	0.17	2.64
HFS	-0.75	0.75	0.76	1.77	VSXC	0.09	0.18	0.20	2.68
HISSbPBE	0.21	0.23	0.26	2.96	wB97	0.05	0.12	0.13	2.65
HSE06	0.17	0.21	0.22	2.77	wB97X	0.06	0.11	0.13	2.59
LC-wPBE	0.19	0.20	0.23	2.79	wB97XD	0.04	0.11	0.12	2.50
M05	0.13	0.17	0.18	2.65	X3LYP	0.10	0.15	0.16	2.63
M052X	0.14	0.19	0.21	2.76	XAlpha	-0.42	0.42	0.44	2.11
M06	0.18	0.20	0.22	2.71					

307 ^a Mean signed deviation. ^b Mean absolute deviation. ^c Root mean squared deviation.

308

309 **Table 5.** Summary n=1-6 [n]acene adiabatic electron affinity (AEA) error statistics compared to the
310 corresponding benchmark dataset ³⁶ and n=1-10 [n]acene extrapolated AEAs at the polymeric limit
311 (VEA_{n→∞}) for various model chemistries at the x/TZVP//B3LYP/6-31G(d) level of theory. Note that
312 semiempirical method VEAs are at the x//B3LYP/6-31G(d) level of theory. Values are in eV.
313

Model chemistry	MSD ^a	MAD ^b	RMSD ^c	AEA _{n→∞}	Model chemistry	MSD	MAD	RMSD	AEA _{n→∞}
AM1	1.04	1.04	1.04	3.40	M062X	0.07	0.15	0.17	2.84
APF	0.12	0.18	0.19	2.86	M06HF	0.07	0.16	0.18	2.94
APFD	0.12	0.18	0.19	2.86	M06L	0.04	0.15	0.17	2.78
B1B95	-0.04	0.12	0.17	2.72	M11L	0.30	0.32	0.35	3.08
B1LYP	-0.07	0.11	0.15	2.67	MN12L	-0.07	0.16	0.21	2.78
B2PLYPD	-0.16	0.16	0.20	2.48	MN12SX	0.12	0.19	0.22	2.88
B2PLYPD3	-0.16	0.16	0.21	2.48	MP2	-0.66	0.66	0.67	1.18
B3LYP	0.10	0.16	0.17	2.82	mPW1LYP	-0.05	0.10	0.14	2.67
B3P86	0.70	0.70	0.72	3.44	mPW1PBE	0.10	0.17	0.18	2.85
B3PW91	0.14	0.19	0.21	2.90	mPW2PLYPD	-0.15	0.15	0.20	2.51
B97D	0.10	0.16	0.17	2.81	mPW3PBE	0.16	0.20	0.22	2.89
B97D3	0.09	0.16	0.17	2.78	O3LYP	0.02	0.14	0.17	2.74
B98	0.05	0.13	0.15	2.80	OPBE	0.12	0.20	0.22	2.87
BHandH	-0.19	0.20	0.25	2.66	OTPSS	0.14	0.21	0.22	2.88
BHandHLYP	-0.15	0.16	0.21	2.66	PBE0	0.10	0.17	0.19	2.87

BLYP	0.03	0.11	0.13	2.73	PDDG	1.09	1.09	1.10	3.42
BMK	-0.03	0.12	0.15	2.73	PM3	1.08	1.08	1.08	3.40
CAM-B3LYP	0.04	0.11	0.13	2.74	PM6	1.21	1.21	1.21	3.60
HCTH/147	0.24	0.27	0.29	2.94	SOGGA11X	0.03	0.13	0.15	2.80
HCTH/407	0.28	0.30	0.32	2.99	tHCTH	0.27	0.29	0.32	2.97
HF	-0.87	0.87	0.88	2.41	tHCTHhyb	0.18	0.22	0.24	2.92
HFB	-0.68	0.68	0.68	1.95	TPSSh	0.06	0.14	0.17	2.75
HFS	-0.73	0.73	0.74	1.93	VSXC	0.07	0.17	0.19	2.84
HISSbPBE	0.13	0.19	0.22	3.05	wB97	0.00	0.10	0.12	2.75
HSE06	0.12	0.18	0.20	2.90	wB97X	0.00	0.10	0.12	2.70
LC-wPBE	0.11	0.15	0.17	2.89	wB97XD	-0.02	0.09	0.12	2.62
M05	0.08	0.15	0.17	2.78	X3LYP	0.05	0.13	0.15	2.78
M052X	0.06	0.15	0.18	2.88	XAlpha	-0.49	0.49	0.51	2.27
M06	0.12	0.17	0.18	2.85					

314 ^a Mean signed deviation. ^b Mean absolute deviation. ^c Root mean squared deviation.

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