Semiempirical, Hartree-Fock, density functional, and second order Moller-Plesset perturbation theory methods do not accurately predict ionization energies and electron affinities of short- through long-chain [n]acenes

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Abstract

Vertical, well-to-well, 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 mid-length [n]acenes, as well as for extrapolations to the polymeric limit, when compared to available experimental and benchmark theoretical data. Provided a minimal basis set size is employed, basis set effects on predicted IEs and EAs are not significant relative to the choice of model chemistry. The poor IE/EA prediction performance for the parent [n]acenes likely extends 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.

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

Introduction

The [n]acenes and their derivatives offer potential in the field of organic electronics [1-3]. Consequently, the molecular properties of these compounds are of interest, both in terms of experimental measurements as well as the development and application of suitable theoretical methods. Unique challenges exist for computational approaches in dealing with these molecules, as evidenced by the various predictions for the multiplicities and open/closed shell natures of their ground states [4-18] [19-21]. Notable high-level work by Deleuze and co-workers may have resolved controversies arising from the prior application of lower-level theory, and their results indicate these molecules should be ground state closed shell singlets [19-21] with positive singlet-triplet gaps that converge on a vanishingly small energetic transition between these multiplicities at the polymer limit (i.e., as $n \rightarrow \infty$). In concert with these efforts, it was recently shown that among the generally available semiempirical, Hartree-Fock (HF), density functional theory (DFT), and second order Moller-Plesset perturbation (MP2) methods, only the B2PLYP and mPW2PLYP functionals (which combine exact HF exchange with an MP2-like correlation to the DFT calculation) appear to accurately describe the singlet-triplet gaps of both the short- through mid-length [n]acenes (e.g., benzene through decacene) as well as extrapolations to the polymeric limit [22, 23].

In the current study, we turn our attention to an examination of how well a broad range of semiempirical, HF, DFT, and MP2 methods perform for predicting the ionization energies (IEs) and electron affinities (EAs) of the [n]acenes. In particular, we give special regard as to whether the theoretical approaches meet a required criteria of accurate IE/EA prediction for both short homologs as well as at the polymeric limit. This type of criteria seems a basic standard to apply for theoretical studies into the use of these types of compounds towards organic electronic and related applications.

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

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

Computational details

Geometry optimizations, frequency calculations, and single point energy (SPE) calculations employed Gaussian 09 (G09) [37] with various combinations of the following semiempirical, HF, DFT, and MP2 model chemistries and basis sets: model chemistries, AM1 [38-40], B1B95 [41], B1LYP [41-43],

B2PLYPD [44, 45], 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], 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], HSE06 [67-73], LC-wPBE [74-77], M05 [78], M052X [79], M06 [80], M062X [80], M06HF [81], M06L [80], MP2 [82-86], mPW1LYP [42, 43, 87], mPW1PBE [87-89], mPW2PLYPD [45, 90], mPW3PBE [87-89], O3LYP [42, 43, 91], OPBE [88, 89, 92, 93], OTPSS [92-94], PBE0 [88, 89, 95], PDDG [96-100], PM3 [101, 102], PM6 [103], tHCTH [104], tHCTHhyb [104], TPSSh [94], VSXC [105], wB97 [106], wB97X [106], wB97XD [107], X3LYP [108], and XAlpha [54-56]; basis sets, 6-31G(d) [109-114], 6-311++G(d,p) [115, 116], 6-311++G(2d,2p) [115, 116], SVP [117, 118], TZV [117, 118], TZVP [117, 118], cc-pVDZ [119-122], and cc-pVTZ [119-122]. Structures were confirmed as true minima absent imaginary frequencies. Geometry visualizations were conducted with Gabedit 2.2.12 [123]. KyPlot v.2.b.15 [124] was employed for all statistical analyses.

Results and discussion

Geometry optimizations and frequency calculations were conducted on the neutral, cationic, and 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. The benzene anion yields one imaginary frequency at the B3LYP/6-31G(d) level. Thus, calculations for the well-to-well electron affinity (WWEA) and adiabatic electron affinity (AEA) of benzene used the B3LYP/6-311++G(d,p) geometries, which are absent imaginary frequencies, for both the neutral and anionic forms. B3LYP/6-31G(d) calculations on the decacene cation failed to converge; therefore, this compound was omitted from well-to-well ionization energy (WWIE) and adiabatic ionization energy (AIE) calculations. Due to computational expense, B3LYP/6-31G(d) frequency calculations could only be completed on the n=1-7 [n]acene cations and n=2-6

[n]acene anions (as noted, the benzene anion frequency calculation was completed at the B3LYP/6-311++G(d,p) level). No imaginary frequencies were observed. Consequently, WWIE/AIE and WWEA/AEA calculations for the n=8-9 [n]acene cations and n=7-10 [n]acene anions, respectively, make use of optimized B3LYP/6-31G(d) geometries for which corresponding frequency calculations were not conducted (and with the assumption of no imaginary frequencies), and also employ estimated zero-point energy and thermal corrections extrapolated from lower homologs.

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 (Table 1; semiempirical calculations are at the x//B3LYP/6-31G(d) level). Experimental VIEs are available for benzene through hexacenes, 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)=VIE in eV; c= 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.

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. 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 short- through mid-range chain lengths.

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(a), 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.

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150 For the semiempirical, HF, DFT, and MP2 VIEs, regression analyses were also conducted using the
151 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 $n \rightarrow \infty$. As shown in Table 1, the
153 n=1-6 projected polymeric limit VIEs are generally about 0.2 to 0.3 eV higher than the corresponding
154 n=1-10 projected polymeric limit VIEs. However, even with the reduced regression dataset (making the
155 analysis directly comparable to that conducted on the available experimental and benchmark theoretical
156 datasets, where only the n=1-6 data is available), none of the model chemistries examined meets the
157 criteria of reliably reproducing [n]acene VIEs for both short and long homologs. The basis set
158 dependence of estimated VIEs was also considered at the B3LYP/y//B3LYP/6-31G(d) level with
159 representative Pople, Ahlrichs, and Dunning type basis sets (Table 2). With the exception of the
160 minimal 6-31G(d) basis set, the basis set effects on extrapolated VIEs are not significant. Thus, model
161 chemistry effects on extrapolated VIEs for the [n]acenes dominate any reasonable basis set size
162 influences.
163

164 Analogous calculations were conducted for the WWIEs of the n=1-9 [n]acenes at the
165 x/TZVP//B3LYP/6-31G(d) level (Table 3). The geometry optimization with the B3LYP/6-31G(d)
166 method failed to converge for decacene, resulting in its omission. Benchmark theoretical WWIEs were
167 calculated from ref. [35] by subtracting the relaxation energies ($E_{relax)}$ these authors calculated at the
168 B3LYP/cc-pVTZ level from the corresponding FPA AIEs. Similar results and trends were obtained for
169 the WWIEs as with the VIEs, including the relative insignificance of basis set effects (Table 4).
170 Deleuze et al. [35] reported the following E_{relax} at the B3LYP/cc-pVTZ level for the n=1-6 [n]acenes
171 (values in eV): benzene, -0.15; naphthalene, -0.09; anthracene, -0.07; tetracene, -0.06; pentacene, -0.05;
172 and hexacene, -0.04. Our values at the B3LYP/TZVP//B3LYP/6-31G(d) level are in excellent

agreement (-0.13, -0.08, -0.06, -0.05, -0.04, and -0.04 eV, respectively). Relaxation energies are predicted to decline with increasing acene chain length for all model chemistries (Table 5), but modest variations in the E_{relax} among the different methods are observed (values in eV): benzene, -0.23 [HFB/MP2] to -0.08 [HF/BHandH]; naphthalene, -0.14 [AM1/PDDG] to -0.06 [BHandH/XAlpha]; anthracene, -0.11 [AM1/PDDG] to -0.05 [M06L/MP2]; tetracene, -0.10 [PDDG] to -0.04 [HFB]; pentacene, -0.09 [PDDG] to -0.02 [HFB]; hexacene, -0.09 [PDDG] to 0.00 [HFB]; heptacene, -0.08 [PDDG] to +0.01 [HFB]; octacene, -0.08 [PDDG] to +0.02 [HFB]; and nonacene, -0.07 [PDDG] to +0.03 [HFB].

Frequency calculations were completed at the B3LYP/6-31G(d) level on the neutral and cationic forms of benzene through heptacene in order to obtain the following zero-point vibrational energy (ZPVE) plus thermal (T) corrections (values in eV): benzene, -0.05; naphthalene, 0.00; anthracene, +0.02; tetracene, +0.02; pentacene, +0.03; hexacene, +0.04; and heptacene, +0.04. These values are in excellent agreement with the B3LYP/cc-pVDZ ZPVE corrections reported by Deleuze et al. [35]: benzene, -0.07; naphthalene, -0.01; anthracene, +0.01; tetracene, +0.02; pentacene, +0.03; and hexacene, +0.03. Owing to computational expense, ZPVE+T corrections were not calculated for octacene and nonacene, but based on the trend between benzene and heptacene, the ZPVE+T correction for these two longer acenes can be reliably approximated as +0.04 eV (all higher acenes beyond nonacene are also expected to have a ZPVE+T correction of about +0.04 eV). Applying the ZPVE+T corrections to the WWIE data in Table 3 yields the estimated AIEs in Table 6. As with the VIE and WWIE calculations, we find no HF, semiempirical, DFT, or MP2 model chemistry that meets the criteria of accurate AIE estimation for both short and long [n]acenes.

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

estimate vertical electron affinities (VEAs; Table 7) and the corresponding presence/absence of significant basis set effects (Table 8; although the anomalous performance of the 6-311++G(d,p) and 6-311++G(2d,2p) Pople-type basis sets is notable), WWEAs (Table 9) and the corresponding presence/absence of significant basis set effects (Table 10), relaxation energies from the anionic form of the neutral geometry to the optimized anionic geometry (Table 11), and AEAs (Table 12). ZPE+T corrections were calculated at the B3LYP/6-31G(d) level for benzene through hexacene, resulting in the following values (values in eV): benzene, 0.24; naphthalene, 0.16; anthracene, 0.13; tetracene, 0.11; pentacene, 0.10; and hexacene, 0.10. These values are in excellent agreement with those calculated by Deleuze et al. [36] at the B3LYP/cc-pVTZ level: benzene, 0.27; naphthalene, 0.16; anthracene, 0.14; tetracene, 0.13; pentacene, 0.12; and hexacene, 0.11. Due to computational expense, ZPE+T corrections could not be calculated for heptacene through decacene. However, the benzene through hexacene [n]acene ZPE+T corrections are well fit by a single exponential decay function regression having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=ZPE+T in eV; c= ZPE+T at the polymeric limit; r=0.9992, a=0.311, b=0.771, and c=0.096), indicating a reliably estimated ZPE+T correction of 0.10 eV for heptacene and all higher [n]acene homologs. As with the ionization energies, all semiempirical, Hartree-Fock, density functional, and second order Moller-Plesset perturbation theory methods fail to accurately predict the electron affinities of short- through long-chain [n]acenes.

Conclusions

Vertical, well-to-well, and adiabatic ionization energies (IEs) and electron affinities (AEs) 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. In comparison to available experimental and benchmark theoretical values, none of the model chemistries considered

met the required criteria of accurate IE/EA prediction for both short- through mid-length [n]acenes as well as for extrapolations to the polymeric limit. Basis set influences of IE/EA predictive capacity were minimal compared to the effects of changing model chemistry. One must also reasonably conclude the poor IE/EA prediction performance of these theoretical methods on the parent [n]acenes also extends to their substituted derivatives and heteroatom substituted analogs, thereby warranting caution in their employment for such property prediction efforts on these important classes of materials.

Acknowledgements

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235 **Figure Captions**

236

237 **Figure 1.** General structure of the polyacenes (**1**) and the individual members from benzene (**2**; n=1)

238 through decacene (**11**; n=10).

239

240 **Figure 2.** Trends in calculated VIEs for benzene through decacene at the x//B3LYP/6-31G(d) level of

241 theory (x=M062X/TZVP, PM3, and B2PLYPD/TZVP) along with benchmark theoretical calculations

242 from ref. [35] and corresponding associated extrapolations to the polymeric limit using a single

243 exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (corresponding

244 regression statistics given in Table 1). Regression estimated VIEs at the polymeric limit are provided

245 along the right y-axis.

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Figures

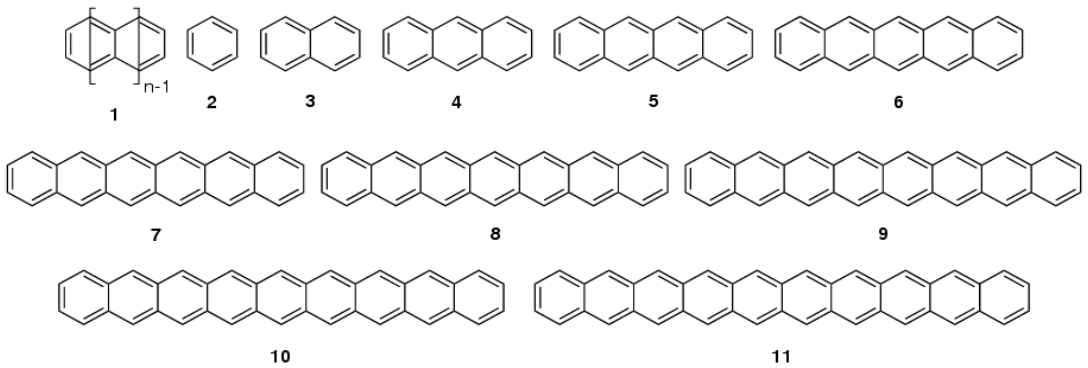

Figure 1.

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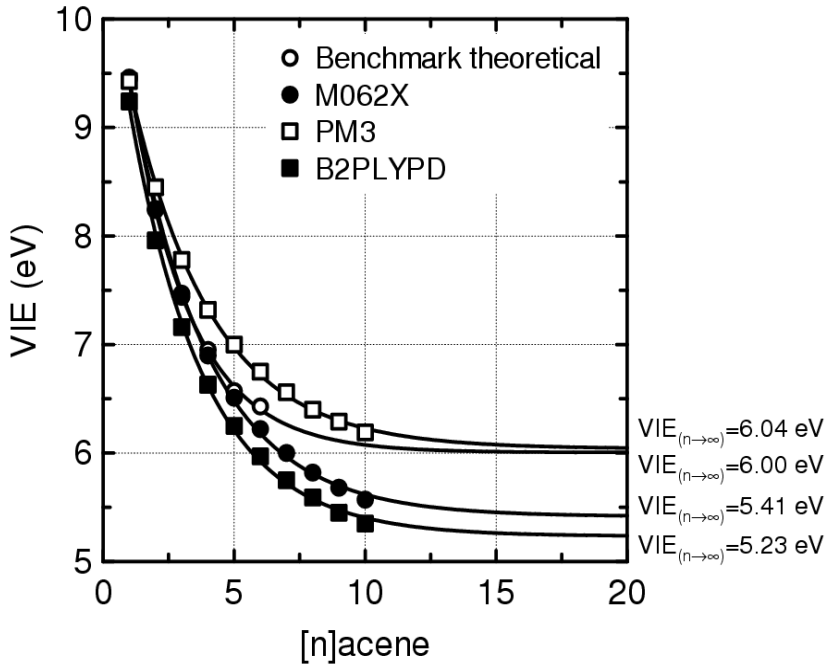

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257 Figure 2.
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259 **Table 1.** Experimental, benchmark theoretical [35], and estimated (at the x/TZVP//B3LYP/6-31G(d) level of theory) vertical ionization energies (VIEs) for the [n]acenes (n=1-10). Error metrics (MSD=mean signed deviation; MAD=mean absolute deviation; and RMSD=root mean squared deviation) are between VIEs obtained at the x/TZVP//B3LYP/6-31G(d) level of theory and the benchmark theoretical [35] values for the n=1-6 [n]acenes. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=VIE in eV; c= VIE at the polymeric limit). Values are in eV. Note that semiempirical method VIEs are at the x//B3LYP/6-31G(d) level of theory.

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	[n]acene										error metrics			regression statistics (n=1-10)				regression statistics (n=1-6)	
	1	2	3	4	5	6	7	8	9	10	MSD	MAD	RMSD	a	b	c	r	c	r
expt.	9.2 [125] 9.22 [126] 9.23 [127, 128] 9.24 [129, 130-135] 9.24±0.02 [136] 9.25 [137, 138] 9.25±0.03 [139] 9.25±0.05 [140]	8.09 [141] 8.15 [130, 133, 138, 142] 8.15±0.02 [136] 8.18±0.03 [143] 8.31±0.03 [144]	7.40 [145, 146] 7.41 [130] 7.41±0.02 [136] 7.42±0.02 [147] 7.44±0.03 [144]	6.97±0.02 [136] 7.01 [148]	6.61±0.02 [136]	6.36±0.02 [136]	n/a[a]	n/a	n/a	n/a	n/a	n/a	n/a	4.91[b]	0.376	5.86	0.9998	5.86	0.9998
benchmark theoretical [35]	9.45	8.24	7.47	6.95	6.57	6.43	n/a	n/a	n/a	n/a	n/a	n/a	n/a	5.31	0.433	6.00	0.9998	6.00	0.9998
HF	7.92	6.95	6.14	5.55	5.11	4.76	4.49	4.26	4.08	3.93	-1.45	1.45	1.45	5.69	0.253	3.50	0.9999	3.60	0.99993
HFS	n/c[c]	6.88	6.07	5.53	5.15	4.86	4.64	4.46	4.31	4.19	-1.43	1.43	1.43	5.25	0.297	3.95	0.9996	4.34	0.9997
HFB	8.16	6.82	6.02	5.48	5.09	4.80	4.58	4.40	4.25	4.13	-1.46	1.46	1.46	5.77	0.345	4.02	0.9991	4.24	0.99993
XAlpha	8.57	7.21	6.41	5.88	5.50	5.21	4.99	4.81	4.66	4.54	-1.06	1.06	1.06	5.76	0.349	4.44	0.9989	4.79	0.9997
BLYP	n/c	7.71	6.90	6.36	5.97	5.68	5.46	5.27	5.13	5.00	-0.61	0.61	0.61	5.27	0.294	4.76	0.9996	5.04	0.99994
BHandHLYP	9.05	7.85	7.05	6.50	6.10	5.80	5.57	5.39	5.25	5.13	-0.46	0.46	0.47	5.61	0.322	4.95	0.9997	5.19	0.99993
B1LYP	9.08	7.79	6.99	6.44	6.05	5.76	5.54	5.36	5.22	5.10	-0.50	0.50	0.51	5.70	0.340	4.97	0.9994	5.25	0.9998
B97D	9.12	7.77	6.97	6.43	6.05	5.76	5.53	5.35	5.21	5.09	-0.50	0.50	0.51	5.77	0.347	4.98	0.9991	5.32	0.9997
M06L	9.16	7.83	7.02	6.47	6.08	5.79	5.56	5.38	5.23	5.11	-0.46	0.46	0.47	5.79	0.342	4.99	0.9992	5.31	0.9998
mPW1LYP	9.11	7.82	7.01	6.47	6.08	5.79	5.56	5.38	5.24	5.12	-0.47	0.47	0.48	5.71	0.339	4.99	0.9993	5.29	0.9999
VSXC	9.14	7.80	6.99	6.45	6.07	5.78	5.55	5.37	5.23	5.11	-0.48	0.48	0.49	5.78	0.347	5.00	0.9991	5.33	0.9998
BHandH	9.10	7.88	7.08	6.53	6.13	5.84	5.61	5.43	5.29	5.18	-0.42	0.42	0.43	5.62	0.328	5.01	0.9996	5.26	0.99993
O3LYP	9.17	7.84	7.03	6.49	6.10	5.81	5.58	5.40	5.26	5.14	-0.45	0.45	0.46	5.77	0.344	5.02	0.9992	5.34	0.9998
TPSSh	9.17	7.85	7.04	6.50	6.12	5.83	5.60	5.42	5.28	5.16	-0.43	0.43	0.44	5.74	0.344	5.04	0.9992	5.37	0.9998
M05	9.01	7.81	7.03	6.51	6.13	5.84	5.63	5.45	5.32	5.20	-0.46	0.46	0.47	5.45	0.331	5.06	0.9995	5.31	0.9999
OPBE	9.24	7.89	7.08	6.54	6.15	5.86	5.64	5.46	5.31	5.19	-0.39	0.39	0.41	5.80	0.347	5.08	0.9991	5.41	0.9998
OTPSS	9.26	7.90	7.09	6.55	6.16	5.87	5.65	5.47	5.32	5.20	-0.38	0.38	0.39	5.82	0.349	5.10	0.9991	5.42	0.9997
X3LYP	9.22	7.91	7.11	6.56	6.18	5.88	5.66	5.48	5.34	5.22	-0.37	0.37	0.39	5.73	0.342	5.10	0.9993	5.39	0.9998
B98	9.23	7.92	7.11	6.57	6.18	5.89	5.67	5.49	5.35	5.23	-0.37	0.37	0.38	5.74	0.344	5.11	0.9993	5.41	0.9998
HSE06	9.25	7.97	7.16	6.62	6.23	5.93	5.70	5.52	5.37	5.25	-0.32	0.32	0.34	5.71	0.333	5.11	0.9993	5.42	0.9998
B1B95	9.24	7.93	7.13	6.59	6.20	5.91	5.68	5.51	5.37	5.25	-0.35	0.35	0.37	5.72	0.343	5.13	0.9993	5.43	0.9998
B3LYP	9.26	7.95	7.14	6.60	6.21	5.92	5.70	5.52	5.38	5.26	-0.34	0.34	0.35	5.74	0.344	5.14	0.9993	5.44	0.9998
HCTH/147	9.30	7.95	7.15	6.61	6.23	5.94	5.71	5.53	5.39	5.27	-0.32	0.32	0.34	5.77	0.347	5.16	0.9991	5.50	0.9997
tHCTH	9.27	7.95	7.15	6.62	6.24	5.95	5.73	5.55	5.40	5.28	-0.32	0.32	0.33	5.70	0.344	5.17	0.9991	5.50	0.9998
mPW1PBE	9.26	7.98	7.18	6.64	6.25	5.96	5.74	5.56	5.42	5.30	-0.31	0.31	0.32	5.67	0.339	5.17	0.9994	5.46	0.9998
PBE0	9.26	7.98	7.18	6.64	6.25	5.97	5.74	5.56	5.42	5.31	-0.30	0.30	0.31	5.67	0.339	5.18	0.9994	5.47	0.9999
M06	9.20	7.94	7.15	6.62	6.24	5.96	5.74	5.56	5.42	5.31	-0.33	0.33	0.34	5.58	0.340	5.18	0.9993	5.47	0.9999
tHCTHhyb	9.31	7.99	7.19	6.65	6.26	5.97	5.75	5.57	5.43	5.31	-0.29	0.29	0.30	5.73	0.344	5.19	0.9992	5.50	0.9998
BMK	9.31	8.04	7.22	6.67	6.28	5.99	5.76	5.58	5.44	5.33	-0.27	0.27	0.28	5.72	0.339	5.19	0.9995	5.46	0.99992

B3PW91	9.29	8.00	7.19	6.65	6.27	5.98	5.75	5.58	5.44	5.32	-0.29	0.29	0.30	5.69	0.342	5.20	0.9993	5.50	0.9999
HCTH/407	9.34	8.01	7.20	6.67	6.28	5.99	5.77	5.59	5.44	5.32	-0.27	0.27	0.29	5.75	0.345	5.21	0.9991	5.53	0.9998
mPW3PBE	9.31	8.01	7.21	6.67	6.28	5.99	5.77	5.59	5.45	5.33	-0.27	0.27	0.29	5.70	0.341	5.21	0.9993	5.50	0.9998
mPW2PLYPD	9.23	7.97	7.17	6.64	6.25	5.97	5.76	5.59	5.45	5.35	-0.31	0.31	0.32	5.60	0.346	5.22	0.9995	5.47	0.9999
B2PLYPD	9.24	7.96	7.16	6.63	6.25	5.97	5.75	5.59	5.45	5.35	-0.32	0.32	0.33	5.62	0.350	5.23	0.9994	5.47	0.9999
CAM-B3LYP	9.30	8.07	7.27	6.73	6.34	6.05	5.83	5.66	5.52	5.42	-0.22	0.22	0.23	5.59	0.337	5.27	0.9996	5.50	0.99991
wB97	9.28	8.13	7.34	6.80	6.40	6.11	5.88	5.71	5.57	5.46	-0.18	0.18	0.19	5.48	0.320	5.27	0.9998	5.47	0.99997
wB97X	9.29	8.11	7.32	6.78	6.39	6.11	5.89	5.72	5.59	5.48	-0.19	0.19	0.20	5.48	0.332	5.32	0.9997	5.56	0.9999
wB97XD	9.27	8.04	7.26	6.73	6.35	6.07	5.86	5.70	5.57	5.47	-0.23	0.23	0.24	5.49	0.345	5.34	0.9996	5.53	0.99996
M052X	9.36	8.19	7.39	6.85	6.46	6.17	5.95	5.78	5.64	5.53	-0.11	0.11	0.13	5.50	0.327	5.36	0.9997	5.57	0.99997
LC-wPBE	9.39	8.26	7.46	6.92	6.52	6.23	6.00	5.82	5.69	5.58	-0.06	0.06	0.09	5.47	0.318	5.38	0.9998	5.57	0.99998
M062X	9.46	8.25	7.44	6.90	6.51	6.22	6.00	5.82	5.68	5.57	-0.06	0.06	0.09	5.58	0.331	5.41	0.9996	5.66	0.99994
M06HF	9.66	8.56	7.76	7.22	6.82	6.52	6.30	6.12	5.98	5.86	0.24	0.24	0.25	5.44	0.311	5.65	0.9998	5.82	0.99998
B3P86	9.86	8.56	7.76	7.22	6.83	6.54	6.32	6.14	6.00	5.89	0.28	0.28	0.29	5.70	0.343	5.76	0.9993	6.05	0.9998
AM1	9.25	8.29	7.63	7.17	6.85	6.60	6.41	6.26	6.14	6.04	0.11	0.18	0.19	4.58	0.316	5.88	0.9997	6.07	0.99997
PM3	9.43	8.45	7.78	7.32	7.00	6.75	6.56	6.40	6.29	6.19	0.27	0.28	0.31	4.63	0.320	6.04	0.9997	6.24	0.99996
PDDG	9.44	8.48	7.82	7.36	7.04	6.79	6.61	6.46	6.34	6.25	0.30	0.31	0.34	4.57	0.320	6.10	0.9997	6.26	0.99997
PM6	9.28	8.41	7.80	7.38	7.07	6.83	6.65	6.50	6.39	6.29	0.28	0.33	0.36	4.25	0.303	6.12	0.9997	6.30	0.99996
MP2	9.57	8.31	7.54	7.09	6.80	6.63	6.54	6.51	6.52	6.57	0.14	0.14	0.15	5.36	0.540	6.46	0.9993	6.37	0.999993

[a] not available. [b] regression statistics for the experiment values obtained using the average of multiple experimental datapoints where available. [c] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

Table 2. Estimated vertical ionization energies (VIEs) for the [n]acenes (n=1-10) at the B3LYP/y//B3LYP/6-31G(d) level of theory. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=VIE in eV; c= VIE at the polymeric limit). Values are in eV.

	[n]acene										regression statistics (n=1-10)				regression statistics (n=1-6)	
basis set	1	2	3	4	5	6	7	8	9	10	a	b	c	r	c	r
6-31G(d)	9.01	7.69	6.87	6.33	5.94	5.64	5.42	5.24	5.10	4.98	5.78	0.344	4.86	0.9993	5.16	0.9998
6-311++G(d,p)	9.27	7.96	7.16	6.62	6.23	5.94	5.71	5.54	n/c[a]	5.27	5.72	0.344	5.16	0.9992	5.46	0.9998
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	5.72	0.342	5.13	0.9993	5.44	0.9998
SVP	9.25	7.92	7.11	6.56	6.17	5.88	5.66	5.48	5.33	5.22	5.79	0.346	5.10	0.9993	5.40	0.9998
TZV	9.31	7.97	n/c	6.60	6.21	5.91	5.69	5.51	5.36	5.25	5.83	0.339	5.11	0.9993	5.44	0.9998
TZVP	9.26	7.95	7.14	6.60	6.21	5.92	5.70	5.52	5.38	5.26	5.74	0.344	5.14	0.9993	5.44	0.9998
cc-pVDZ	9.16	7.85	7.04	6.49	6.10	5.81	5.59	5.41	5.27	5.15	5.76	0.344	5.03	0.9993	5.32	0.9998
cc-pVTZ	9.23	7.92	7.11	6.57	6.18	n/c	5.66	5.48	5.34	5.22	5.77	0.344	5.09	0.9994	5.52	0.99991

[a] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

Table 3. Benchmark theoretical [35] and estimated (at the x/TZVP//B3LYP/6-31G(d) level of theory) well-to-well ionization energies (WWIEs) for the [n]acenes (n=1-9). Error metrics (MSD=mean signed deviation; MAD=mean absolute deviation; and RMSD=root mean squared deviation) are between WWIEs obtained at the x/TZVP//B3LYP/6-31G(d) level of theory and the benchmark theoretical [35] values for the n=1-6 [n]acenes. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=WWIE in eV; c= WWIE at the polymeric limit). Values are in eV. Note that semiempirical method WWIEs are at the x//B3LYP/6-31G(d) level of theory.

	[n]acene									error metrics			regression statistics (n=1-9)				regression statistics (n=1-6)	
	1[a]	2	3	4	5	6	7	8	9	MSD	MAD	RMSD	a	b	c	r	c	r
benchmark theoretical [35]	9.37	8.23	7.49	6.97	6.60	6.46	n/a	n/a	n/a	n/a	n/a	n/a	5.10	0.416	6.01	0.9997	6.01	0.9997
HF	7.83	6.84	6.06	5.49	5.06	4.73	4.46	4.24	4.07	-1.52	1.52	1.52	5.53	0.264	3.57	0.99994	3.71	0.99998
HFB	7.93	6.70	5.94	5.44	5.07	4.80	4.59	4.42	4.28	-1.54	1.54	1.54	5.38	0.354	4.11	0.9994	4.35	0.9998
HFS	8.08	6.79	6.01	5.48	5.11	4.83	4.62	4.44	4.30	-1.47	1.47	1.47	5.58	0.359	4.14	0.9993	4.38	0.9998
XAlpha	8.47	7.15	6.35	5.82	5.44	5.16	4.94	4.76	4.62	-1.12	1.12	1.13	5.69	0.361	4.46	0.9993	4.72	0.9998
BLYP	8.93	7.62	6.84	6.31	5.93	5.65	5.43	5.26	5.11	-0.64	0.64	0.65	5.63	0.359	4.95	0.9993	5.20	0.9998
BHandHLYP	8.95	7.77	6.98	6.44	6.05	5.75	5.53	5.35	5.21	-0.53	0.53	0.54	5.51	0.331	4.97	0.9997	5.15	0.99993
BHandH	9.03	7.82	7.02	6.47	6.08	5.78	5.55	5.37	5.23	-0.49	0.49	0.50	5.60	0.334	4.99	0.9997	5.20	0.99993
B1LYP	8.95	7.71	6.92	6.39	6.01	5.72	5.50	5.33	5.19	-0.57	0.57	0.58	5.55	0.347	4.99	0.9996	5.21	0.9999
M06L	9.05	7.76	6.96	6.42	6.03	5.74	5.52	5.34	5.19	-0.52	0.52	0.54	5.69	0.350	5.00	0.9994	5.24	0.9998
mPW1LYP	8.98	7.74	6.95	6.42	6.03	5.75	5.53	5.35	5.21	-0.54	0.54	0.55	5.56	0.346	5.01	0.9996	5.23	0.9999
B97D	8.97	7.68	6.90	6.38	6.00	5.72	5.50	5.32	5.18	-0.58	0.58	0.59	5.58	0.355	5.01	0.9993	5.27	0.9998
VSXC	9.01	7.72	6.93	6.40	6.02	5.73	5.51	5.34	5.19	-0.56	0.56	0.57	5.63	0.354	5.02	0.9994	5.26	0.9998
TPSSh	9.03	7.77	6.98	6.45	6.07	5.78	5.56	5.38	5.24	-0.51	0.51	0.52	5.58	0.348	5.05	0.9995	5.29	0.9998
O3LYP	9.04	7.76	6.97	6.43	6.05	5.76	5.54	5.37	5.23	-0.52	0.52	0.53	5.63	0.353	5.05	0.9995	5.27	0.9998
M05	8.90	7.72	6.97	6.45	6.07	5.79	5.58	5.41	5.28	-0.54	0.54	0.54	5.34	0.341	5.07	0.9997	5.26	0.9999
OPBE	9.11	7.81	7.01	6.48	6.10	5.81	5.59	5.41	5.27	-0.47	0.47	0.48	5.67	0.356	5.10	0.9994	5.35	0.9998
OTPSS	9.13	7.82	7.02	6.49	6.11	5.82	5.60	5.43	5.28	-0.45	0.45	0.47	5.68	0.358	5.11	0.9994	5.36	0.9998
X3LYP	9.09	7.83	7.05	6.51	6.13	5.84	5.62	5.45	5.31	-0.44	0.44	0.45	5.58	0.349	5.12	0.9995	5.34	0.9998
B98	9.08	7.83	7.05	6.52	6.14	5.85	5.63	5.46	5.32	-0.44	0.44	0.45	5.55	0.348	5.13	0.9995	5.35	0.9998
B1B95	9.13	7.86	7.07	6.53	6.15	5.86	5.64	5.46	5.32	-0.42	0.42	0.43	5.62	0.349	5.13	0.9995	5.36	0.9998
B3LYP	9.13	7.87	7.08	6.55	6.17	5.88	5.66	5.49	5.35	-0.40	0.40	0.42	5.58	0.351	5.16	0.9995	5.39	0.9998
PBE0	9.14	7.91	7.12	6.59	6.20	5.92	5.70	5.52	5.38	-0.38	0.38	0.39	5.54	0.344	5.18	0.9996	5.40	0.9999
mPW1PBE	9.13	7.90	7.12	6.58	6.20	5.91	5.69	5.52	5.38	-0.38	0.38	0.39	5.53	0.344	5.18	0.9996	5.38	0.9999
tHCTH	9.15	7.87	7.09	6.56	6.19	5.90	5.68	5.51	5.37	-0.39	0.39	0.40	5.58	0.355	5.19	0.9994	5.44	0.9998
M06	9.09	7.87	7.10	6.57	6.19	5.91	5.70	5.52	5.39	-0.40	0.40	0.41	5.46	0.347	5.19	0.9996	5.40	0.9999
HSE06	9.13	7.89	7.10	6.56	6.18	5.89	5.66	5.48	n/c	-0.40	0.40	0.41	5.57	0.354	5.19	0.9997	5.37	0.9999
HCTH/147	9.18	7.88	7.09	6.56	6.18	5.89	5.67	5.50	5.36	-0.39	0.39	0.41	5.65	0.357	5.19	0.9994	5.43	0.9998
BMK	9.14	7.94	7.16	6.63	6.24	5.95	5.73	5.56	5.42	-0.34	0.34	0.35	5.48	0.338	5.20	0.9997	5.39	0.9999
tHCTHhyb	9.17	7.91	7.12	6.60	6.22	5.93	5.71	5.54	5.40	-0.36	0.36	0.37	5.56	0.351	5.21	0.9995	5.45	0.9998
B3PW91	9.17	7.92	7.13	6.60	6.22	5.93	5.71	5.54	5.40	-0.36	0.36	0.37	5.57	0.349	5.21	0.9995	5.43	0.9999
mPW3PBE	9.19	7.94	7.15	6.62	6.23	5.95	5.73	5.55	5.41	-0.34	0.34	0.36	5.57	0.347	5.22	0.9995	5.44	0.9999
mPW2PLYPD	9.11	7.89	7.11	6.58	6.20	5.92	5.71	5.55	5.42	-0.38	0.38	0.39	5.48	0.352	5.23	0.9997	5.40	0.9999
HCTH/407	9.23	7.93	7.14	6.61	6.23	5.95	5.72	5.55	5.41	-0.34	0.34	0.36	5.64	0.357	5.24	0.9994	5.49	0.9998
B2PLYPD	9.10	7.88	7.10	6.57	6.20	5.92	5.71	5.55	5.42	-0.39	0.39	0.40	5.46	0.354	5.24	0.9997	5.42	0.99991
wB97	9.12	8.03	7.27	6.75	6.37	6.08	5.86	5.69	5.56	-0.25	0.25	0.26	5.25	0.322	5.30	0.9998	5.45	0.99996
wB97X	9.14	8.02	7.25	6.73	6.35	6.07	5.86	5.69	5.56	-0.26	0.26	0.27	5.29	0.333	5.33	0.9998	5.48	0.99997
CAM-B3LYP	9.18	7.99	7.21	6.68	6.30	6.01	5.80	5.63	n/c	-0.29	0.29	0.30	5.44	0.352	5.34	0.9998	5.46	0.99992
wB97XD	9.14	7.96	7.19	6.67	6.30	6.03	5.82	5.66	5.54	-0.30	0.30	0.31	5.35	0.351	5.35	0.9997	5.52	0.99994
M052X	9.23	8.10	7.32	6.79	6.41	6.13	5.91	5.74	5.60	-0.19	0.19	0.20	5.35	0.331	5.37	0.9998	5.53	0.99998

LC-wPBE	9.27	8.17	7.40	6.87	6.48	6.19	5.97	5.80	5.66	-0.12	0.12	0.14	5.32	0.321	5.39	0.9999	5.54	0.99997
M062X	9.28	8.16	7.38	6.85	6.47	6.18	5.96	5.79	5.65	-0.13	0.13	0.15	5.35	0.327	5.40	0.9998	5.56	0.99997
M06HF	9.46	8.46	7.69	7.17	6.78	6.49	6.27	6.10	5.96	0.16	0.16	0.17	5.17	0.306	5.65	0.99993	5.73	0.99996
B3P86	9.74	8.49	7.70	7.16	6.78	6.50	6.28	6.10	5.96	0.21	0.21	0.23	5.58	0.349	5.77	0.9995	5.99	0.9999
AM1	9.13	8.15	7.52	7.08	6.77	6.53	6.35	6.21	6.10	0.01	0.12	0.14	4.47	0.338	5.92	0.9997	6.08	0.9999
PM3	9.31	8.32	7.68	7.24	6.92	6.68	6.49	6.35	6.24	0.17	0.19	0.21	4.53	0.336	6.05	0.9997	6.22	0.9999
PDDG	9.32	8.34	7.70	7.26	6.94	6.71	6.53	6.38	6.28	0.19	0.21	0.23	4.50	0.339	6.10	0.9997	6.25	0.99993
PM6	9.13	8.28	7.72	7.32	7.03	6.81	6.65	6.51	6.41	0.20	0.28	0.30	4.00	0.323	6.22	0.9997	6.34	0.99991
MP2	9.33	8.24	7.49	7.04	6.76	6.59	6.50	6.47	6.49	0.05	0.07	0.09	4.88	0.493	6.37	0.9994	6.26	0.99991

[a] the benzene cation has a single imaginary frequency at the B3LYP/6-31G(d) level; thus, calculations were conducted at the x/TZVP//B3LYP/6-311++G(d,p) level where the benzene cation is absent imaginary frequencies.

Table 4. Estimated well-to-well ionization energies (WWIEs) for the [n]acenes (n=1-9) at the B3LYP/y//B3LYP/6-31G(d) level of theory. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=WWIE in eV; c= WWIE at the polymeric limit). Values are in eV.

	[n]acene									regression statistics (n=1-9)				regression statistics (n=1-6)	
basis set	1	2	3	4	5	6	7	8	9	a	b	c	r	c	r
6-31G(d)	8.86	7.59	6.80	6.27	5.89	5.60	5.38	5.21	5.07	5.60	0.352	4.89	0.9995	5.12	0.9998
6-311++G(d,p)	9.13	7.88	7.09	6.56	6.18	5.90	5.68	5.51	n/c[a]	5.55	0.364	5.25	0.9997	5.41	0.9999
6-311++G(2d,2p)	9.12	7.86	7.08	6.55	6.17	5.88	5.66	5.49	5.35	5.56	0.350	5.16	0.9995	5.39	0.9998
SVP	9.09	7.83	7.04	6.51	6.13	5.84	5.62	5.45	5.31	5.58	0.351	5.12	0.9995	5.35	0.9998
TZV	9.16	7.88	n/c	6.55	6.16	5.88	5.66	5.48	5.34	5.63	0.347	5.14	0.9995	5.40	0.9999
TZVP	9.13	7.87	7.08	6.55	6.17	5.88	5.66	5.49	5.35	5.58	0.351	5.16	0.9995	5.39	0.9998
cc-pVDZ	9.01	7.75	6.97	6.44	6.06	5.78	5.56	5.38	5.25	5.55	0.351	5.06	0.9995	5.30	0.9998
cc-pVTZ	9.10	7.84	7.05	6.52	6.13	n/c	5.62	5.45	5.31	5.61	0.350	5.11	0.9996	5.45	0.99991

[a] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

Table 5. Estimated relaxation energies (E_{relax}) from the cationic form of the neutral geometry to the optimized cationic geometry for the [n]acenes (n=1-9) at the x/TZVP//B3LYP/6-31G(d) level of theory. Values are in eV. Note that semiempirical method E_{relax} are at the x//B3LYP/6-31G(d) level of theory.

	[n]acene								
model chemistry	1	2	3	4	5	6	7	8	9
MP2	-0.23	-0.07	-0.05	-0.05	-0.04	-0.04	-0.04	-0.04	-0.03
HFB	-0.23	-0.12	-0.07	-0.04	-0.02	0.00	0.01	0.02	0.03
M06HF	-0.20	-0.10	-0.07	-0.05	-0.04	-0.03	-0.02	-0.02	-0.02
M062X	-0.18	-0.09	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03
BMK	-0.17	-0.09	-0.06	-0.05	-0.04	-0.03	-0.03	-0.02	-0.02
wB97	-0.16	-0.10	-0.07	-0.05	-0.04	-0.03	-0.02	-0.02	-0.01
PM6	-0.15	-0.13	-0.08	-0.05	-0.03	-0.02	0.00	0.01	0.02
B97D	-0.15	-0.09	-0.06	-0.05	-0.05	-0.04	-0.03	-0.03	-0.03
B98	-0.14	-0.09	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03
wB97X	-0.14	-0.09	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.02
tHCTHhyb	-0.14	-0.08	-0.06	-0.05	-0.05	-0.04	-0.04	-0.03	-0.03
TPSSh	-0.14	-0.08	-0.06	-0.06	-0.05	-0.04	-0.04	-0.04	-0.03
VSXC	-0.14	-0.08	-0.07	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
M052X	-0.14	-0.09	-0.07	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
B2PLYPD	-0.14	-0.08	-0.06	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
wB97XD	-0.14	-0.08	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04	-0.03
B1LYP	-0.13	-0.08	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03
O3LYP	-0.13	-0.08	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04	-0.03
B3LYP	-0.13	-0.08	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03
mPW1LYP	-0.13	-0.08	-0.06	-0.05	-0.04	-0.04	-0.04	-0.03	-0.03
X3LYP	-0.13	-0.08	-0.06	-0.05	-0.04	-0.04	-0.04	-0.03	-0.03
mPW2PLYPD	-0.13	-0.08	-0.06	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
OTPSS	-0.13	-0.08	-0.07	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
OPBE	-0.13	-0.08	-0.07	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04
LC-wPBE	-0.13	-0.09	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03
B3PW91	-0.13	-0.08	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04
mPW3PBE	-0.13	-0.08	-0.06	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
HCTH/147	-0.12	-0.08	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04	-0.03
PBE0	-0.12	-0.08	-0.06	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04
mPW1PBE	-0.12	-0.08	-0.06	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04
HSE06	-0.12	-0.08	-0.06	-0.06	-0.05	-0.05	-0.04	-0.04	n/c[a]
CAM-B3LYP	-0.12	-0.08	-0.06	-0.05	-0.04	-0.04	-0.04	-0.03	n/c
AM1	-0.12	-0.14	-0.11	-0.09	-0.08	-0.07	-0.06	-0.05	-0.04
B3P86	-0.12	-0.07	-0.06	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04
tHCTH	-0.12	-0.07	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04
PM3	-0.12	-0.13	-0.10	-0.09	-0.08	-0.07	-0.06	-0.06	-0.05
PDDG	-0.12	-0.14	-0.11	-0.10	-0.09	-0.09	-0.08	-0.08	-0.07
M06	-0.12	-0.07	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04
HCTH/407	-0.11	-0.07	-0.06	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
M06L	-0.11	-0.07	-0.05	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04
B1B95	-0.11	-0.07	-0.06	-0.05	-0.05	-0.05	-0.05	-0.05	-0.04

BHandHLYP	-0.11	-0.08	-0.06	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04
M05	-0.10	-0.08	-0.07	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04
XAlpha	-0.10	-0.06	-0.06	-0.05	-0.05	-0.05	-0.05	-0.05	-0.04
HF	-0.08	-0.11	-0.08	-0.05	-0.04	-0.03	-0.03	-0.02	-0.02
BHandH	-0.08	-0.06	-0.06	-0.06	-0.06	-0.06	-0.06	-0.06	-0.06
HFS	n/c	-0.09	-0.07	-0.05	-0.04	-0.03	-0.02	-0.02	-0.01
BLYP	n/c	-0.09	-0.06	-0.05	-0.04	-0.03	-0.02	-0.02	-0.01

[a] calculation failed to converge.

293 **Table 6.** Experimental, benchmark theoretical [35], and estimated (at the x/TZVP//B3LYP/6-31G(d) level of theory) adiabatic ionization energies (AIEs) for the [n]acenes (n=1-9). Error metrics (MSD=mean signed deviation; MAD=mean absolute deviation; and RMSD=root mean squared deviation) are between AIEs obtained at the x/TZVP//B3LYP/6-31G(d) level of theory and the benchmark theoretical [35] values for the n=1-6 [n]acenes. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=AIE in eV; c= AIE at the polymeric limit). Values are in eV. Note that semiempirical method WWIEs are at the x//B3LYP/6-31G(d) level of theory.

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	[n]acene									error metrics			regression statistics (n=1-9)				regression statistics (n=1-6)	
	1[a]	2	3	4	5	6	7	8	9	MSD	MAD	RMSD	a	b	c	r	c	r
expt.	9.24±0.00 [149]	8.14±0.00 [149]	7.44±0.01 [149]	6.97±0.05 [149]	6.63±0.05 [149]	6.44±0.04 [150] 6.44 [151] 6.36 [152]	n/a[b]	n/a	n/a	n/a	n/a	n/a	4.86[c]	0.403	5.99	0.9999	5.99	0.9999
benchmark theoretical [35]	9.22	8.14	7.42	6.91	6.56	6.42	n/a	n/a	n/a	n/a	n/a	n/a	4.91	0.409	5.97	0.9997	5.97	0.9997
HF	7.78	6.84	6.08	5.52	5.10	4.76	4.50	4.28	4.11	-1.43	1.43	1.44	5.42	0.256	3.58	0.99996	3.67	0.99997
HFB	7.88	6.70	5.96	5.46	5.10	4.83	4.62	4.46	4.32	-1.46	1.46	1.46	5.24	0.347	4.14	0.9995	4.36	0.9998
HFS	8.03	6.79	6.02	5.51	5.14	4.87	4.65	4.48	4.34	-1.39	1.39	1.39	5.44	0.353	4.17	0.9994	4.42	0.9998
XAlpha	8.41	7.15	6.37	5.85	5.47	5.19	4.98	4.80	4.66	-1.04	1.04	1.04	5.53	0.353	4.48	0.9994	4.72	0.9998
BLYP	8.88	7.62	6.85	6.34	5.96	5.69	5.47	5.30	5.15	-0.55	0.55	0.57	5.49	0.353	4.98	0.9993	5.24	0.9998
BHandHLYP	8.89	7.77	7.00	6.47	6.08	5.79	5.57	5.39	5.25	-0.45	0.45	0.46	5.35	0.322	4.99	0.9998	5.16	0.99996
BHandH	8.97	7.82	7.04	6.50	6.11	5.82	5.59	5.41	5.27	-0.40	0.40	0.42	5.44	0.325	5.01	0.9998	5.20	0.99996
B1LYP	8.90	7.71	6.94	6.42	6.04	5.76	5.54	5.37	5.23	-0.48	0.48	0.50	5.40	0.340	5.02	0.9996	5.23	0.9999
M06L	9.00	7.76	6.98	6.45	6.06	5.78	5.55	5.38	5.23	-0.44	0.44	0.46	5.54	0.343	5.03	0.9995	5.27	0.9999
mPW1LYP	8.93	7.73	6.97	6.44	6.06	5.78	5.56	5.39	5.25	-0.46	0.46	0.47	5.42	0.340	5.04	0.9996	5.25	0.9999
B97D	8.92	7.68	6.92	6.40	6.03	5.75	5.54	5.36	5.22	-0.50	0.50	0.51	5.44	0.349	5.04	0.9994	5.28	0.9998
VSXC	8.95	7.71	6.94	6.42	6.05	5.77	5.55	5.38	5.23	-0.47	0.47	0.49	5.47	0.349	5.05	0.9994	5.30	0.9998
TPSSh	8.97	7.77	6.99	6.47	6.10	5.82	5.60	5.42	5.28	-0.43	0.43	0.44	5.43	0.342	5.08	0.9995	5.31	0.99991
O3LYP	8.99	7.76	6.98	6.46	6.08	5.80	5.58	5.41	5.27	-0.43	0.43	0.45	5.49	0.348	5.08	0.9995	5.30	0.9999
M05	8.85	7.72	6.98	6.47	6.10	5.83	5.62	5.45	5.32	-0.45	0.45	0.46	5.20	0.336	5.10	0.9997	5.29	0.99993
OPBE	9.06	7.80	7.02	6.50	6.13	5.85	5.63	5.45	5.31	-0.39	0.39	0.40	5.52	0.352	5.13	0.9994	5.39	0.9998
X3LYP	9.04	7.83	7.06	6.54	6.16	5.88	5.66	5.49	5.35	-0.36	0.36	0.38	5.44	0.343	5.15	0.9996	5.37	0.9999
OTPSS	9.08	7.82	7.04	6.51	6.14	5.86	5.64	5.47	5.32	-0.37	0.37	0.39	5.54	0.352	5.15	0.9994	5.39	0.9999
B1B95	9.07	7.86	7.09	6.56	6.18	5.89	5.67	5.50	5.36	-0.34	0.34	0.36	5.46	0.341	5.15	0.9996	5.36	0.9999
B98	9.03	7.83	7.06	6.54	6.17	5.89	5.67	5.50	5.36	-0.36	0.36	0.37	5.41	0.343	5.16	0.9996	5.39	0.9999
B3LYP	9.08	7.87	7.10	6.58	6.20	5.92	5.70	5.53	5.39	-0.32	0.32	0.34	5.44	0.343	5.19	0.9996	5.41	0.9999
PBE0	9.08	7.91	7.13	6.61	6.23	5.95	5.73	5.56	5.42	-0.29	0.29	0.31	5.39	0.338	5.20	0.9997	5.40	0.99994
mPW1PBE	9.08	7.90	7.13	6.61	6.23	5.95	5.73	5.56	5.42	-0.30	0.30	0.31	5.39	0.339	5.21	0.9996	5.41	0.99991
M06	9.03	7.87	7.11	6.60	6.23	5.95	5.73	5.56	5.43	-0.31	0.31	0.33	5.30	0.338	5.21	0.9996	5.42	0.99991
HSE06	9.07	7.89	7.12	6.59	6.21	5.92	5.70	5.52	n/c	-0.31	0.31	0.33	5.41	0.344	5.21	0.9997	5.36	0.99991
tHCTH	9.10	7.87	7.11	6.59	6.22	5.94	5.72	5.55	5.41	-0.31	0.31	0.33	5.43	0.347	5.22	0.9994	5.46	0.9998
HCTH/147	9.12	7.87	7.10	6.58	6.21	5.93	5.71	5.54	5.40	-0.31	0.31	0.33	5.48	0.352	5.22	0.9994	5.47	0.9998
BMK	9.08	7.94	7.18	6.65	6.27	5.99	5.77	5.60	5.46	-0.26	0.26	0.27	5.33	0.331	5.23	0.9998	5.40	0.99995
tHCTHhyb	9.11	7.91	7.14	6.62	6.25	5.97	5.75	5.58	5.44	-0.28	0.28	0.30	5.41	0.343	5.24	0.9996	5.47	0.9999
B3PW91	9.11	7.92	7.15	6.62	6.25	5.97	5.75	5.58	5.44	-0.28	0.28	0.29	5.41	0.341	5.24	0.9996	5.45	0.99992
mPW3PBE	9.13	7.94	7.16	6.64	6.26	5.98	5.77	5.59	5.45	-0.26	0.26	0.28	5.42	0.342	5.25	0.9996	5.45	0.99992
mPW2PLYPD	9.05	7.89	7.12	6.61	6.23	5.96	5.75	5.59	5.46	-0.30	0.30	0.31	5.32	0.345	5.26	0.9997	5.43	0.99993
HCTH/407	9.17	7.93	7.16	6.64	6.26	5.98	5.76	5.59	5.45	-0.26	0.26	0.28	5.48	0.348	5.26	0.9995	5.49	0.9998
B2PLYPD	9.05	7.88	7.11	6.60	6.23	5.96	5.75	5.59	5.46	-0.31	0.31	0.32	5.32	0.348	5.27	0.9997	5.45	0.99993
wB97	9.07	8.03	7.29	6.77	6.40	6.12	5.90	5.73	5.60	-0.17	0.17	0.18	5.11	0.315	5.33	0.9999	5.46	0.999991

CAM-B3LYP	9.13	7.99	7.23	6.71	6.33	6.05	5.83	5.67	n/c[d]	-0.21	0.21	0.22	5.30	0.343	5.35	0.9998	5.48	0.99994
wB97X	9.09	8.02	7.27	6.75	6.38	6.11	5.90	5.73	5.60	-0.17	0.17	0.19	5.15	0.327	5.36	0.9998	5.50	0.999994
wB97XD	9.08	7.96	7.21	6.70	6.33	6.06	5.86	5.70	5.58	-0.22	0.22	0.23	5.19	0.342	5.37	0.9998	5.51	0.99995
M052X	9.17	8.10	7.34	6.82	6.44	6.16	5.95	5.78	5.64	-0.11	0.11	0.13	5.20	0.322	5.39	0.9999	5.52	0.99999
M062X	9.22	8.16	7.40	6.88	6.50	6.22	6.00	5.83	5.69	-0.05	0.06	0.09	5.20	0.318	5.42	0.9999	5.57	0.99999
LC-wPBE	9.21	8.17	7.42	6.89	6.51	6.23	6.01	5.84	5.70	-0.04	0.05	0.08	5.17	0.313	5.42	0.9999	5.54	0.999998
M06HF	9.41	8.46	7.70	7.19	6.81	6.53	6.31	6.14	6.00	0.24	0.24	0.25	5.03	0.300	5.68	0.99991	5.76	0.99992
B3P86	9.68	8.48	7.71	7.19	6.81	6.53	6.31	6.14	6.00	0.29	0.29	0.31	5.42	0.342	5.80	0.9996	6.01	0.9999
AM1	9.08	8.15	7.53	7.11	6.80	6.57	6.39	6.25	6.14	0.09	0.14	0.16	4.33	0.331	5.95	0.9997	6.11	0.99993
PM3	9.26	8.32	7.69	7.26	6.95	6.71	6.53	6.39	6.28	0.25	0.25	0.28	4.39	0.331	6.08	0.9997	6.23	0.99993
PDDG	9.26	8.34	7.72	7.29	6.97	6.74	6.56	6.42	6.32	0.28	0.28	0.30	4.34	0.328	6.11	0.9998	6.24	0.99995
PM6	9.07	8.28	7.73	7.35	7.07	6.85	6.68	6.55	6.45	0.28	0.33	0.36	3.85	0.310	6.23	0.9998	6.37	0.99994
MP2	9.28	8.24	7.51	7.07	6.79	6.63	6.54	6.51	6.53	0.14	0.14	0.15	4.71	0.487	6.41	0.9993	6.29	0.9999

[a] the benzene cation has a single imaginary frequency at the B3LYP/6-31G(d) level; thus, calculations were conducted at the x/TZVP//B3LYP/6-311++G(d,p) level where the benzene cation is absent imaginary frequencies. [b] Not available. [c] Regression statistics for the experiment values obtained using the average of multiple experimental datapoints where available. [d] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

302 **Table 7.** Benchmark theoretical [36] and estimated (at the x/TZVP//B3LYP/6-31G(d) level of theory) vertical electron affinities (VEAs) for the [n]acenes (n=1-10). Error metrics (MSD=mean signed deviation; MAD=mean absolute deviation; and RMSD=root mean squared deviation) are between VEAs obtained at the x/TZVP//B3LYP/6-31G(d) level of theory and the benchmark theoretical [36] values for the n=1-6 [n]acenes. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=VEA in eV; c= VEA at the polymeric limit). Values are in eV. Note that semiempirical method WWIEs are at the x//B3LYP/6-31G(d) level of theory.

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	[n]acene										error metrics			regression statistics (n=1-10)				regression statistics (n=1-6)	
	1	2	3	4	5	6	7	8	9	10	MSD	MAD	RMSD	a	b	c	r	c	r
benchmark theoretical [36]	-1.53	-0.48	0.28	0.82	1.21	1.47	n/a[a]	n/a	n/a	n/a	n/a	n/a	n/a	-5.17	0.338	2.16	0.99999	2.16	0.99999
MP2	-2.17	-1.05	-0.23	0.28	0.62	0.83	0.95	1.01	1.02	0.98	-0.58	0.58	0.58	-5.25	0.457	1.12	0.9991	1.30	0.9999
HFB	-2.48	-1.27	n/c[b]	0.10	0.50	0.81	1.04	1.23	1.39	1.51	-0.77	0.77	0.77	-5.68	0.311	1.72	0.9996	1.44	0.99993
HFS	-2.53	-1.29	-0.45	0.13	0.54	0.85	1.10	1.29	1.45	1.58	-0.75	0.75	0.76	-5.85	0.316	1.77	0.9996	1.49	0.99997
XAlpha	-2.22	-0.96	-0.12	0.46	0.88	1.19	1.43	1.63	1.79	1.92	-0.42	0.42	0.44	-5.89	0.318	2.11	0.9996	1.83	0.99995
HF	-2.53	-1.43	-0.57	0.07	0.55	0.92	1.22	1.47	1.66	1.83	-0.80	0.80	0.81	-6.19	0.256	2.28	0.99991	2.08	0.99999
B2PLYPD	-1.86	-0.65	0.19	0.77	1.18	1.49	1.72	1.90	2.05	2.17	-0.11	0.12	0.16	-5.78	0.322	2.36	0.9998	2.16	0.99998
mPW2PLYPD	-1.85	-0.64	0.20	0.78	1.19	1.50	1.74	1.93	2.07	2.19	-0.10	0.11	0.15	-5.79	0.320	2.39	0.9998	2.17	0.99998
wB97XD	-1.70	-0.49	0.34	0.92	1.33	1.64	1.87	2.06	2.20	2.31	0.04	0.11	0.12	-5.77	0.322	2.50	0.9998	2.31	0.99998
B1LYP	-1.79	-0.57	0.27	0.85	1.27	1.58	1.83	2.02	2.17	2.30	-0.03	0.09	0.12	-5.84	0.315	2.50	0.9997	2.26	0.99998
mPW1LYP	-1.77	-0.55	0.29	0.87	1.29	1.61	1.85	2.04	2.20	2.32	0.00	0.10	0.12	-5.84	0.314	2.53	0.9997	2.30	0.99996
BLYP	-1.75	-0.49	n/c	0.91	1.32	1.63	1.87	2.06	2.22	2.35	0.03	0.12	0.14	-5.83	0.315	2.55	0.9996	2.24	0.99992
O3LYP	-1.76	-0.50	0.35	0.93	1.34	1.66	1.90	2.09	2.25	2.38	0.04	0.12	0.14	-5.90	0.320	2.56	0.9996	2.29	0.99994
BHandHLYP	-1.81	-0.63	0.22	0.81	1.25	1.57	1.83	2.03	2.18	2.31	-0.06	0.11	0.14	-5.88	0.303	2.56	0.9998	2.36	0.99999
BHandH	-1.85	-0.65	0.21	0.81	1.25	1.58	1.83	2.04	2.19	2.32	-0.07	0.12	0.16	-5.96	0.304	2.57	0.9998	2.37	0.99999
wB97X	-1.68	-0.50	0.34	0.93	1.35	1.67	1.91	2.10	2.25	2.37	0.06	0.11	0.13	-5.80	0.311	2.59	0.9998	2.42	0.99999
B1B95	-1.77	-0.52	0.33	0.92	1.34	1.66	1.91	2.10	2.26	2.39	0.03	0.13	0.15	-5.93	0.316	2.59	0.9997	2.33	0.99996
BMK	-1.80	-0.56	0.30	0.89	1.33	1.65	1.90	2.10	2.26	2.38	0.01	0.12	0.15	-5.98	0.312	2.60	0.9998	2.37	0.99997
CAM-B3LYP	-1.63	-0.44	0.40	0.98	1.40	1.71	1.95	2.14	2.29	2.41	0.11	0.14	0.15	-5.79	0.314	2.62	0.9998	2.42	0.99999
X3LYP	-1.67	-0.44	0.40	0.98	1.40	1.71	1.95	2.15	2.30	2.43	0.10	0.15	0.16	-5.85	0.316	2.63	0.9997	2.38	0.99997
M06L	-1.73	-0.44	0.41	0.99	1.41	1.72	1.97	2.16	2.32	2.46	0.10	0.16	0.18	-5.96	0.322	2.63	0.9995	2.33	0.99993
B98	-1.71	-0.47	0.38	0.97	1.39	1.71	1.95	2.15	2.30	2.43	0.08	0.14	0.16	-5.91	0.316	2.63	0.9997	2.39	0.99997
TPSSh	-1.71	-0.45	0.40	0.98	1.41	1.72	1.97	2.16	2.32	2.45	0.10	0.16	0.17	-5.93	0.318	2.64	0.9996	2.38	0.99995
B97D	-1.68	-0.41	n/c	1.00	1.41	1.72	1.96	2.16	2.31	2.44	0.11	0.17	0.18	-5.87	0.316	2.64	0.9996	2.33	0.99993
wB97	-1.69	-0.52	0.33	0.92	1.35	1.68	1.93	2.12	2.28	2.40	0.05	0.12	0.13	-5.85	0.304	2.65	0.9999	2.47	0.99998
M05	-1.67	-0.41	0.43	1.01	1.43	1.74	1.98	2.18	2.33	2.46	0.13	0.17	0.18	-5.89	0.320	2.65	0.9996	2.38	0.99995
VSXC	-1.79	-0.47	0.40	1.00	1.43	1.75	2.00	2.20	2.36	2.50	0.09	0.18	0.20	-6.11	0.322	2.68	0.9995	2.39	0.99994
B3LYP	-1.62	-0.39	0.44	1.02	1.44	1.68	2.00	2.19	2.35	2.47	0.13	0.16	0.17	-5.81	0.311	2.68	0.9994	2.28	0.99996
OTPSS	-1.69	-0.38	0.47	1.05	1.47	1.79	2.03	2.23	2.38	2.52	0.16	0.21	0.22	-5.99	0.324	2.69	0.9995	2.39	0.9999
OPBE	-1.70	-0.39	n/c	1.04	1.46	1.78	2.02	2.22	2.38	2.51	0.14	0.21	0.22	-5.99	0.317	2.71	0.9995	2.38	0.9999
M06	-1.59	-0.35	0.48	1.06	1.48	1.79	2.03	2.23	2.38	2.51	0.18	0.20	0.22	-5.84	0.316	2.71	0.9996	2.45	0.99995
PBE0	-1.63	-0.39	0.45	1.04	1.47	1.79	2.03	2.23	2.38	2.51	0.16	0.19	0.21	-5.91	0.314	2.72	0.9997	2.49	0.99996
mPW1PBE	-1.63	-0.39	0.45	1.04	1.47	1.79	2.03	2.23	2.38	2.51	0.16	0.19	0.21	-5.91	0.314	2.72	0.9997	2.49	0.99996
M062X	-1.67	-0.44	0.42	1.02	1.45	1.78	2.03	2.23	2.38	2.51	0.13	0.18	0.20	-5.97	0.311	2.73	0.9998	2.52	0.99998
B3PW91	-1.60	-0.35	0.49	1.08	1.50	1.81	2.06	2.25	2.41	2.54	0.19	0.22	0.24	-5.90	0.317	2.74	0.9996	2.47	0.99997
tHCTHhyb	-1.59	-0.33	0.52	1.10	1.52	1.84	2.08	2.28	2.43	2.56	0.21	0.23	0.25	-5.92	0.319	2.75	0.9996	2.49	0.99994
mPW3PBE	-1.58	-0.34	0.51	1.09	1.51	1.83	2.08	2.27	2.43	2.56	0.21	0.23	0.25	-5.90	0.315	2.76	0.9997	2.50	0.99996
M052X	-1.68	-0.44	0.43	1.03	1.47	1.80	2.05	2.25	2.41	2.53	0.14	0.19	0.21	-6.03	0.312	2.76	0.9998	2.55	0.99997
HSE06	-1.63	-0.38	0.47	1.06	1.49	1.81	2.06	2.26	2.42	2.56	0.17	0.21	0.22	-5.96	0.312	2.77	0.9996	2.50	0.99996
LC-wPBE	-1.55	-0.37	0.47	1.06	1.50	1.82	2.07	2.27	2.42	2.55	0.19	0.20	0.23	-5.86	0.304	2.79	0.9998	2.61	0.99999

HCTH/147	-1.54	-0.26	0.58	1.16	1.57	1.88	2.13	2.32	2.48	2.61	0.27	0.27	0.30	-5.91	0.322	2.79	0.9995	2.48	0.99993
tHCTH	-1.49	-0.22	0.62	1.20	1.61	1.92	2.16	2.36	2.51	2.64	0.31	0.31	0.34	-5.89	0.322	2.82	0.9995	2.53	0.99994
HCTH/407	-1.50	-0.21	n/c	1.21	1.62	1.93	2.17	2.37	2.53	2.66	0.31	0.31	0.35	-5.92	0.317	2.86	0.9995	2.52	0.99992
M06HF	-1.66	-0.46	0.43	1.05	1.50	1.85	2.11	2.31	2.48	2.61	0.16	0.20	0.23	-6.11	0.300	2.88	0.9999	2.72	0.99998
B3P86	-1.03	0.21	1.06	1.64	2.06	2.38	2.63	2.82	2.98	3.11	0.76	0.76	0.77	-5.90	0.315	3.31	0.9997	3.05	0.99996
AM1	-0.11	0.74	1.39	1.86	2.21	2.47	2.68	2.85	2.98	3.09	1.13	1.13	1.14	-4.56	0.277	3.35	0.9999	3.22	0.999991
PM3	-0.07	0.81	1.47	1.93	2.27	2.53	2.74	2.90	3.03	3.13	1.20	1.20	1.20	-4.56	0.288	3.36	0.9999	3.20	0.99998
PDDG	-0.08	0.83	1.49	1.95	2.30	2.57	2.77	2.94	3.07	3.18	1.21	1.21	1.22	-4.63	0.288	3.41	0.9998	3.24	0.99997
PM6	0.01	0.92	1.57	2.03	2.38	2.65	2.86	3.04	3.18	3.29	1.30	1.30	1.31	-4.64	0.280	3.54	0.9997	3.32	0.99996

[a] not available. [b] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

Table 8. Estimated vertical electron affinities (VEAs) for the [n]acenes (n=1-10) at the B3LYP/y//B3LYP/6-31G(d) level of theory. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=VEA in eV; c= VEA at the polymeric limit). Values are in eV.

	[n]acene										regression statistics (n=1-10)				regression statistics (n=1-6)	
basis set	1	2	3	4	5	6	7	8	9	10	a	b	c	r	c	r
6-31G(d)	-2.30	-0.90	0.01	0.62	1.06	1.38	1.64	1.84	2.00	2.13	-6.35	0.334	2.29	0.9995	1.98	0.99993
6-311++G(d,p)	-0.60	-0.31	0.51	1.07	1.49	1.80	2.04	2.23	n/c[a]	2.51	-4.90	0.194	3.27	0.994	6.21	0.992
6-311++G(2d,2p)	-0.59	-0.29	0.51	1.08	1.49	1.80	2.04	2.24	2.39	2.52	-4.86	0.194	3.26	0.995	6.11	0.992
SVP	-1.93	-0.58	0.30	0.90	1.33	1.66	1.91	2.11	2.26	2.39	-6.18	0.328	2.57	0.9996	2.28	0.9999
TZV	-1.75	-0.49	n/c	0.94	1.37	1.68	1.92	2.12	2.27	2.40	-5.92	0.314	2.61	0.9997	2.34	0.99995
TZVP	-1.62	-0.39	0.44	1.02	1.44	1.68	2.00	2.19	2.35	2.47	-5.81	0.311	2.68	0.9994	2.28	0.99996
cc-pVDZ	-1.99	-0.64	0.24	0.85	1.28	1.60	1.85	2.05	2.21	2.35	-6.19	0.327	2.52	0.9995	2.23	0.99994
cc-pVTZ	-1.71	-0.44	0.41	1.00	1.42	n/c	1.98	2.18	2.33	2.46	-5.97	0.322	2.65	0.9997	2.31	0.99998

[a] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

315 **Table 9.** Estimated (at the x/TZVP//B3LYP/6-31G(d) level of theory) well-to-well electron affinities (WWEAs) for the [n]acenes (n=1-10). Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=WWEA in eV; c=WWEA at the polymeric limit). Values are in eV. Note that semiempirical method WWEAs are at the x//B3LYP/6-31G(d) level of theory.

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	[n]acene										error metrics			regression statistics (n=1-10)				regression statistics (n=1-6)	
	1	2	3	4	5	6	7	8	9	10	MSD	MAD	RMSD	a	b	c	r	c	r
MP2	-2.12	-0.98	-0.19	0.32	0.64	0.84	0.95	0.99	0.99	0.95	-0.80	0.80	0.81	-5.22	0.478	1.08	0.999	1.26	0.99994
HFS	-2.30	-1.11	n/c	0.26	0.66	0.96	1.19	1.37	1.53	n/c	-0.87	0.87	0.89	-5.63	0.322	1.80	0.9998	1.60	0.99997
HFB	-2.14	-1.01	n/c[b]	0.28	0.66	0.95	1.17	1.35	1.50	1.62	-0.81	0.81	0.82	-5.35	0.308	1.82	0.9997	1.56	0.99995
XAlpha	-2.09	-0.87	n/c	0.52	0.93	1.24	1.47	1.66	1.81	1.94	-0.61	0.61	0.65	-5.75	0.314	2.14	0.9997	1.89	0.99995
HF	-2.36	-1.34	-0.53	0.07	0.53	0.89	1.18	1.42	1.62	1.78	-1.01	1.01	1.02	-5.89	0.246	2.26	0.99991	2.06	0.99999
B2PLYPD	-1.72	-0.55	0.26	0.82	1.22	1.52	1.74	1.92	2.06	2.17	-0.30	0.30	0.34	-5.59	0.323	2.35	0.9998	2.17	0.99998
mPW2PLYPD	-1.72	-0.55	0.26	0.82	1.23	1.53	1.75	1.93	2.08	2.19	-0.29	0.29	0.34	-5.61	0.320	2.38	0.9998	2.20	0.99998
wB97XD	-1.56	-0.41	0.39	0.95	1.35	1.65	1.88	2.06	2.19	2.30	-0.16	0.16	0.23	-5.55	0.318	2.50	0.9998	2.32	0.99998
BHandH	-1.80	-0.63	0.21	0.80	1.22	1.55	1.80	1.99	2.15	2.28	-0.33	0.33	0.39	-5.82	0.303	2.52	0.9998	2.32	0.99998
BHandHLYP	-1.71	-0.58	0.24	0.82	1.24	1.56	1.80	2.00	2.15	2.28	-0.29	0.29	0.34	-5.69	0.299	2.53	0.9998	2.35	0.999991
mPW1LYP	-1.62	-0.45	0.36	0.92	1.33	1.63	1.87	2.06	2.21	2.33	-0.19	0.19	0.26	-5.64	0.311	2.54	0.9997	2.30	0.99998
B1LYP	-1.64	-0.47	n/c	0.90	1.31	1.61	1.85	2.04	2.19	2.31	-0.22	0.22	0.29	-5.64	0.307	2.54	0.9998	2.29	0.99998
wB97X	-1.54	-0.41	0.40	0.96	1.37	1.68	1.91	2.09	2.24	2.35	-0.14	0.16	0.22	-5.58	0.310	2.57	0.9999	2.41	0.99998
BMK	-1.62	-0.44	0.38	0.95	1.37	1.68	1.92	2.11	2.26	2.39	-0.17	0.18	0.26	-5.72	0.310	2.60	0.9998	2.39	0.99997
BLYP	-1.54	-0.34	n/c	1.01	1.41	1.71	1.94	2.12	2.28	2.40	-0.11	0.15	0.22	-5.61	0.313	2.60	0.9996	2.32	0.99993
B1B95	-1.66	-0.46	n/c	0.95	1.36	1.67	1.91	2.10	2.25	2.38	-0.19	0.20	0.29	-5.77	0.310	2.60	0.9998	2.36	0.99998
O3LYP	-1.61	-0.40	n/c	0.99	1.40	1.70	1.94	2.13	2.28	2.40	-0.14	0.17	0.26	-5.73	0.313	2.61	0.9997	2.35	0.99997
wB97	-1.53	-0.41	0.39	0.96	1.37	1.68	1.92	2.11	2.26	2.38	-0.14	0.16	0.22	-5.58	0.302	2.62	0.9998	2.43	0.999992
TPSSh	-1.55	-0.35	0.48	1.05	1.46	1.76	2.00	2.19	2.35	n/c	-0.08	0.15	0.21	-5.73	0.324	2.62	0.9998	2.42	0.99998
CAM-B3LYP	-1.50	-0.36	0.44	1.01	1.41	1.72	1.95	2.14	2.28	2.40	-0.10	0.14	0.20	-5.58	0.310	2.62	0.9998	2.43	0.99998
X3LYP	-1.52	-0.35	0.47	1.03	1.44	1.74	1.98	2.17	2.32	2.44	-0.08	0.14	0.20	-5.65	0.312	2.65	0.9997	2.41	0.99998
M05	-1.52	-0.32	0.49	1.06	1.47	1.77	2.01	2.19	2.34	2.46	-0.06	0.14	0.20	-5.69	0.318	2.65	0.9997	2.43	0.99997
M06L	-1.60	-0.37	0.46	1.03	1.45	1.75	1.99	2.18	2.34	2.47	-0.10	0.16	0.24	-5.80	0.317	2.66	0.9996	2.39	0.99996
B98	-1.54	-0.35	n/c	1.03	1.44	1.75	1.98	2.17	2.32	2.45	-0.09	0.16	0.23	-5.69	0.309	2.67	0.9997	2.43	0.99996
B97D	-1.49	-0.28	n/c	1.08	1.48	1.78	2.01	2.20	2.35	2.48	-0.04	0.16	0.21	-5.65	0.313	2.68	0.9996	2.39	0.99994
B3LYP	-1.47	-0.29	0.52	1.08	1.49	1.79	2.03	2.21	2.37	2.49	-0.04	0.14	0.19	-5.64	0.313	2.69	0.9997	2.45	0.99997
VSXC	-1.60	-0.35	0.49	1.07	1.48	1.80	2.04	2.23	2.39	2.52	-0.07	0.17	0.24	-5.87	0.318	2.71	0.9996	2.44	0.99994
M062X	-1.54	-0.36	0.47	1.05	1.47	1.78	2.03	2.22	2.37	2.49	-0.07	0.16	0.22	-5.76	0.310	2.71	0.9998	2.50	0.99999
mPW1PBE	-1.50	-0.31	0.51	1.08	1.50	1.81	2.05	2.24	2.39	2.51	-0.04	0.15	0.20	-5.73	0.312	2.72	0.9998	2.51	0.99997
M06	-1.46	-0.28	n/c	1.09	1.50	1.81	2.04	2.23	2.38	2.50	-0.03	0.17	0.20	-5.65	0.309	2.72	0.9998	2.49	0.99996
PBE0	-1.50	-0.31	n/c	1.09	1.50	1.81	2.05	2.24	2.39	2.52	-0.04	0.18	0.22	-5.73	0.308	2.74	0.9998	2.50	0.99998
OPBE	-1.54	-0.28	n/c	1.12	1.53	1.84	2.08	2.26	2.42	2.55	-0.02	0.20	0.24	-5.83	0.317	2.74	0.9996	2.45	0.99992
M052X	-1.55	-0.36	n/c	1.06	1.48	1.80	2.04	2.24	2.39	2.51	-0.07	0.19	0.25	-5.81	0.306	2.75	0.9998	2.54	0.99998
LC-wPBE	-1.42	-0.30	0.51	1.08	1.50	1.81	2.05	2.24	2.39	2.51	-0.03	0.14	0.17	-5.62	0.302	2.75	0.9999	2.58	0.999994
OTPSS	-1.52	-0.27	n/c	1.14	1.54	1.85	2.09	2.28	2.43	2.56	-0.01	0.20	0.24	-5.82	0.317	2.76	0.9996	2.46	0.99995
mPW3PBE	-1.45	-0.25	0.57	1.14	1.55	1.86	2.10	2.29	2.44	2.56	0.02	0.16	0.20	-5.73	0.315	2.76	0.9997	2.53	0.99996
B3PW91	-1.46	-0.27	n/c	1.13	1.54	1.84	2.08	n/c	2.42	2.55	0.00	0.18	0.22	-5.73	0.309	2.77	0.9997	2.52	0.99999
HSE06	-1.49	-0.30	0.53	1.10	1.52	1.83	2.08	2.27	2.43	2.56	-0.02	0.16	0.21	-5.76	0.308	2.78	0.9997	2.53	0.99997
tHCTHhyb	-1.42	-0.22	n/c	1.17	1.58	1.88	2.12	2.31	2.46	2.58	0.04	0.19	0.22	-5.71	0.312	2.79	0.9997	2.54	0.99998
M06HF	-1.53	-0.38	0.46	1.06	1.49	1.82	2.07	2.27	2.42	2.55	-0.07	0.17	0.22	-5.83	0.299	2.81	0.9999	2.65	0.999993
HCTH/147	-1.39	-0.16	0.67	1.23	1.63	1.94	2.17	2.36	2.51	2.64	0.10	0.21	0.23	-5.75	0.322	2.81	0.9996	2.55	0.99994
tHCTH	-1.34	-0.12	0.70	1.26	1.67	1.97	2.20	2.39	2.54	2.67	0.14	0.23	0.24	-5.72	0.320	2.85	0.9996	2.59	0.99995

HCTH/407	-1.36	-0.12	0.71	1.27	1.68	1.98	2.22	2.40	2.56	2.69	0.14	0.23	0.25	-5.77	0.322	2.86	0.9995	2.59	0.99995
PM3	-0.09	0.85	1.49	1.94	2.27	2.52	2.71	2.87	2.99	3.09	0.94	0.94	0.94	-4.52	0.306	3.27	0.9997	3.07	0.99995
AM1	-0.14	0.80	1.44	1.90	2.24	2.49	2.69	2.85	2.98	3.08	0.90	0.90	0.90	-4.57	0.300	3.28	0.9997	3.07	0.99996
PDDG	-0.10	0.86	1.50	1.95	2.28	2.54	2.73	2.89	3.01	3.11	0.95	0.95	0.95	-4.56	0.307	3.29	0.9997	3.08	0.9999
B3P86	-0.90	0.29	1.12	1.69	2.10	2.41	2.64	2.83	2.99	3.11	0.56	0.56	0.60	-5.73	0.315	3.31	0.9997	3.09	0.99998
PM6	0.02	0.99	1.62	2.07	2.40	2.66	2.86	3.03	3.16	3.28	1.07	1.07	1.07	-4.58	0.297	3.47	0.9994	3.19	0.9998

[a] not available. [b] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

Table 10. Estimated vertical electron affinities (VEAs) for the [n]acenes (n=1-10) at the B3LYP/y//B3LYP/6-31G(d) level of theory. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=VEA in eV; c= VEA at the polymeric limit). Values are in eV.

	[n]acene										regression statistics (n=1-10)				regression statistics (n=1-6)	
basis set	1	2	3	4	5	6	7	8	9	10	a	b	c	r	c	r
6-31G(d)	-2.10	-0.77	0.11	0.70	1.12	1.44	1.68	1.88	2.03	2.16	-6.10	0.331	2.32	0.9995	2.04	0.99993
6-311++G(d,p)	-1.29	-0.20	0.59	1.14	1.54	1.84	2.07	2.26	n/c[a]	2.53	-5.44	0.303	2.75	0.9998	2.57	0.999991
6-311++G(2d,2p)	-1.29	-0.20	0.58	1.13	1.53	1.83	2.07	2.26	2.41	n/c	-5.43	0.305	2.73	0.9999	2.56	0.999991
SVP	-1.72	-0.43	0.42	1.00	1.42	1.73	1.97	2.16	2.31	2.44	-5.95	0.327	2.61	0.9996	2.34	0.99993
TZV	-1.56	-0.37	n/c	1.02	1.42	1.73	1.96	2.15	n/c	2.43	-5.69	0.311	2.63	0.9997	2.40	0.99997
TZVP	-1.47	-0.29	0.52	1.08	1.49	1.79	2.03	2.21	2.37	2.49	-5.64	0.313	2.69	0.9997	2.45	0.99997
cc-pVDZ	-1.78	-0.49	0.36	0.94	1.36	1.67	1.91	2.10	2.26	2.39	-5.95	0.325	2.56	0.9995	2.28	0.99993
cc-pVTZ	-1.56	-0.35	0.48	1.05	1.46	n/c	2.00	2.19	2.35	2.47	-5.77	0.319	2.66	0.9997	2.35	0.999993

[a] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

Table 11. Estimated relaxation energies (E_{relax}) from the anionic form of the neutral geometry to the optimized anionic geometry for the [n]acenes (n=1-10) at the x/TZVP//B3LYP/6-31G(d) level of theory. Values are in eV. Note that semiempirical method E_{relax} are at the x//B3LYP/6-31G(d) level of theory.

	[n]acene									
model chemistry	1	2	3	4	5	6	7	8	9	10
AM1	-0.03	0.06	0.05	0.04	0.03	0.02	0.01	0.00	-0.01	-0.01
PM3	-0.03	0.04	0.02	0.01	0.00	-0.01	-0.02	-0.03	-0.04	-0.05
PDDG	-0.02	0.03	0.01	0.00	-0.02	-0.03	-0.04	-0.05	-0.06	-0.07
HFS	n/c[a]	0.18	n/c	0.13	0.12	0.10	0.09	0.08	0.08	n/c
BLYP	n/c	0.15	n/c	0.10	0.09	0.08	0.07	0.06	0.06	0.05
PM6	0.01	0.07	0.05	0.03	0.02	0.01	0.00	0.00	-0.01	-0.02
MP2	0.05	0.07	0.05	0.03	0.02	0.00	-0.01	-0.02	-0.03	-0.04
BHandH	0.05	0.01	0.00	-0.02	-0.03	-0.03	-0.04	-0.04	-0.05	-0.05
BHandHLYP	0.10	0.05	0.02	0.01	-0.01	-0.01	-0.02	-0.03	-0.03	-0.03
B1B95	0.11	0.06	n/c	0.03	0.02	0.01	0.00	0.00	-0.01	-0.01
M06	0.13	0.07	n/c	0.04	0.02	0.02	0.01	0.00	0.00	0.00
XAlpha	0.13	0.08	n/c	0.06	0.05	0.05	0.04	0.03	0.03	0.03
LC-wPBE	0.13	0.07	0.04	0.01	0.00	-0.01	-0.02	-0.03	-0.03	-0.03
M06L	0.13	0.08	0.06	0.05	0.04	0.03	0.03	0.02	0.02	0.01
B3P86	0.13	0.08	0.06	0.04	0.03	0.02	0.02	0.01	0.01	0.00
CAM-B3LYP	0.13	0.08	0.05	0.03	0.02	0.01	0.00	-0.01	n/c	-0.01
M052X	0.13	0.08	n/c	0.03	0.01	0.00	-0.01	-0.02	-0.02	-0.02
mPW1PBE	0.13	0.08	0.06	0.04	0.03	0.02	0.02	0.01	0.01	0.00
HSE06	0.13	0.08	0.06	0.04	0.03	0.02	0.02	0.01	n/c	0.00
PBE0	0.13	0.08	n/c	0.04	0.03	0.02	0.02	0.01	0.01	0.00
mPW2PLYPD	0.13	0.09	0.06	0.04	0.03	0.02	0.01	0.01	0.00	0.00
M062X	0.13	0.08	0.05	0.03	0.02	0.01	0.00	-0.01	-0.01	-0.02
HCTH/407	0.14	0.09	n/c	0.06	0.06	0.05	0.04	0.04	0.03	0.03
M06HF	0.14	0.08	0.04	0.01	-0.01	-0.03	-0.04	-0.05	-0.05	-0.05
mPW3PBE	0.14	0.09	0.06	0.05	0.04	0.03	0.02	0.02	0.01	0.01
wB97XD	0.14	0.08	0.05	0.04	0.02	0.01	0.00	0.00	-0.01	-0.01
B3PW91	0.14	0.09	n/c	0.05	0.04	0.03	0.02	n/c	0.01	0.01
wB97X	0.14	0.09	0.06	0.03	0.02	0.01	0.00	-0.01	-0.01	-0.02
B2PLYPD	0.14	0.10	0.07	0.05	0.04	0.03	0.02	0.02	0.01	0.01
tHCTH	0.15	0.10	0.08	0.07	0.06	0.05	0.04	0.04	0.03	0.03
mPW1LYP	0.15	0.09	0.07	0.05	0.04	0.03	0.02	0.02	0.01	0.01
X3LYP	0.15	0.10	0.07	0.05	0.04	0.03	0.02	0.02	0.01	0.01
O3LYP	0.15	0.10	n/c	0.06	0.05	0.04	0.04	0.03	0.03	0.02
M05	0.15	0.09	0.06	0.05	0.04	0.03	0.02	0.02	0.01	0.01
B1LYP	0.15	0.10	n/c	0.05	0.04	0.03	0.02	0.02	0.01	0.01
B3LYP	0.15	0.10	0.07	0.06	0.04	0.11	0.03	0.02	0.02	0.01
HCTH/147	0.16	0.11	0.09	0.07	0.06	0.05	0.05	0.04	0.04	0.03
OPBE	0.16	0.11	n/c	0.08	0.07	0.06	0.06	0.05	0.04	0.04
OTPSS	0.16	0.11	n/c	0.08	0.07	0.06	0.06	0.05	0.04	0.04
TPSSh	0.16	0.11	0.08	0.06	0.05	0.04	0.03	0.03	0.02	n/c

wB97	0.16	0.11	0.07	0.04	0.02	0.01	0.00	-0.01	-0.01	-0.02
tHCTHhyb	0.17	0.11	n/c	0.07	0.06	0.05	0.04	0.03	0.03	0.02
B98	0.17	0.11	n/c	0.06	0.05	0.04	0.03	0.03	0.02	0.02
HF	0.18	0.09	0.04	0.01	-0.01	-0.03	-0.04	-0.04	-0.05	-0.05
BMK	0.18	0.12	0.08	0.06	0.04	0.03	0.02	0.01	0.01	0.00
VSXC	0.19	0.12	0.09	0.07	0.06	0.05	0.04	0.03	0.03	0.02
B97D	0.20	0.13	n/c	0.08	0.07	0.06	0.05	0.04	0.04	0.03
HFB	0.34	0.26	n/c	0.18	0.16	0.14	0.13	0.12	0.11	0.11

[a] calculation failed to converge.

Table 12. Experimental, benchmark theoretical [36], and estimated (at the x/TZVP//B3LYP/6-31G(d) level of theory) adiabatic electron affinities (AEAs) for the [n]acenes (n=1-10). Error metrics (MSD=mean signed deviation; MAD=mean absolute deviation; and RMSD=root mean squared deviation) are between AEAs obtained at the x/TZVP//B3LYP/6-31G(d) level of theory and the benchmark theoretical [36] values for the n=1-6 [n]acenes. Regression analysis parameters employ a single exponential decay function having a y-axis offset of the general form $y=ae^{-bx}+c$ (x=n, y(x)=AEA in eV; c= AEA at the polymeric limit). Values are in eV. Note that semiempirical method AEAs are at the x//B3LYP/6-31G(d) level of theory.

	[n]acene										error metrics			regression statistics (n=1-10)				regression statistics (n=1-6)	
	1[a]	2	3	4	5	6	7	8	9	10	MSD	MAD	RMSD	a	b	c	r	c	r
expt.	-1.12±0.03	0.1480±0.0060 [153] <0.134±0.043 [154, 155] 0.140±0.050 [156] -0.1908 [157] -0.200±0.050 [158] -0.18 [159] 0.2 [160]	0.41998 [161] <0.481±0.039 [154, 155] 0.5560±0.0080 [153] 0.570±0.020 [162] 0.660±0.060 [163] [153] 0.60±0.10 [164] 0.5300±0.0050 [165] 0.530±0.020 [166]	0.880±0.040 [162] 1.0580±0.0050 [167] 1.067±0.043 [168]	1.392±0.043 [168]	n/a[a]	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a[b]	n/a	n/a	n/a	n/a	n/a
benchmark theoretical [36]	-1.07	-0.19	0.53	1.03	1.39	1.63	n/a	n/a	n/a	n/a	n/a	n/a	n/a	-4.72	0.311	2.38	0.9998	2.38	0.9998
MP2	-1.89	-0.82	-0.06	0.43	0.74	0.93	1.05	1.09	1.09	1.05	-0.66	0.66	0.67	-4.96	0.468	1.18	0.999	1.35	0.9999
HFS	-2.06	-0.95	n/c	0.37	0.76	1.05	1.29	1.47	1.63	n/c	-0.72	0.72	0.74	-5.40	0.308	1.93	0.9998	1.72	0.99999
HFB	-1.91	-0.86	n/c	0.39	0.77	1.05	1.27	1.45	1.60	1.72	-0.67	0.67	0.68	-5.15	0.296	1.95	0.9997	1.71	0.99998
XAlpha	-1.85	-0.72	n/c	0.64	1.03	1.33	1.57	1.76	1.91	2.04	-0.47	0.47	0.50	-5.53	0.301	2.27	0.9997	2.02	0.99999
HF	-2.12	-1.19	-0.40	0.19	0.64	0.99	1.28	1.52	1.72	1.88	-0.87	0.87	0.88	-5.72	0.235	2.41	0.99992	2.28	0.99992
B2PLYPD	-1.48	-0.40	0.39	0.93	1.32	1.61	1.84	2.02	2.16	2.27	-0.16	0.16	0.20	-5.37	0.309	2.48	0.9998	2.30	0.99999
mPW2PLYPD	-1.48	-0.40	0.39	0.93	1.33	1.62	1.85	2.03	2.18	2.29	-0.15	0.15	0.20	-5.39	0.306	2.51	0.9998	2.33	0.99999
wB97XD	-1.33	-0.25	0.52	1.07	1.46	1.75	1.98	2.16	2.29	2.40	-0.02	0.09	0.12	-5.35	0.309	2.62	0.9999	2.46	0.999997
BHandHLYP	-1.47	-0.42	0.37	0.93	1.35	1.66	1.90	2.10	2.25	2.38	-0.15	0.16	0.21	-5.49	0.288	2.66	0.9999	2.51	0.999993
BHandH	-1.56	-0.48	0.33	0.91	1.33	1.65	1.90	2.09	2.25	2.38	-0.19	0.20	0.25	-5.62	0.290	2.66	0.9999	2.50	0.999992
mPW1LYP	-1.38	-0.30	0.49	1.03	1.43	1.73	1.97	2.16	2.31	2.43	-0.05	0.10	0.14	-5.43	0.298	2.67	0.9998	2.45	0.99998
B1LYP	-1.40	-0.32	n/c	1.01	1.41	1.71	1.95	2.14	2.29	2.41	-0.07	0.12	0.16	-5.43	0.293	2.67	0.9999	2.46	0.999996
wB97X	-1.30	-0.25	0.52	1.07	1.47	1.77	2.01	2.19	2.34	2.45	0.00	0.10	0.12	-5.36	0.296	2.70	0.9999	2.54	0.999997
B1B95	-1.42	-0.30	n/c[b]	1.06	1.47	1.77	2.01	2.20	2.35	2.48	-0.04	0.14	0.18	-5.56	0.298	2.72	0.9998	2.51	0.999995
BMK	-1.39	-0.29	0.51	1.07	1.47	1.78	2.02	2.21	2.36	2.49	-0.03	0.12	0.15	-5.52	0.299	2.73	0.9998	2.52	0.99999
BLYP	-1.30	-0.19	n/c	1.12	1.51	1.81	2.04	2.22	2.38	2.50	0.03	0.13	0.15	-5.40	0.299	2.73	0.9997	2.49	0.99997
O3LYP	-1.37	-0.24	n/c	1.10	1.50	1.80	2.04	2.23	2.38	2.50	0.00	0.14	0.17	-5.51	0.300	2.74	0.9998	2.49	0.99998
CAM-B3LYP	-1.26	-0.21	0.57	1.12	1.52	1.82	2.05	2.24	n/c	2.50	0.04	0.11	0.13	-5.37	0.298	2.74	0.9999	2.59	0.999992
wB97	-1.29	-0.26	0.52	1.07	1.48	1.78	2.02	2.21	2.36	2.48	0.00	0.10	0.12	-5.38	0.290	2.75	0.9999	2.60	0.99999
TPSSh	-1.31	-0.19	0.61	1.16	1.56	1.86	2.10	2.29	2.45	n/c	0.06	0.14	0.17	-5.51	0.311	2.75	0.9998	2.55	0.99998
X3LYP	-1.28	-0.19	0.60	1.14	1.54	1.84	2.08	2.27	2.42	2.54	0.05	0.13	0.15	-5.44	0.300	2.78	0.9998	2.55	0.99998
M06L	-1.36	-0.21	0.59	1.15	1.55	1.85	2.09	2.28	2.44	2.57	0.04	0.15	0.17	-5.58	0.306	2.78	0.9996	2.52	0.99998
M05	-1.29	-0.17	0.62	1.17	1.57	1.87	2.11	2.29	2.44	2.56	0.08	0.15	0.17	-5.49	0.306	2.78	0.9998	2.56	0.99998
B98	-1.30	-0.20	n/c	1.14	1.54	1.85	2.08	2.27	2.42	2.55	0.05	0.14	0.17	-5.48	0.296	2.80	0.9998	2.60	0.99998
B97D	-1.25	-0.13	n/c	1.19	1.58	1.88	2.11	2.30	2.45	2.58	0.10	0.17	0.18	-5.44	0.299	2.81	0.9997	2.55	0.99997
B3LYP	-1.23	-0.14	0.65	1.19	1.59	1.89	2.13	2.31	2.47	2.59	0.10	0.16	0.17	-5.44	0.300	2.82	0.9998	2.60	0.99998
VSXC	-1.36	-0.20	0.62	1.18	1.59	1.90	2.14	2.33	2.49	2.62	0.07	0.17	0.19	-5.66	0.306	2.84	0.9997	2.59	0.99997

M062X	-1.30	-0.20	0.60	1.17	1.57	1.88	2.13	2.32	2.47	2.59	0.07	0.15	0.17	-5.55	0.298	2.84	0.9998	2.64	0.999991
mPW1PBE	-1.27	-0.16	0.64	1.20	1.60	1.91	2.15	2.34	2.49	2.61	0.10	0.17	0.18	-5.53	0.302	2.85	0.9998	2.64	0.99999
M06	-1.23	-0.13	n/c	1.21	1.60	1.91	2.14	2.33	2.48	2.60	0.11	0.18	0.19	-5.46	0.298	2.85	0.9998	2.63	0.99998
PBE0	-1.27	-0.16	n/c	1.20	1.61	1.91	2.15	2.34	2.49	2.62	0.10	0.18	0.20	-5.54	0.297	2.87	0.9998	2.66	0.999998
OPBE	-1.30	-0.13	n/c	1.24	1.64	1.94	2.18	2.36	2.52	2.65	0.12	0.21	0.23	-5.61	0.306	2.87	0.9997	2.60	0.99998
OTPSS	-1.29	-0.12	n/c	1.25	1.65	1.95	2.19	2.38	2.53	2.66	0.13	0.22	0.23	-5.62	0.306	2.88	0.9997	2.61	0.99998
M052X	-1.32	-0.21	n/c	1.17	1.59	1.90	2.14	2.34	2.49	2.61	0.07	0.17	0.20	-5.62	0.295	2.88	0.9999	2.70	0.999999
mPW3PBE	-1.21	-0.10	0.70	1.25	1.66	1.96	2.20	2.39	2.54	2.66	0.16	0.20	0.22	-5.52	0.302	2.89	0.9998	2.68	0.99999
LC-wPBE	-1.19	-0.15	0.63	1.19	1.60	1.91	2.15	2.34	2.49	2.61	0.11	0.15	0.17	-5.43	0.289	2.89	0.99992	2.75	0.999994
HSE06	-1.26	-0.15	0.65	1.22	1.62	1.93	2.18	2.37	n/c	2.66	0.12	0.18	0.20	-5.57	0.298	2.90	0.9997	2.67	0.999991
B3PW91	-1.22	-0.11	n/c	1.24	1.64	1.94	2.18	n/c	2.52	2.65	0.14	0.20	0.22	-5.51	0.297	2.90	0.9998	2.66	0.999995
tHCTHhyb	-1.18	-0.06	n/c	1.28	1.68	1.98	2.22	2.41	2.56	2.68	0.18	0.23	0.24	-5.50	0.299	2.92	0.9998	2.68	0.99999
M06HF	-1.29	-0.22	0.59	1.17	1.60	1.92	2.17	2.37	2.52	2.65	0.07	0.16	0.18	-5.63	0.288	2.94	0.99992	2.81	0.999992
HCTH/147	-1.15	0.00	0.80	1.34	1.74	2.04	2.27	2.46	2.61	2.74	0.24	0.27	0.29	-5.53	0.310	2.94	0.9996	2.69	0.99996
tHCTH	-1.11	0.03	0.83	1.38	1.77	2.07	2.30	2.49	2.64	2.77	0.27	0.29	0.32	-5.52	0.310	2.97	0.9996	2.72	0.99998
HCTH/407	-1.12	0.03	0.83	1.38	1.78	2.08	2.32	2.50	2.66	2.79	0.28	0.30	0.32	-5.55	0.308	2.99	0.9996	2.74	0.99997
PM3	0.14	1.01	1.61	2.05	2.37	2.62	2.81	2.97	3.09	3.19	1.08	1.08	1.08	-4.33	0.290	3.40	0.9998	3.22	0.99995
AM1	0.09	0.96	1.57	2.01	2.34	2.59	2.79	2.95	3.08	3.18	1.04	1.04	1.04	-4.38	0.286	3.40	0.9998	3.21	0.99996
PDDG	0.14	1.02	1.63	2.06	2.39	2.64	2.83	2.99	3.11	3.21	1.09	1.09	1.10	-4.35	0.292	3.42	0.9998	3.23	0.99993
B3P86	-0.67	0.45	1.24	1.80	2.20	2.51	2.74	2.93	3.09	3.21	0.70	0.70	0.72	-5.52	0.302	3.44	0.9998	3.23	0.99998
PM6	0.25	1.15	1.75	2.18	2.51	2.76	2.96	3.13	3.26	3.38	1.21	1.21	1.21	-4.39	0.283	3.60	0.9995	3.33	0.9999

[a] not available. [b] excessive scatter in the experimental AEA dataset precludes reliable regression analysis. [c] calculation failed to converge, and resulting error metrics and regression statistics omit this datapoint from the corresponding analysis.

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Electronic supplementary material

Semiempirical, Hartree-Fock, density functional, and second order Moller-Plesset perturbation theory methods do not accurately predict ionization energies and electron affinities of short- through long-chain [n]acenes

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B3LYP/6-31G(d) optimized geometries of neutral [n]acenes

benzene
C,-2.1024350367,2.7684261838,0.
C,-3.2924054082,2.0370655744,0.
C,-0.8739208597,2.1035389105,0.
C,-3.2540363572,0.640695652,0.
C,-0.8355687627,0.7073184931,0.
C,-2.0256614591,-0.0241308599,0.
H,0.0521743901,2.6728213411,0.
H,0.1204183816,0.1897932184,0.
H,-2.1322366388,3.8550982588,0.
H,-4.2484678658,2.5544456156,0.
H,-4.1802209909,0.0715527558,0.
H,-1.9956893926,-1.1107951435,0.

naphthalene
C,-2.118444498,2.8046440598,0.
C,-3.3350004959,2.0782362577,0.
C,-0.9130799056,2.1397370861,0.
C,-3.3214231547,0.7017114086,0.
C,-0.8635627452,0.7195342525,0.
C,-2.0946548086,-0.0155528505,0.
H,0.0222439927,2.6949382531,0.
C,0.3632054109,0.0022694752,0.
H,-2.1415996453,3.8911134667,0.
H,-4.2804757979,2.61398684,0.
H,-4.2538571832,0.1416706881,0.
C,-2.0451380094,-1.4357562499,0.
C,0.3767829621,-1.3742551286,0.
C,-0.8397735662,-2.1006628323,0.
H,1.2956396265,0.5623102048,0.
H,1.3222578928,-1.9100060884,0.
H,-0.8166178288,-3.1871322971,0.
H,-2.9804622461,-1.9909565458,0.

anthracene
C,-2.1095172445,2.8570582802,0.
C,-3.3503654272,2.1538123923,0.
C,-0.923447811,2.1716002049,0.
C,-3.3716663706,0.7840825822,0.
C,-0.8997651337,0.7418352051,0.
C,-2.1572029122,0.0291874076,0.
H,0.0241068891,2.7054160654,0.
C,0.2959389143,0.0127317045,0.
H,-2.1120632797,3.9437088024,0.
H,-4.2813228596,2.7142895895,0.

H,-4.3164700801,0.245411981,0.
C,-2.1460087031,-1.3712325117,0.
C,0.3071337172,-1.3876878351,0.
C,-0.9503040037,-2.1003358148,0.
H,1.2428489703,0.5493892071,0.
C,1.5215979915,-2.1425819399,0.
C,-0.9266200346,-3.5301005073,0.
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H,0.2619959017,-5.3022083734,0.

tetracene
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pentacene
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hexacene
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nonacene
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decacene
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H,-2.0972262691,18.3895771242,0.369186632
C,-1.076216741,20.8819717456,0.4412528443
C,1.0290303744,22.1462591391,0.4913763945
C,-0.4296759966,22.1063062447,0.4778839911
H,2.829859222,20.9891828271,0.4773844671
H,-2.1639113506,20.8524169521,0.4311924315
C,-1.1465468349,23.3524893785,0.5034022109
C,1.6760232397,23.4297993514,0.5295074278
C,-0.4852426076,24.5449195168,0.5393466322
C,0.9498928821,24.5842279835,0.5526191465
H,2.7630911042,23.4576972919,0.5395111755
H,1.4535404439,25.546620959,0.5813703854
H,-2.2335111947,23.3208428672,0.4932997312
H,-1.041257802,25.4782871277,0.5582998706

B3LYP/6-311++G(d,p) optimized geometries of neutral [n]acenes

benzene
C,-2.1023616046,2.7660722355,0.
C,-3.2902839551,2.0359162058,0.
C,-0.8760364082,2.102274208,0.
C,-3.2519500354,0.6419968065,0.
C,-0.8377061855,0.7084245618,0.
C,-2.0256876039,-0.0217693242,0.
H,0.0477531659,2.6700865366,0.
H,0.1158948631,0.1922359318,0.
H,-2.1321305413,3.8500042066,0.
H,-4.2439279887,2.5520235436,0.
H,-4.1757887428,0.0742629249,0.
H,-1.9958249635,-1.105697837,0.

B3LYP/6-31G(d) optimized geometries of cationic [n]acenes

naphthalene
C,-2.1386052488,2.8144518028,0.
C,-3.3340714284,2.100637122,0.
C,-0.9085628831,2.1323663006,0.
C,-3.3170769565,0.6942388705,0.
C,-0.8642238159,0.7191393622,0.
C,-2.0939939504,-0.0151582624,0.
H,0.0208252355,2.6952915671,0.
C,0.3588591902,0.0097422293,0.
H,-2.1506782547,3.8996060947,0.
H,-4.283645513,2.6260080886,0.
H,-4.2534956202,0.143088059,0.
C,-2.0496548831,-1.4283852008,0.
C,0.3758536621,-1.3966560222,0.
C,-0.8196125174,-2.110470703,0.
H,1.295277854,0.5608930408,0.
H,1.3254277467,-1.9220269889,0.
H,-0.8075395115,-3.1956249949,0.
H,-2.9790430017,-1.9913104673,0.

anthracene
C,-2.122200271,2.8586625532,0.
C,-3.3452267278,2.1655171045,0.
C,-0.9175812073,2.1627517692,0.
C,-3.3670891362,0.7745027456,0.
C,-0.9060979187,0.7482188634,0.
C,-2.1594250682,0.0379006149,0.
H,0.0252149552,2.7023299548,0.
C,0.2977755202,0.0137725933,0.
H,-2.1186700913,3.9440167165,0.
H,-4.2781934723,2.72011531,0.
H,-4.3143912555,0.2428751419,0.
C,-2.1478438286,-1.3722725761,0.
C,0.3093567508,-1.3964006073,0.
C,-0.9439704025,-2.1067188489,0.
H,1.2437982422,0.5499272588,0.
C,1.5170208122,-2.1330027541,0.
C,-0.9324871311,-3.5212517522,0.
H,-3.0938665514,-1.908427242,0.
C,1.4951583832,-3.5240171113,0.
C,0.2721319235,-4.2171625547,0.
H,2.4643229368,-1.6013751521,0.
H,2.4281251319,-4.0786153152,0.
H,-1.8752832924,-4.0608299323,0.
H,0.2686017472,-5.3025167153,0.

tetracene
C,0.015657587,-0.000559999,-0.0069574158
C,1.4298850349,0.0001216821,-0.0045165431
C,2.1321004206,1.1908186653,0.0014991471
C,1.4440499372,2.4315988381,0.0053226147
C,-0.0008856001,2.4309022339,0.0028276967
C,-0.6877222238,1.1894592594,-0.0033671252
C,2.1294018214,3.6607237937,0.0114662087
C,1.4458157068,4.8895798306,0.0152456467
C,-0.0050557115,4.888880343,0.0127417497
C,-0.6874394834,3.6593657627,0.0066028106
C,2.1281995479,6.1190942363,0.0213820497
C,1.441645517,7.3475578972,0.0251582164
C,-0.003289885,7.3468613331,0.0226657868
C,-0.6886418468,6.1177361708,0.0165228525
C,2.1284823261,8.5890004696,0.0313541801
C,1.4251022078,9.7790199065,0.0349440726
C,0.0108750871,9.7783382167,0.0325032899
C,-0.6913405549,8.5876410593,0.0264873832
H,-0.5185340878,-0.9454820402,-0.0116926196
H,1.9650007066,-0.9442848103,-0.0074056353
H,3.2183501951,1.1887079961,0.003363535
H,-1.7739693868,1.1863012561,-0.0052523546
H,3.2166907388,3.659485556,0.0133345915
H,-1.77472668,3.6570791325,0.0047189576
H,3.2154867247,6.1213812115,0.0232665547
H,-1.7759307728,6.1189747217,0.0146537633
H,3.2147294596,8.5921588644,0.0332386012
H,1.95929453,10.7239416038,0.0396772569
H,-0.5242410073,10.7227444781,0.0353919894
H,-1.7775903085,8.5897520201,0.0246227369

pentacene
C,0.0154198931,0.0045805648,-0.0153369313
C,1.4352142487,0.0061507572,-0.011038989
C,2.1351140193,1.1919100261,0.0004844584
C,1.4464827594,2.4368311529,0.0082909439
C,-0.001342464,2.4352297423,0.0039091923
C,-0.6871583447,1.1887884903,-0.0080570488
C,2.1306813945,3.6623266341,0.0200850643
C,1.4473008408,4.8902863909,0.0277708137
C,-0.0077060891,4.8886770016,0.0233677278
C,-0.6883094345,3.6592085508,0.0115538915
C,2.1294305051,6.1200190571,0.0395915995
C,1.4445229352,7.3482395615,0.047276907
C,-0.0104839981,7.3466300978,0.0428743918

C,-0.6926136665,6.1168974572,0.0310521174
C,2.1251261904,8.5777080896,0.0590920322
C,1.4381592043,9.8016868607,0.0667388685
C,-0.0096660165,9.8000853487,0.0623587145
C,-0.6938646008,8.5745897726,0.0505631958
C,2.1239748502,11.0481283185,0.0787067184
C,1.4213965695,12.2323362057,0.085990079
C,0.0016022633,12.2307656852,0.0816945053
C,-0.6982974281,11.0450063617,0.0701676943
H,-0.5161922021,-0.9418760726,-0.0244531087
H,1.968964177,-0.9391274678,-0.0169307925
H,3.2214107371,1.191781917,0.0037628524
H,-1.7734520243,1.1862572767,-0.0113534888
H,3.2179262824,3.6615935303,0.0233602349
H,-1.7755499374,3.6560702345,0.0082485023
H,3.2167529636,6.1212218651,0.0428831728
H,-1.7799361278,6.1156947128,0.027763365
H,3.2123666896,8.5808465808,0.0623983667
H,-1.781109486,8.5753228126,0.047290082
H,3.2102685383,11.0506596171,0.0820038673
H,1.9530086505,13.1787928227,0.0951088399
H,-0.5321477693,13.1760438481,0.0875905056
H,-1.784594121,11.0451343009,0.0668916396

hexacene
C,0.0151648842,0.0090002993,-0.0257871242
C,1.4388357333,0.011240623,-0.0370140461
C,2.1371066448,1.1935990075,-0.0207566358
C,1.4484832711,2.4419621611,0.0076610878
C,-0.0014275459,2.4396805711,0.0190665773
C,-0.6864813529,1.1891555845,0.0014662612
C,2.1316510659,3.663864073,0.0247484232
C,1.448165775,4.8928092969,0.0527579684
C,-0.0081129123,4.8905179667,0.0642088344
C,-0.6880837713,3.6594272306,0.046928997
C,2.1302244894,6.1224149421,0.0699900643
C,1.4460874042,7.3489013855,0.0979365218
C,-0.0130526776,7.3466056757,0.1094113442
C,-0.6936822483,6.1179718893,0.0921946371
C,2.1267165202,8.5775351618,0.1151443102
C,1.4411472943,9.8049898234,0.1431126236
C,-0.0151313103,9.8026985761,0.1545634973
C,-0.6971900704,8.5730920198,0.1373516309
C,2.1211175555,11.0360810636,0.1603615442
C,1.4344609614,12.2558289695,0.1881817782
C,-0.0154496284,12.2535474741,0.1995833355
C,-0.6986173108,11.0316443184,0.182532702

C,2.1195136745,13.5063548771,0.2057354382
C,1.4178671895,14.6865116357,0.2329430886
C,-0.0058037757,14.6842716533,0.2441337061
C,-0.7040737549,13.5019118521,0.2279332578
H,-0.5141032584,-0.9388019913,-0.03906357
H,1.970809353,-0.9348916127,-0.0586302
H,3.2234137812,1.1956883841,-0.0292985529
H,-1.7727895184,1.1878257233,0.0100101844
H,3.2188109327,3.6650246839,0.0161776755
H,-1.7752421073,3.657166165,0.0554653014
H,3.2174733996,6.1238662742,0.0614229336
H,-1.780930528,6.1160015951,0.1007299656
H,3.2139647019,8.5795059728,0.1065914293
H,-1.7844390521,8.5716414451,0.1458965615
H,3.2082758222,11.038342763,0.1518148171
H,-1.7857771949,11.0304847128,0.1910814847
H,3.2058218438,13.5076850099,0.197183695
H,1.9471349555,15.6343146962,0.2461658209
H,-0.5377783168,15.630404692,0.2657003939
H,-1.7903809184,13.4998233399,0.2364622364

heptacene
C,0.0155455817,0.0134019207,-0.0518202676
C,1.4417903788,0.0156232653,-0.0449263187
C,2.1390680771,1.1959162712,-0.0164993841
C,1.4505267384,2.4469447368,0.0067764491
C,-0.0012634244,2.444683632,-0.0002415861
C,-0.6856474245,1.1915168735,-0.0301547814
C,2.132901232,3.6660975854,0.0359558976
C,1.4495154432,4.8965623334,0.0588196397
C,-0.0083855105,4.8942917215,0.0517712679
C,-0.6876823077,3.6617046317,0.0223205851
C,2.1309162128,6.1252094472,0.0881955002
C,1.4473435795,7.3508028925,0.1109523502
C,-0.0143623615,7.348526358,0.1038857845
C,-0.6938621957,6.1208099896,0.0745388857
C,2.1274404004,8.5798380799,0.1403285556
C,1.4432663947,9.8067485971,0.1631092558
C,-0.01843951,9.8044720723,0.1560424735
C,-0.6985363678,8.5754367668,0.1266663242
C,2.1227662201,11.0344647948,0.1924531053
C,1.4372895772,12.260983225,0.2152176506
C,-0.0206112995,12.2587126389,0.2081691585
C,-0.7020121183,11.030065376,0.1787962731
C,2.1165864004,13.493570143,0.2446626249
C,1.4301675552,14.7105913867,0.2672195273
C,-0.0216224927,14.708330331,0.2602005277

C,-0.7039970544,13.4891772704,0.2310259674
C,2.1145516241,15.9637581019,0.2971242909
C,1.413358663,17.1418733288,0.318783134
C,-0.0128859827,17.1396520587,0.3118875938
C,-0.7101637623,15.9593588036,0.2834675393
H,-0.5136178587,-0.9343909453,-0.07450098
H,1.9740980367,-0.9305164048,-0.0624753715
H,3.2255072737,1.1976463708,-0.0112476086
H,-1.7720867389,1.189862745,-0.035407692
H,3.2201578559,3.6664608034,0.041182687
H,-1.7749345108,3.658681111,0.0170351517
H,3.218226107,6.1260675902,0.0934327098
H,-1.7811693109,6.118281235,0.0692631367
H,3.2148011727,8.5815317103,0.145584049
H,-1.7858971371,8.5737433816,0.121407862
H,3.2100733154,11.0369937994,0.1977261494
H,-1.7893219842,11.0292075284,0.1735558659
H,3.2038385807,13.4965938957,0.2499459634
H,-1.7912536458,13.4888143446,0.2257962251
H,3.2009909285,15.965412389,0.3023753969
H,1.942522332,18.0896662479,0.3414563065
H,-0.5451937468,18.0857918093,0.3294288264
H,-1.796602938,15.9576289636,0.2782133291

octacene
C,-0.0037386715,-0.0032433839,-0.0617580835
C,1.4244285966,-0.0057830143,-0.0540068883
C,2.1249402367,1.1706473127,-0.023312144
C,1.4409427702,2.426197201,0.0016176846
C,-0.0122064504,2.4287813065,-0.0062692131
C,-0.7003539907,1.1756713909,-0.0386461788
C,2.1268290688,3.6407651625,0.0331040666
C,1.447761938,4.875375273,0.0575847365
C,-0.0109222788,4.8779692654,0.0496675379
C,-0.6940703201,3.6457815105,0.0177935587
C,2.132995057,6.1005088851,0.0893108315
C,1.4538122169,7.3285673621,0.1136428213
C,-0.0088557098,7.331168573,0.1057035746
C,-0.6920978871,6.1055328751,0.0739768774
C,2.1379203411,8.5557118711,0.1454107864
C,1.4584509475,9.7838254605,0.1697445921
C,-0.0053704328,9.7864288361,0.1617985477
C,-0.688899485,8.5607391603,0.1300665115
C,2.1419799698,11.0095149783,0.2014785917
C,1.4619363075,12.239085545,0.2258443385
C,-0.0007316266,12.2416869055,0.2179040163
C,-0.6848398603,11.0145424462,0.1861332926

C,2.1451785134,13.4647209047,0.2575777546
C,1.4640031241,14.6922845187,0.2818927197
C,0.0053188732,14.6948788279,0.2739735905
C,-0.6799143982,13.4697454166,0.2422408673
C,2.1471513537,15.9244717538,0.3137767583
C,1.4652878312,17.1414719819,0.3378476226
C,0.0121386369,17.1440565544,0.3299582859
C,-0.6737480272,15.9294890016,0.2984619408
H,-0.5355433807,-0.9495921487,-0.0862757627
H,1.9530991231,-0.9540175861,-0.0727689567
H,3.2114513628,1.1691147179,-0.0174057063
H,-1.7868638487,1.1780029356,-0.0445336078
H,3.2141130008,3.6377739191,0.0389817698
H,-1.7813578747,3.6466571222,0.0118687424
H,3.2202971541,6.0977953105,0.0951949771
H,-1.779402746,6.1066862809,0.0680577338
H,3.2252859105,8.5535673684,0.1513088224
H,-1.7762659711,8.5624621229,0.1241598694
H,3.2293462367,11.0077919292,0.2073868473
H,-1.772205651,11.0166871168,0.1802361219
H,3.2324831793,13.4635671339,0.2634991964
H,-1.7672166884,13.472459361,0.2363568243
H,3.2344387782,15.9235956104,0.3197049391
C,2.1534357338,18.3945812561,0.3702384913
C,-0.6718584356,18.3996064764,0.35489949
H,-1.7610320805,15.9324807293,0.2925842354
C,0.028653633,19.5760363039,0.3856051256
C,1.4568208724,19.5734961243,0.3933589489
H,3.2399455186,18.3922491368,0.3761288052
H,1.9886258572,20.5198444639,0.4178864726
H,-1.758369613,18.4011396111,0.3489920981
H,-0.500016715,20.5242708218,0.4043751246

nonacene
C,11.0204486581,-0.71613061,0.0022636051
C,11.0200935477,0.7134244749,0.0040201994
C,9.842882535,1.4110832017,0.0048113355
C,8.586623061,0.7251258658,0.0038974685
C,8.5869905023,-0.7291200757,0.0021111593
C,9.8435959656,-1.414408471,0.0013399148
C,7.3720619249,1.4081873786,0.0046654045
C,6.1367549952,0.7270630399,0.0037541964
C,6.1371248157,-0.7323930583,0.0019627555
C,7.3727714666,-1.4128339113,0.0012013018
C,4.9110775534,1.4095269503,0.0045132966
C,3.6833213048,0.7284171992,0.0035941669
C,3.6836777565,-0.7350570731,0.001799803

C,4.911765213,-1.4154991796,0.0010477302
C,2.4544360047,1.4098723128,0.0043393828
C,1.2278934506,0.7286375313,0.0034101516
C,1.2282190817,-0.7364755219,0.001615409
C,2.4550810245,-1.4170991544,0.0008751596
C,-0.0002905141,1.4096032069,0.0041461512
C,-1.228189013,0.7281235989,0.003162235
C,-1.2279012822,-0.7369894456,0.0013689777
C,0.0003016172,-1.4179438119,0.0006846162
C,-2.4550168335,1.4088449525,0.0038434649
C,-3.6836166607,0.7268757629,0.0028542023
C,-3.6833602774,-0.7365985609,0.0010644272
C,-2.4544780101,-1.418126582,0.0003847568
C,-4.911657939,1.4074717994,0.0035276157
C,-6.1370495349,0.724495059,0.0025312864
C,-6.1368082682,-0.7349610986,0.0007471735
C,-4.9111627727,-1.4175544141,0.0000734803
H,11.9682492566,-1.2460373518,0.0016648725
H,11.9676272478,1.2438052451,0.0047247213
H,9.8420832442,2.4976952646,0.0061462485
H,9.8433883936,-2.5010205566,0.0000046063
H,7.3728788695,2.4955553784,0.006000451
H,7.3742068726,-2.5002011609,-0.0001340342
H,4.911760981,2.4968886092,0.0058478129
H,4.9130569502,-2.5028598021,-0.0002853787
H,2.4545491658,2.4972962865,0.0056758987
H,2.4557413248,-2.5045220977,-0.0004528167
H,-0.0005182447,2.4970391012,0.0054516034
H,0.0005293062,-2.5053773151,-0.0006677904
H,-2.4555853482,2.4962688544,0.0051760243
H,-2.4546829928,-2.5055496297,-0.0009429454
H,-4.9127964763,2.4948330491,0.004855456
C,-7.3726416575,1.405102391,0.0031990132
C,-7.3721697969,-1.415918989,-0.000249185
H,-4.9119993638,-2.5049155473,-0.0012578372
C,-8.586675153,-0.7327134387,0.0004239513
C,-8.5869165239,0.7215325769,0.0022012891
H,-7.3739138518,2.4924699089,0.0045261053
C,-9.8434631786,1.406963958,0.0028702648
H,-7.3731499026,-2.5032867975,-0.0015802883
C,-9.8429935077,-1.4185277926,-0.0005827938
C,-11.0203820364,0.7088127975,0.0018592404
C,-11.0201383833,-0.7207423269,0.000112224
H,-9.8431188501,2.4935763669,0.0041974705
H,-11.9681376535,1.2387969781,0.0023795625
H,-9.8423309757,-2.5051396214,-0.0019114769
H,-11.9677170881,-1.2510457038,-0.0006630969

B3LYP/6-311++G(d,p) optimized geometries of cationic [n]acenes

benzene
C,-2.0719540776,2.7948980264,0.
C,-3.2796245851,2.0300172484,0.
C,-0.8683462229,2.1434938107,0.
C,-3.2596618281,0.6008073233,0.
C,-0.8483813596,0.7142920124,0.
C,-2.0560576285,-0.0505947811,0.
H,0.067469586,2.6887618425,0.
H,0.1059554146,0.1976603121,0.
H,-2.1272549799,3.8765728333,0.
H,-4.2339669319,2.5466387915,0.
H,-4.1954844332,0.0555513169,0.
H,-2.0007429539,-1.1322687362,0.

B3LYP/6-31G(d,p) optimized geometries of anionic [n]acenes

benzene
C,-2.1024683209,2.7697236496,0.
C,-3.3122685281,2.0698248861,0.
C,-0.8558980792,2.1373804967,0.
C,-3.2721096222,0.6069181487,0.
C,-0.8157394498,0.6744864522,0.
C,-2.0255410453,-0.0254186369,0.
H,0.0647820118,2.7212400457,0.
H,0.1356343207,0.142081061,0.
H,-2.1326311393,3.8657883608,0.
H,-4.2636499511,2.6022159989,0.
H,-4.1927980502,0.0230724806,0.
H,-1.9953621463,-1.1214829434,0.

naphthalene
C,-2.1492980456,2.8301853713,0.
C,-3.3428501374,2.1175135953,0.
C,-0.9163101256,2.1449681404,0.
C,-3.3244959134,0.7070367302,0.
C,-0.8550528448,0.7246153631,0.
C,-2.1031649215,-0.0206342633,0.
H,0.0198754663,2.7042296666,0.
C,0.3662781471,-0.0030556304,0.
H,-2.1608734715,3.9210373657,0.
H,-4.2976761443,2.6451492278,0.
H,-4.2609136325,0.1481639607,0.
C,-2.0419076407,-1.4409870406,0.
C,0.3846323711,-1.4135324955,0.
C,-0.8089197207,-2.1262042715,0.
H,1.3026958663,0.5558171391,0.
H,1.339458378,-1.941168128,0.
H,-0.7973442948,-3.2170562659,0.
H,-2.9780932326,-2.0002485668,0.

anthracene
C,-2.1392303214,2.886194507,0.
C,-3.3600974928,2.1942728264,0.
C,-0.9377137713,2.177770206,0.
C,-3.3696302519,0.7994910682,0.
C,-0.9053066266,0.7585942722,0.
C,-2.1687329415,0.0425523597,0.
H,0.0116507368,2.7138514683,0.
C,0.2953574766,0.0124021766,0.
H,-2.1280629806,3.9757787476,0.
H,-4.3006170977,2.7444922271,0.

H,-4.3173069163,0.2604316838,0.
C,-2.1454257864,-1.3709021601,0.
C,0.3186646242,-1.4010523537,0.
C,-0.944761696,-2.1170942568,0.
H,1.2442080814,0.5501595335,0.
C,1.5195619229,-2.1579910779,0.
C,-0.9123545708,-3.5362701927,0.
H,-3.0942763979,-1.9086595209,0.
C,1.5100291505,-3.5527728303,0.
C,0.2891619775,-4.2446945081,0.
H,2.4672385935,-1.6189316962,0.
H,2.4505487658,-4.102992223,0.
H,-1.8617190781,-4.0723514483,0.
H,0.277994649,-5.3342787438,0.

tetracene
C,0.0165903781,-0.0395288938,-0.0071105121
C,1.428990313,-0.0388480686,-0.0046731052
C,2.1205484991,1.1617166379,0.0013632756
C,1.4469094381,2.4140370705,0.0052536785
C,-0.0037278634,2.4133376478,0.0027505969
C,-0.6761418899,1.1603683344,-0.0034635873
C,2.123606567,3.6501251074,0.011408991
C,1.4515203405,4.8895824708,0.0152514283
C,-0.0107603533,4.8888774314,0.0127277916
C,-0.6816338278,3.6487726696,0.0065673888
C,2.1223938674,6.129687177,0.021413227
C,1.4444877447,7.3651223125,0.0252322334
C,-0.0061493685,7.3644229724,0.022728315
C,-0.682846544,6.1283347504,0.0165722101
C,2.1169019781,8.6180914845,0.031450857
C,1.4241693572,9.8179888777,0.0351020149
C,0.0117698269,9.8173080744,0.0326643256
C,-0.6797886253,8.6167432356,0.0266244134
H,-0.5266575963,-0.9832811112,-0.0118545355
H,1.9731611054,-0.9820759494,-0.0075405593
H,3.210461312,1.1648043386,0.0032554532
H,-1.766057136,1.1624050715,-0.0053338005
H,3.2138499471,3.6497645245,0.0132884843
H,-1.7718763493,3.6473607418,0.0046834166
H,3.2126363295,6.1310994875,0.0233001164
H,-1.7730899205,6.1286956702,0.0146960091
H,3.2068171156,8.6160551502,0.0333220244
H,1.967417929,10.7617407794,0.0398498363
H,-0.5324012239,10.7605358504,0.0355358502
H,-1.7697013505,8.6136558351,0.0247341607

pentacene
C,0.0161195479,-0.0385411965,-0.0156804492
C,1.4346120815,-0.0369722977,-0.0113876935
C,2.1241245708,1.1580651805,0.0001833984
C,1.4479340722,2.4123492327,0.00810187
C,-0.0027384106,2.4107445023,0.0037112463
C,-0.6760924813,1.1549677847,-0.0082919917
C,2.1238126938,3.6439652594,0.019920568
C,1.4515048402,4.8818174416,0.0277204434
C,-0.0118910111,4.8801987143,0.0232918328
C,-0.6813992855,3.6408623048,0.0114305889
C,2.1232682955,6.1200122518,0.0395775961
C,1.4487077616,7.3567178523,0.0473612321
C,-0.0146881054,7.3550991069,0.0429333066
C,-0.686451567,6.1169043023,0.0310752732
C,2.1182160132,8.5960542502,0.0592196889
C,1.4395551567,9.8261719902,0.0669386436
C,-0.0111173517,9.8245673784,0.0625497743
C,-0.6869959988,8.592951283,0.0507325388
C,2.112909044,11.0819488159,0.0789387052
C,1.4206970296,12.2754578416,0.0863261684
C,0.0022045142,12.2738887997,0.0820347578
C,-0.6873080162,11.07885135,0.0704674174
H,-0.5238240258,-0.9836416852,-0.0248157601
H,1.9766904328,-0.9808758117,-0.0172483591
H,3.2136933067,1.1621642719,0.0035043665
H,-1.7656676512,1.1566561726,-0.0115667645
H,3.2138406637,3.6442135579,0.0232128958
H,-1.7714250661,3.6386990574,0.0081250694
H,3.2130396515,6.1212178361,0.0428759466
H,-1.776222911,6.1156988345,0.0277782914
H,3.2082418123,8.598217597,0.0625255749
H,-1.7770239671,8.5927030354,0.0474425027
H,3.2024842734,11.0802602532,0.0822119795
H,1.960640711,13.2205582303,0.0954577456
H,-0.5398739161,13.2177923621,0.0878932417
H,-1.7768767056,11.0747522491,0.067148339

hexacene
C,0.0157605236,-0.0367698055,-0.02660204
C,1.438371639,-0.0345314442,-0.0377963144
C,2.1271578859,1.1564948513,-0.0213335806
C,1.449284634,2.4124383341,0.0071117454
C,-0.0021446663,2.4101545323,0.0185278652
C,-0.6764261186,1.1520833859,0.0007207685
C,2.1248292397,3.6400007242,0.024347773
C,1.4514409423,4.8774176538,0.0524148111

C,-0.01134469,4.8751159963,0.0639192623
C,-0.6811940445,3.6355855808,0.0464181126
C,2.1238033949,6.1141469642,0.0698422819
C,1.4501644325,7.3489089434,0.0978600012
C,-0.0171305625,7.3466002285,0.1093994696
C,-0.6872381983,6.1097239685,0.0919505693
C,2.1202718542,8.5857852482,0.1153069138
C,1.4443783598,9.8203933062,0.1433366472
C,-0.0184072433,9.8180916609,0.1548400009
C,-0.6907697045,8.581362159,0.137413195
C,2.1142275564,11.059923821,0.1608324394
C,1.4351780093,12.2853550391,0.1887159822
C,-0.0162512534,12.2830711397,0.2001298848
C,-0.691795879,11.0555085411,0.1828983996
C,2.1094590695,13.543426334,0.2065171376
C,1.4172723505,14.7322797967,0.2338312746
C,-0.0053388102,14.7300413241,0.2450178432
C,-0.6941247509,13.5390147336,0.2285633895
H,-0.521856765,-0.9827853132,-0.0397505979
H,1.9786896916,-0.9788505789,-0.0594295984
H,3.2164100172,1.1611784797,-0.0298469665
H,-1.7656866499,1.1533387057,0.0093440528
H,3.2146325171,3.6409248988,0.0157625124
H,-1.7709950014,3.6330798958,0.0549763414
H,3.2133463284,6.1153736744,0.0612650476
H,-1.776779661,6.1075217959,0.1005114193
H,3.2098133987,8.5879874801,0.1067479279
H,-1.7803125563,8.580135537,0.1459909124
H,3.2040285805,11.0624295502,0.1522774427
H,-1.7815990728,11.0545846203,0.1914832119
H,3.1987196924,13.5421710073,0.1978970192
H,1.9548896818,15.6782952482,0.2469754908
H,-0.5456572859,15.6743605738,0.2666379356
H,-1.7833768856,13.5343313922,0.2370740255

heptacene
C,0.0159704689,-0.0346864219,-0.0528284378
C,1.4415248852,-0.0324662104,-0.0459368472
C,2.1300602918,1.1554685787,-0.0173953635
C,1.4509119034,2.4130886155,0.0060605597
C,-0.0015362325,2.4108265301,-0.0009607651
C,-0.6765055493,1.1510975149,-0.0309625686
C,2.1263061155,3.6371299706,0.035306749
C,1.4517339187,4.8752037742,0.0583696947
C,-0.0105329351,4.8729263784,0.0513007428
C,-0.6809910052,3.6327577741,0.0217358791
C,2.1245582193,6.1100102224,0.0878329886

C,1.4505058457,7.3435074116,0.1108017838
C,-0.017500178,7.3412210743,0.1037047568
C,-0.687453584,6.1056306734,0.0742386787
C,2.1211513343,8.5798283821,0.140287418
C,1.4464044357,9.8140541248,0.1632688253
C,-0.021601585,9.8117677776,0.1561715353
C,-0.6922470724,8.5754466645,0.1266858312
C,2.1163578357,11.0496443526,0.1927363083
C,1.4394371582,12.2823487983,0.215675328
C,-0.0228296895,12.2800713848,0.2086056548
C,-0.6956539853,11.0452647881,0.1791410785
C,2.1098951929,13.5225172031,0.2452431899
C,1.4304403383,14.744448556,0.2679415338
C,-0.0220077359,14.7421864391,0.2609191739
C,-0.6974019428,13.5181449689,0.2316704494
C,2.1054096092,16.0041773858,0.2979470064
C,1.4129335118,17.1899613575,0.3198149892
C,-0.0126207696,17.1877411228,0.3129225831
C,-0.7011561618,15.9998062834,0.2843776003
H,-0.5199104996,-0.9812343835,-0.0755091768
H,1.980545808,-0.9773400832,-0.0634209429
H,3.2190976372,1.1601143348,-0.0120681583
H,-1.7655526876,1.1523509603,-0.036164302
H,3.2159524837,3.6381982162,0.0405609132
H,-1.7706352799,3.6304318709,0.0164550734
H,3.213971564,6.1110959014,0.0930866489
H,-1.7768648938,6.1033229167,0.068959112
H,3.2105228779,8.5815251614,0.1455539987
H,-1.781618609,8.5737501576,0.121419135
H,3.2057691482,11.0519523738,0.1980162565
H,-1.7850673188,11.0441793784,0.1738870339
H,3.1995394647,13.5248433035,0.2505248472
H,-1.7870482983,13.517076903,0.2264156221
H,3.1944567407,16.0029240452,0.3031499855
H,1.948814604,18.1365091821,0.3424986839
H,-0.5516418828,18.1326148361,0.3304092277
H,-1.790193499,15.9951606588,0.2790497108

octacene
C,-0.0035594505,-0.0528880102,-0.0629011067
C,1.4240803949,-0.0554277221,-0.0551538107
C,2.1167033429,1.127928438,-0.0243412729
C,1.4409991302,2.3891178678,0.0007678528
C,-0.0123869363,2.3917033344,-0.0071193373
C,-0.6922614743,1.1329254703,-0.0395846434
C,2.1206086016,3.6081004253,0.0323234574
C,1.4493449549,4.8493107276,0.0570011539

C,-0.0125904117,4.8519111421,0.0490671084
C,-0.6879577632,3.6130965003,0.0170817535
C,2.1268499314,6.0799101967,0.0888115869
C,1.456352049,7.3150900401,0.1133564242
C,-0.0114374771,7.3177006396,0.1053898244
C,-0.6860185613,6.0849134989,0.0735453176
C,2.1318084719,8.5486645176,0.1452249058
C,1.4613711561,9.7838200752,0.1697698913
C,-0.0082875272,9.7864337998,0.1617921714
C,-0.6828075538,8.5536704158,0.1299473476
C,2.1358914152,11.0165836838,0.2016160087
C,1.4645206634,12.2525534108,0.226174551
C,-0.0032688638,12.2551635634,0.2182059936
C,-0.6787246068,11.0215890333,0.1863364718
C,2.1391014734,13.4853410755,0.2580224693
C,1.465672266,14.718343089,0.2825016912
C,0.0037368718,14.7209425567,0.2745641207
C,-0.6737669623,13.49034277,0.2427506016
C,2.1410388874,15.9571583404,0.3144918085
C,1.4654668122,17.1785509539,0.3386936172
C,0.0120807864,17.1811351012,0.3308020065
C,-0.6675274414,15.9621520879,0.2992420797
H,-0.5414208247,-0.9980553726,-0.0874274274
H,1.9588101574,-1.0025031799,-0.0738596285
H,3.2055509941,1.1288593872,-0.0183670677
H,-1.7810995394,1.1377302285,-0.0454279203
H,3.2100863182,3.6056396429,0.0382231104
H,-1.7774370445,3.6145113687,0.0111566086
H,3.216121019,6.0773503699,0.0947078575
H,-1.7752914874,6.0862282267,0.0676180151
H,3.2210415563,8.5465078786,0.1511308724
H,-1.7720411351,8.5553880396,0.1240287634
H,3.2251252175,11.0148662598,0.2075333686
H,-1.7679574689,11.0237457404,0.1804277444
H,3.2283745789,13.4840266208,0.2639505897
H,-1.7630378583,13.4929024511,0.2368507892
H,3.2305183025,15.955743927,0.3204194948
C,2.1453402324,18.437329429,0.3711639607
C,-0.663624496,18.4423237923,0.3559115836
H,-1.757004997,15.9646124448,0.2933385487
C,0.0289972057,19.6256805537,0.3867288945
C,1.4566370153,19.6231422358,0.3944808832
H,3.2341783547,18.4325253909,0.3770108683
H,1.9944974031,20.5683100406,0.4190112155
H,-1.7524720481,18.4413921093,0.3499337649
H,-0.5057336348,20.5727553975,0.4054350666

nonacene
C,0.075058564,-0.0963748222,-0.0717649072
C,1.5040982659,-0.0818747157,-0.0624672113
C,2.1828460142,1.1079071314,-0.0296477834
C,1.4914421141,2.3619861957,-0.00387291
C,0.0373528452,2.3472321308,-0.0133339237
C,-0.6280641359,1.079382849,-0.0479363829
C,2.1566879941,3.5867368886,0.0296994765
C,1.4698829056,4.8207792953,0.0550285584
C,0.0082437009,4.8059508257,0.0455174593
C,-0.6529874847,3.5582275635,0.0114174303
C,2.1332043524,6.0575034393,0.0888820989
C,1.4473165527,7.2845475454,0.1140514732
C,-0.0199478138,7.2696647022,0.1045021216
C,-0.6804107826,6.0289602746,0.0705718182
C,2.1086735316,8.5253140639,0.1479964002
C,1.4232077812,9.7513502168,0.1731490108
C,-0.0466404554,9.7364460136,0.1635810812
C,-0.7067104455,8.4967629468,0.1296710043
C,2.0835082102,10.9920519432,0.2070950842
C,1.3978079461,12.2191110306,0.232277093
C,-0.0720403689,12.2042137541,0.2227078146
C,-0.7323342081,10.9635089245,0.1887632815
C,2.057895166,13.4587842842,0.2662064463
C,1.3711376416,14.6858858588,0.2913909828
C,-0.0961270058,14.6710213683,0.2818376403
C,-0.7574892941,13.4302595869,0.2478754042
C,2.0316267727,15.9265747865,0.3253556525
C,1.342989393,17.149594714,0.3504371532
C,-0.1186502377,17.1347922307,0.3409199018
C,-0.7819890383,15.8980801923,0.3070349625
H,-0.4506672974,-1.0481528525,-0.0979126628
H,2.0493262808,-1.0227843777,-0.0816477318
H,3.2714061179,1.1214764409,-0.0225058531
H,-1.7166761644,1.0708581333,-0.0549594478
H,3.2459435518,3.5970231292,0.0367708895
H,-1.742227954,3.5464097618,0.0043139025
H,3.2222790392,6.0676515398,0.095950262
H,-1.7694681388,6.0170153005,0.0634652986
H,3.1977170013,8.5358730242,0.155077149
H,-1.7957456974,8.4852369082,0.1225744394
H,3.1725466784,11.0030908836,0.2141902742
H,-1.8213747311,10.9524698592,0.1816783801
H,3.1469286997,13.4703031316,0.2733151262
H,-1.8465346346,13.4197072515,0.2408021242
H,3.1206830172,15.938504862,0.3324741263
C,2.004252765,18.3972989998,0.3845793214

C,-0.8054233807,18.3688526469,0.366284109
H,-1.871065136,15.8879460699,0.299970393
C,-0.1401506999,19.5935869903,0.3999007321
C,1.3139390147,19.6083090338,0.4093690767
H,3.0934926605,18.4090942322,0.3916955185
C,1.9793888659,20.8761385494,0.4440296951
H,-1.8946799328,18.3585881247,0.3592146479
C,-0.8315218978,20.8476840931,0.4257260887
C,1.2762967563,22.0519140368,0.4678903567
C,-0.1527432687,22.0374470484,0.4585848332
H,3.0680011456,20.8846368999,0.451058759
H,1.8020476463,23.0036770897,0.4940674353
H,-1.9200822214,20.8341410353,0.4185783047
H,-0.6979465667,22.9783709356,0.477788221

decacene
C,0.1952695833,-0.002064957,-0.0787801245
C,1.6249388456,0.0370649298,-0.0652948884
C,2.2832529878,1.2370328844,-0.029105843
C,1.5698033421,2.4797207284,-0.0038243618
C,0.1155500817,2.4399175057,-0.0175404769
C,-0.5282577872,1.1600788818,-0.0556245478
C,2.2139811671,3.7139919426,0.0331140065
C,1.5053931998,4.9367789683,0.0579454864
C,0.0442918607,4.8967905593,0.0441665913
C,-0.5957564951,3.6370842162,0.0066143415
C,2.1476556398,6.1831408738,0.095189086
C,1.4401051628,7.3983225324,0.1198528074
C,-0.0263407586,7.3581910544,0.1060268898
C,-0.6657690876,6.1061297167,0.0686587012
C,2.0804342493,8.6494292989,0.1572210496
C,1.3734746266,9.8627950126,0.1818689968
C,-0.0957926234,9.8225894327,0.1680214292
C,-0.7347287118,8.572368733,0.1306816809
C,2.0126688055,11.1145966489,0.2192724114
C,1.3058264109,12.3286084946,0.2439691493
C,-0.1642947641,12.2883795206,0.2301192146
C,-0.8030786223,11.0375196587,0.1927374021
C,1.944621268,13.57946722,0.2813741965
C,1.2373269955,14.7943995493,0.3061244541
C,-0.2319399166,14.7541889221,0.2922884566
C,-0.8711259748,13.5023902788,0.2548504844
C,1.8762725508,16.0446163357,0.3435404926
C,1.1678798477,17.2587960471,0.3682944236
C,-0.2985657165,17.2186543548,0.3544910215
C,-0.9388900272,15.967553668,0.3170348704
H,-0.3131201332,-0.9630027682,-0.1075963684

H,2.1855780729,-0.8946128561,-0.0840265005
H,3.3712634062,1.2693098173,-0.0187766759
H,-1.616405894,1.1327899436,-0.0658216464
H,3.3027535634,3.7431278014,0.0433737407
H,-1.6844924486,3.6066139511,-0.0036631286
H,3.2362705483,6.2120478842,0.1054437214
H,-1.7543357977,6.0754346884,0.0583826645
H,3.1690204633,8.6786445158,0.1674847777
H,-1.8232849231,8.5419830005,0.1204207323
H,3.1012523031,11.1441890884,0.2295442906
H,-1.891654128,11.0075180324,0.1824917147
H,3.0331935126,13.6094631995,0.2916514104
H,-1.9597130906,13.4728019176,0.2446186121
H,2.9648265285,16.0749902581,0.3538192242
C,1.8073110241,18.5108531442,0.4057817983
C,-1.0061133491,18.4338332226,0.3793052882
H,-2.027479326,15.9383488634,0.3068142378
C,-0.3638552951,19.6801890657,0.4166771166
C,1.0972457989,19.7201916895,0.4304248008
H,2.8958766657,18.5415381251,0.4160594658
C,1.7372888558,20.9798952323,0.468126315
H,-2.0947302094,18.4049352882,0.369093289
C,-1.072448532,20.9029702663,0.4416939711
C,1.0259757564,22.1770561361,0.4924676002
C,-0.4282773924,22.13723875,0.4787882223
H,2.8260245863,21.0103628002,0.4783926271
H,-2.1612217628,20.8738363651,0.4314760299
C,-1.141738099,23.3799170364,0.5042834009
C,1.6697725843,23.4568941179,0.5307264533
C,-0.4834341336,24.5798845438,0.5406285766
C,0.9462350951,24.6190293335,0.5540746209
H,2.7579210974,23.4841854982,0.5408988432
H,1.4546125207,25.5799691722,0.5830150534
H,-2.2297485279,23.3476372151,0.4939900565
H,-1.0440854806,25.5115526476,0.5595182629

Table S1. Molecular energies (298.15 K and 1 atm) of the neutral compounds at the optimized neutral geometries for the n=1-10 [n]acenes at the x/TZVP//B3LYP/6-31G(d) level of theory (note that semiempirical method energies are at the x//B3LYP/6-31G(d) level of theory).

	[n]acene									
model chemistry	1	2	3	4	5	6	7	8	9	10
AM1	0.035586	0.065669	0.101919	0.140960	0.181525	0.223000	0.265037	0.307569	0.350160	0.393046
B1B95	-232.204127	-385.824919	-539.439235	-693.050901	-846.661290	-1000.271015	-1153.880393	-1307.489545	-1461.098626	-1614.707599
B1LYP	-232.192414	-385.799895	-539.401061	-692.999625	-846.596935	-1000.193591	-1153.789893	-1307.385983	-1460.981978	-1614.577888
B2PLYPD	-232.075557	-385.611632	-539.141776	-692.669499	-846.196107	-999.722177	-1153.247999	-1306.773683	-1460.299344	-1613.824969
B3LYP	-232.328219	-386.016675	-539.698972	-693.378770	-847.057382	-1000.735385	-1154.413064	-1308.090554	-1461.767954	-1615.445282
B3P86	-233.078858	-387.234311	-541.383523	-695.530226	-849.675745	-1003.820661	-1157.965265	-1312.109678	-1466.254017	-1620.398274
B3PW91	-232.232519	-385.859989	-539.481220	-693.099942	-846.717479	-1000.334413	-1153.951033	-1307.567463	-1461.183817	-1614.800092
B97D	-232.144714	-385.713611	-539.277313	-692.838973	-846.399713	-999.960009	-1153.520080	-1307.080046	-1460.639929	-1614.199793
B98	-232.226083	-385.850890	-539.469479	-693.085537	-846.700389	-1000.314620	-1153.928520	-1307.542224	-1461.155837	-1614.769380
BHandH	-230.504574	-383.034238	-535.556621	-688.075866	-840.593513	-993.110280	-1145.626568	-1298.142509	-1450.658357	-1603.174010
BHandHLYP	-232.174622	-385.768374	-539.354965	-692.938418	-846.520255	-1000.101197	-1153.681630	-1307.261708	-1460.841677	-1614.421464
BLYP	-232.216826	-385.842633	-539.463034	-693.081363	-846.698771	-1000.315734	-1153.932464	-1307.549099	-1461.165633	-1614.782164
BMK	-232.149211	-385.730226	-539.304488	-692.875869	-846.445809	-1000.014968	-1153.583687	-1307.152123	-1460.720449	-1614.288660
CAM-B3LYP	-232.184085	-385.783711	-539.376316	-692.965882	-846.553903	-1000.141072	-1153.727760	-1307.314122	-1460.900373	-1614.486467
HCTH/147	-232.303740	-385.968752	-539.628177	-693.285479	-846.941841	-1000.597755	-1154.253450	-1307.909037	-1461.564552	-1615.220039
HCTH/407	-232.296215	-385.953611	-539.605365	-693.254979	-846.903648	-1000.551866	-1154.199868	-1307.847761	-1461.495586	-1615.143377
HF	-230.771827	-383.462402	-536.144585	-688.822642	-841.498342	-994.172594	-1146.845918	-1299.518535	-1452.190899	-1604.862878
HFB	-230.827827	-383.562567	-536.292124	-689.019649	-841.746268	-994.472445	-1147.198363	-1299.924208	-1452.649897	-1605.375637
HFS	-227.496763	-378.109455	-528.716731	-679.321954	-829.926284	-980.530186	-1131.133871	-1281.737485	-1432.340976	-1582.944478
HSE06	-232.056009	-385.576746	-539.091201	-692.603109	-846.113807	-999.623881	-1153.133631	-1306.643179	-1460.152648	-1613.662029
LC-wPBE	-232.141943	-385.707292	-539.264903	-692.818983	-846.371165	-999.922241	-1153.472654	-1307.022576	-1460.572349	-1614.121863
M05	-232.115115	-385.674109	-539.226714	-692.776691	-846.325403	-999.873457	-1153.421160	-1306.968640	-1460.516041	-1614.063344
M052X	-232.295147	-385.973979	-539.645706	-693.314367	-846.981469	-1000.647713	-1154.313479	-1307.978905	-1461.644242	-1615.309413
M06	-232.129570	-385.697831	-539.259829	-692.819237	-846.377386	-999.934871	-1153.492003	-1307.048907	-1460.605729	-1614.162444
M062X	-232.215251	-385.842856	-539.463519	-693.081163	-846.697266	-1000.312518	-1153.927287	-1307.541727	-1461.156055	-1614.770228
M06HF	-232.262534	-385.921684	-539.572944	-693.220521	-846.866082	-1000.510452	-1154.154094	-1307.797189	-1461.440118	-1615.082768
M06L	-232.284453	-385.952488	-539.614703	-693.274653	-846.933573	-1000.591988	-1154.250153	-1307.908182	-1461.566138	-1615.224041
MP2	-231.593266	-384.820162	-538.041058	-691.259572	-844.477092	-997.694237	-1150.911324	-1304.128466	-1457.345734	-1610.563135
mPW1LYP	-232.189531	-385.797107	-539.398366	-692.997023	-846.594425	-1000.191173	-1153.787569	-1307.383752	-1460.979840	-1614.575842
mPW1PBE	-232.172643	-385.766493	-539.353918	-692.938725	-846.522282	-1000.105193	-1153.687765	-1307.270124	-1460.852406	-1614.434593
mPW2PLYPD	-232.076658	-385.613505	-539.144205	-692.672365	-846.199330	-999.725702	-1153.251789	-1306.777706	-1460.303591	-1613.829418
mPW3PBE	-232.154861	-385.734478	-539.307849	-692.878710	-846.448387	-1000.017462	-1153.586225	-1307.154798	-1460.723295	-1614.291713
O3LYP	-232.237739	-385.868940	-539.494137	-693.116970	-846.738719	-1000.359930	-1153.980868	-1307.601652	-1461.222363	-1614.843020
OPBE	-232.218556	-385.839204	-539.454145	-693.066948	-846.678818	-1000.290251	-1153.901479	-1307.512600	-1461.123666	-1614.734704
OTPSS	-232.221465	-385.844250	-539.461331	-693.076277	-846.690292	-1000.303871	-1153.917246	-1307.530516	-1461.143728	-1614.756914
PBE0	-232.035930	-385.543306	-539.044267	-692.542613	-846.039711	-999.536164	-1153.032280	-1306.528183	-1460.024009	-1613.519740
PDDG	0.037631	0.067126	0.102977	0.141659	0.181893	0.223047	0.264726	0.306987	0.349151	0.391679

PM3	0.037767	0.065978	0.100368	0.137552	0.176269	0.215902	0.256083	0.296795	0.337497	0.378521
PM6	0.038923	0.065059	0.096847	0.131310	0.167323	0.204317	0.241978	0.280198	0.318569	0.357265
tHCTH	-232.257416	-385.890745	-539.518476	-693.144076	-846.768733	-1000.392938	-1154.016924	-1307.640798	-1461.264603	-1614.888376
tHCTHhyb	-232.286136	-385.946018	-539.599892	-693.251374	-846.901742	-1000.551547	-1154.201060	-1307.850407	-1461.499671	-1615.148880
TPSSh	-232.340656	-386.040664	-539.734682	-693.426327	-847.116875	-1000.806874	-1154.496591	-1308.186148	-1461.875630	-1615.565056
VSXC	-232.426229	-386.186876	-539.941857	-693.694675	-847.446517	-1001.197885	-1154.949015	-1308.700028	-1462.450964	-1616.201867
wB97	-232.264696	-385.918683	-539.565100	-693.208028	-846.849070	-1000.489008	-1154.128270	-1307.767047	-1461.405653	-1615.044018
wB97X	-232.251458	-385.894969	-539.531048	-693.163801	-846.794803	-1000.424808	-1154.054223	-1307.683220	-1461.312082	-1614.940738
wB97XD	-232.237640	-385.870035	-539.495496	-693.117937	-846.738846	-1000.358916	-1153.978518	-1307.597795	-1461.216978	-1614.836007
X3LYP	-232.210614	-385.826753	-539.436670	-693.044051	-846.650221	-1000.255767	-1153.860980	-1307.465996	-1461.070921	-1614.675768
XAlpha	-228.986406	-380.564538	-532.137055	-683.707467	-835.276959	-986.846014	-1138.414867	-1289.983626	-1441.552305	-1593.120950

Table S2. Molecular energies (298.15 K and 1 atm) of the cationic compounds at the optimized neutral geometries for the n=1-10 [n]acenes at the x/TZVP//B3LYP/6-31G(d) level of theory (note that semiempirical method energies are at the x//B3LYP/6-31G(d) level of theory).

	[n]acene									
model chemistry	1	2	3	4	5	6	7	8	9	10
AM1	0.375606	0.370309	0.382194	0.404606	0.433195	0.465660	0.500698	0.537629	0.575809	0.615067
B1B95	-231.864723	-385.533339	-539.177258	-692.808857	-846.433520	-1000.053908	-1153.671518	-1307.287160	-1460.901454	-1614.514685
B1LYP	-231.858569	-385.513551	-539.144316	-692.762844	-846.374473	-999.981841	-1153.586421	-1307.189045	-1460.790293	-1614.390498
B2PLYPD	-231.736048	-385.319101	-538.878492	-692.425871	-845.966442	-999.502836	-1153.036533	-1306.568345	-1460.098880	-1613.628439
B3LYP	-231.987818	-385.724466	-539.436393	-693.136116	-846.829005	-1000.517692	-1154.203638	-1307.887667	-1461.570342	-1615.251999
B3P86	-232.716567	-386.919718	-541.098400	-695.264915	-849.424625	-1003.580154	-1157.732968	-1311.883868	-1466.033441	-1620.181988
B3PW91	-231.891034	-385.566145	-539.216871	-692.855424	-846.487168	-1000.114727	-1153.739564	-1307.362488	-1460.984079	-1614.604647
B97D	-231.809671	-385.428058	-539.021317	-692.602691	-846.177542	-999.748432	-1153.316753	-1306.883297	-1460.448561	-1614.012895
B98	-231.886932	-385.559849	-539.208092	-692.844091	-846.473225	-1000.098135	-1153.720290	-1307.340515	-1460.959384	-1614.577231
BHandH	-230.170043	-382.744572	-535.296469	-687.835877	-840.368051	-992.895689	-1145.420349	-1297.942862	-1450.463925	-1602.983786
BHandHLYP	-231.841968	-385.479922	-539.096034	-692.699708	-846.296148	-999.888031	-1153.476899	-1307.063601	-1460.648821	-1614.232843
BLYP	n/c[a]	-385.559248	-539.209483	-692.847680	-846.479300	-1000.106934	-1153.731977	-1307.355244	-1460.977206	-1614.598248
BMK	-231.807148	-385.434849	-539.038995	-692.630581	-846.215011	-999.794982	-1153.372020	-1306.946987	-1460.520517	-1614.092944
CAM-B3LYP	-231.842163	-385.487080	-539.109065	-692.718538	-846.320822	-999.918604	-1153.513418	-1307.106120	-1460.697360	-1614.287450
HCTH/147	-231.961979	-385.676498	-539.365503	-693.042538	-846.713024	-1000.379543	-1154.043497	-1307.705671	-1461.366575	-1615.026540
HCTH/407	-231.952872	-385.659407	-539.340692	-693.010021	-846.672807	-1000.331628	-1153.987889	-1307.642370	-1461.295585	-1614.947855
HF	-230.480893	-383.206952	-535.918995	-688.618724	-841.310680	-993.997583	-1146.680999	-1299.361838	-1452.040851	-1604.718357
HFB	-230.527880	-383.311861	-536.071023	-688.818330	-841.559122	-994.295946	-1147.030157	-1299.762614	-1452.493712	-1605.223943
HFS	n/c	-377.856691	-528.493609	-679.118554	-829.736983	-980.351468	-1130.963395	-1281.573583	-1432.182455	-1582.790430
HSE06	-231.716100	-385.283904	-538.827925	-692.359831	-845.884927	-999.405824	-1152.923989	-1306.440226	-1459.955124	-1613.468987
LC-wPBE	-231.796720	-385.403797	-538.990685	-692.564800	-846.131473	-999.693379	-1153.252098	-1306.808511	-1460.363351	-1613.916905
M05	-231.784121	-385.387182	-538.968247	-692.537600	-846.100226	-999.658690	-1153.214423	-1306.768222	-1460.320674	-1613.872082
M052X	-231.950998	-385.673108	-539.374138	-693.062575	-846.743925	-1000.420805	-1154.094741	-1307.766563	-1461.436960	-1615.106206
M06	-231.791390	-385.406112	-538.996922	-692.575823	-846.147969	-999.715927	-1153.281150	-1306.844438	-1460.406382	-1613.967278
M062X	-231.867763	-385.539839	-539.189966	-692.827516	-846.457966	-1000.083930	-1153.706939	-1307.327843	-1460.947302	-1614.565621
M06HF	-231.907436	-385.606987	-539.287846	-692.955365	-846.615470	-1000.270707	-1153.922711	-1307.572365	-1461.220450	-1614.867242
M06L	-231.947798	-385.664736	-539.356828	-693.036803	-846.710087	-1000.379289	-1154.045846	-1307.710559	-1461.373968	-1615.036392
MP2	-231.241737	-384.514750	-537.763836	-690.999019	-844.227089	-997.450524	-1150.670919	-1303.889112	-1457.105950	-1610.321661
mPW1LYP	-231.854693	-385.509839	-539.140710	-692.759338	-846.371064	-999.978529	-1153.583206	-1307.185926	-1460.787271	-1614.387571
mPW1PBE	-231.832477	-385.473216	-539.090101	-692.694769	-846.292564	-999.886118	-1153.476910	-1307.065750	-1460.653240	-1614.239680
mPW2PLYPD	-231.737284	-385.320605	-538.880581	-692.428468	-845.969473	-999.506239	-1153.040257	-1306.572346	-1460.103129	-1613.632903
mPW3PBE	-231.812661	-385.439982	-539.042865	-692.633567	-846.217456	-999.797160	-1153.374143	-1306.949213	-1460.522949	-1614.095662
O3LYP	-231.900572	-385.580835	-539.235792	-692.878564	-846.514586	-1000.146489	-1153.775719	-1307.403082	-1461.029133	-1614.654194
OPBE	-231.879036	-385.549388	-539.194099	-692.826740	-846.452797	-1000.074874	-1153.694386	-1307.312112	-1460.928581	-1614.544106
OTPSS	-231.881245	-385.553898	-539.200793	-692.835603	-846.463822	-1000.088057	-1153.709725	-1307.329606	-1460.948225	-1614.565904
PBE0	-231.695533	-385.249879	-538.780303	-692.298512	-845.809849	-999.316947	-1152.821284	-1306.323672	-1459.824709	-1613.324698
PDDG	0.384371	0.378831	0.390188	0.412217	0.440494	0.472710	0.507512	0.544336	0.582285	0.621405

PM3	0.384297	0.376651	0.386367	0.406742	0.433355	0.463901	0.497053	0.532170	0.568500	0.605956
PM6	0.379941	0.374246	0.383631	0.402435	0.427045	0.455410	0.486348	0.519189	0.553328	0.588560
tHCTH	-231.916565	-385.598616	-539.255669	-692.900855	-846.539539	-1000.174277	-1153.806466	-1307.436880	-1461.066034	-1614.694248
tHCTHhyb	-231.943987	-385.652329	-539.335745	-693.007035	-846.671581	-1000.331998	-1153.989729	-1307.645584	-1461.300117	-1614.953660
TPSSh	-232.003768	-385.752188	-539.475821	-693.187339	-846.892125	-1000.592796	-1154.290794	-1307.986921	-1461.681736	-1615.375560
VSXC	-232.090174	-385.900304	-539.684927	-693.457541	-847.223549	-1000.985542	-1154.744937	-1308.502529	-1462.258838	-1616.014194
wB97	-231.923755	-385.619790	-539.295403	-692.958289	-846.613771	-1000.264497	-1153.912041	-1307.557291	-1461.200959	-1614.843364
wB97X	-231.910165	-385.596966	-539.262180	-692.914671	-846.559846	-1000.200378	-1153.837828	-1307.473069	-1461.106793	-1614.739308
wB97XD	-231.896823	-385.574411	-539.228869	-692.870741	-846.505476	-1000.135750	-1153.763092	-1307.388349	-1461.012176	-1614.634875
X3LYP	-231.871807	-385.535942	-539.175482	-692.802802	-846.423264	-1000.039502	-1153.652985	-1307.264537	-1460.874730	-1614.483894
XAlpha	-228.671556	-380.299474	-531.901458	-683.491483	-835.074998	-986.654576	-1138.231624	-1289.806919	-1441.380946	-1592.954036

[a] calculation failed to converge.

Table S3. Molecular energies (298.15 K and 1 atm) of the anionic compounds at the optimized neutral geometries for the n=1-10 [n]acenes at the x/TZVP//B3LYP/6-31G(d) level of theory (note that semiempirical method energies are at the x//B3LYP/6-31G(d) level of theory).

	[n]acene									
model chemistry	1	2	3	4	5	6	7	8	9	10
AM1	0.039530	0.038397	0.050721	0.072682	0.100470	0.132137	0.166474	0.202803	0.240515	0.279398
B1B95	-232.139091	-385.805750	-539.451373	-693.084666	-846.710686	-1000.332133	-1153.950554	-1307.566895	-1461.181688	-1614.795363
B1LYP	-232.126701	-385.778947	-539.410855	-693.030730	-846.643474	-1000.251723	-1153.856979	-1307.460195	-1461.061859	-1614.662442
B2PLYPD	-232.007100	-385.587816	-539.148722	-692.697620	-846.239426	-999.776783	-1153.311213	-1306.843656	-1460.374629	-1613.904577
B3LYP	-232.268556	-386.002221	-539.715294	-693.416356	-847.110350	-1000.797180	-1154.486519	-1308.171130	-1461.854212	-1615.536238
B3P86	-233.040910	-387.242089	-541.422398	-695.590572	-849.751616	-1003.908187	-1158.061800	-1312.213390	-1466.363456	-1620.512445
B3PW91	-232.173836	-385.847008	-539.499309	-693.139477	-846.772519	-1000.401092	-1154.026706	-1307.650300	-1461.272369	-1614.893365
B97D	-232.082837	-385.698378	n/c[a]	-692.875599	-846.451519	-1000.023237	-1153.592186	-1307.159274	-1460.724916	-1614.289593
B98	-232.163228	-385.833796	-539.483509	-693.121049	-846.751428	-1000.377312	-1154.000212	-1307.621082	-1461.240408	-1614.858667
BHandH	-230.436492	-383.010432	-535.564326	-688.105694	-840.639453	-993.168339	-1145.693968	-1298.217315	-1450.738988	-1603.259393
BHandHLYP	-232.108060	-385.745338	-539.362990	-692.968302	-846.566082	-1000.159025	-1153.748715	-1307.336136	-1460.921875	-1614.506369
BLYP	-232.152673	-385.824591	n/c	-693.114787	-846.747283	-1000.375605	-1154.001170	-1307.624897	-1461.247169	-1614.868497
BMK	-232.082916	-385.709486	-539.315400	-692.908756	-846.494603	-1000.075684	-1153.653575	-1307.229277	-1460.803335	-1614.376233
CAM-B3LYP	-232.124297	-385.767645	-539.390880	-693.001793	-846.605277	-1000.204019	-1153.799580	-1307.392940	-1460.984655	-1614.575176
HCTH/147	-232.247103	-385.959141	-539.649546	-693.327988	-846.999589	-1000.666965	-1154.331566	-1307.994299	-1461.655591	-1615.315905
HCTH/407	-232.241242	-385.945770	n/c	-693.299281	-846.963185	-1000.622861	-1154.279764	-1307.934798	-1461.588394	-1615.241008
HF	-230.678771	-383.409894	-536.123558	-688.825033	-841.518419	-994.206447	-1146.890754	-1299.572399	-1452.252034	-1604.930141
HFB	-230.736740	-383.515896	n/c	-689.023317	-841.764760	-994.502105	-1147.236708	-1299.969525	-1452.700851	-1605.431300
HFS	-227.403681	-378.062156	-528.700224	-679.326550	-829.946123	-980.561507	-1131.174121	-1281.784903	-1432.394193	-1583.002542
HSE06	-231.996280	-385.562630	-539.108377	-692.641998	-846.168459	-999.690419	-1153.209394	-1306.726328	-1460.241723	-1613.756029
LC-wPBE	-232.084992	-385.693521	-539.282145	-692.858060	-846.426155	-999.989189	-1153.548793	-1307.105981	-1460.661394	-1614.215468
M05	-232.053702	-385.658975	-539.242427	-692.813716	-846.377840	-999.937457	-1153.494080	-1307.048647	-1460.601669	-1614.153590
M052X	-232.233286	-385.957817	-539.661458	-693.352342	-847.035544	-1000.713849	-1154.388881	-1308.061631	-1461.732714	-1615.402561
M06	-232.071166	-385.684813	-539.277463	-692.858094	-846.431611	-1000.000642	-1153.566694	-1307.130700	-1460.693170	-1614.254539
M062X	-232.153762	-385.826617	-539.478958	-693.118619	-846.750667	-1000.377864	-1154.001814	-1307.623517	-1461.243551	-1614.862376
M06HF	-232.201349	-385.904814	-539.588608	-693.259104	-846.921366	-1000.578273	-1154.231544	-1307.882246	-1461.531089	-1615.178523
M06L	-232.220968	-385.936212	-539.629601	-693.310923	-846.985275	-1000.655302	-1154.322486	-1307.987746	-1461.651539	-1615.314313
MP2	-231.513388	-384.781465	-538.032507	-691.270024	-844.499883	-997.724826	-1150.946414	-1304.165618	-1457.383128	-1610.599328
mPW1LYP	-232.124615	-385.776997	-539.409015	-693.028991	-846.641833	-1000.250178	-1153.855531	-1307.458843	-1461.060603	-1614.661280
mPW1PBE	-232.112653	-385.752024	-539.370624	-692.977010	-846.576180	-1000.170807	-1153.762422	-1307.351971	-1460.939971	-1614.526867
mPW2PLYPD	-232.008708	-385.589994	-539.151522	-692.700967	-846.243239	-999.780994	-1153.315767	-1306.848506	-1460.379743	-1613.909921
mPW3PBE	-232.096629	-385.722021	-539.326501	-692.918832	-846.504029	-1000.084754	-1153.662518	-1307.238262	-1460.812480	-1614.385623
O3LYP	-232.173031	-385.850636	-539.506868	-693.150999	-846.788112	-1000.420859	-1154.050727	-1307.678642	-1461.305074	-1614.930479
OPBE	-232.156207	-385.824731	n/c	-693.105277	-846.732542	-1000.355542	-1153.975749	-1307.594070	-1461.210953	-1614.826849
OTPSS	-232.159462	-385.830209	-539.478686	-693.114999	-846.744389	-1000.369518	-1153.991859	-1307.612317	-1461.231338	-1614.849376
PBE0	-231.975893	-385.528828	-539.060985	-692.580924	-846.093644	-999.601821	-1153.106986	-1306.610085	-1460.111634	-1613.612079
PDDG	0.040505	0.036639	0.048298	0.069854	0.097356	0.128755	0.162783	0.198878	0.236192	0.274730

PM3	0.040172	0.036074	0.046523	0.066753	0.092867	0.122866	0.155514	0.190183	0.226154	0.263311
PM6	0.038545	0.031250	0.039203	0.056571	0.079847	0.107005	0.136846	0.168643	0.201858	0.236204
tHCTH	-232.202591	-385.882698	-539.541303	-693.187994	-846.827860	-1000.463507	-1154.096384	-1307.727392	-1461.356962	-1614.985550
tHCTHhyb	-232.227777	-385.933858	-539.618874	-693.291772	-846.957602	-1000.619017	-1154.277511	-1307.934024	-1461.589027	-1615.242989
TPSSh	-232.277821	-386.024083	-539.749307	-693.462437	-847.168510	-1000.870177	-1154.568933	-1308.265711	-1461.960987	-1615.655223
VSXC	-232.360608	-386.169609	-539.956623	-693.731318	-847.498932	-1001.262163	-1155.022509	-1308.780913	-1462.537822	-1616.293711
wB97	-232.202438	-385.899607	-539.577046	-693.241806	-846.898750	-1000.550634	-1154.199080	-1307.845119	-1461.489367	-1615.132296
wB97X	-232.189591	-385.876627	-539.543577	-693.197882	-846.844496	-1000.486169	-1154.124509	-1307.760526	-1461.394819	-1615.027848
wB97XD	-232.175163	-385.851865	-539.507998	-693.151630	-846.787779	-1000.419170	-1154.047381	-1307.673393	-1461.297771	-1614.920967
X3LYP	-232.149308	-385.810551	-539.451260	-693.079938	-846.701521	-1000.318643	-1153.932802	-1307.544945	-1461.155552	-1614.765091
XAlpha	-228.904934	-380.529314	-532.132758	-683.724343	-835.309124	-986.889691	-1138.467495	-1290.043438	-1441.617931	-1593.191432

[a] calculation failed to converge.

Table S4. Molecular energies (298.15 K and 1 atm) of the cationic compounds at the optimized cationic geometries for the n=1-10 [n]acenes at the x/TZVP//B3LYP/6-31G(d) level of theory (note that semiempirical method energies are at the x//B3LYP/6-31G(d) level of theory).

	[n]acene									
model chemistry	1	2	3	4	5	6	7	8	9	10
AM1	0.371488	0.365247	0.378195	0.401258	0.430297	0.463096	0.498514	0.535690	0.574206	n/c[a]
B1B95	-231.869138	-385.535928	-539.179421	-692.810840	-846.435404	-1000.055723	-1153.673241	-1307.288829	-1460.903031	n/c
B1LYP	-231.863642	-385.516553	-539.146572	-692.764706	-846.376084	-999.983267	-1153.587684	-1307.190186	-1460.791318	n/c
B2PLYPD	-231.741175	-385.322152	-538.880877	-692.427932	-845.968299	-999.504548	-1153.038110	-1306.569837	-1460.100260	n/c
B3LYP	-231.992816	-385.727402	-539.438624	-693.137978	-846.830629	-1000.519135	-1154.204921	-1307.888825	-1461.571385	n/c
B3P86	-232.721224	-386.922465	-541.100666	-695.266954	-849.426523	-1003.581940	-1157.734634	-1311.885446	-1466.034913	n/c
B3PW91	-231.895876	-385.568994	-539.219162	-692.857440	-846.489007	-1000.116427	-1153.741127	-1307.363946	-1460.985422	n/c
B97D	-231.814914	-385.431231	-539.023694	-692.604646	-846.179215	-999.749872	-1153.318010	-1306.884386	-1460.449516	n/c
B98	-231.892270	-385.562977	-539.210409	-692.845976	-846.474830	-1000.099532	-1153.721506	-1307.341593	-1460.960332	n/c
BHandH	-230.173488	-382.746846	-535.298581	-687.837969	-840.370178	-992.897857	-1145.422505	-1297.945046	-1450.466056	n/c
BHandHLYP	-231.846467	-385.482774	-539.098280	-692.701650	-846.297930	-999.889722	-1153.478483	-1307.065143	-1460.650272	n/c
BLYP	-231.888237	-385.562480	-539.211786	-692.849456	-846.480707	-1000.108041	-1153.732848	-1307.355900	-1460.977713	n/c
BMK	-231.813429	-385.438301	-539.041350	-692.632349	-846.216419	-999.796147	-1153.372982	-1306.947821	-1460.521213	n/c
CAM-B3LYP	-231.846938	-385.489987	-539.111248	-692.720354	-846.322421	-999.920061	-1153.514735	-1307.107358	n/c	n/c
HCTH/147	-231.966564	-385.679314	-539.367780	-693.044532	-846.714817	-1000.381156	-1154.044947	-1307.706972	-1461.367750	n/c
HCTH/407	-231.957199	-385.662065	-539.342931	-693.012050	-846.674684	-1000.333361	-1153.989480	-1307.643828	-1461.296927	n/c
HF	-230.484592	-383.211104	-535.921817	-688.620712	-841.312206	-993.998820	-1146.681971	-1299.362666	-1452.041498	n/c
HFB	-230.535261	-383.316316	-536.073652	-688.819850	-841.559857	-994.296071	-1147.029842	-1299.761902	-1452.492762	n/c
HFS	-227.198872	-377.860018	-528.496005	-679.120411	-829.738447	-980.352590	-1130.964267	-1281.574196	-1432.182906	n/c
HSE06	-231.720853	-385.286741	-538.830238	-692.361884	-845.886813	-999.407579	-1152.925612	-1306.441751	n/c	n/c
LC-wPBE	-231.801796	-385.406959	-538.992960	-692.566603	-846.132999	-999.694730	-1153.253266	-1306.809594	-1460.364294	n/c
M05	-231.788120	-385.390245	-538.970724	-692.539774	-846.102196	-999.660495	-1153.216061	-1306.769734	-1460.322048	n/c
M052X	-231.956338	-385.676378	-539.376672	-693.064730	-846.745855	-1000.422592	-1154.096379	-1307.768133	-1461.438400	n/c
M06	-231.795923	-385.408696	-538.999029	-692.577710	-846.149726	-999.717589	-1153.282700	-1306.845913	-1460.407760	n/c
M062X	-231.874597	-385.543063	-539.192290	-692.829362	-846.459529	-1000.085314	-1153.708160	-1307.328978	-1460.948320	n/c
M06HF	-231.915116	-385.610836	-539.290359	-692.957146	-846.616823	-1000.271815	-1153.923605	-1307.573189	-1461.221128	n/c
M06L	-231.952141	-385.667138	-539.358845	-693.038665	-846.711855	-1000.380968	-1154.047425	-1307.712049	-1461.375372	n/c
MP2	-231.250485	-384.517477	-537.765737	-691.000805	-844.228701	-997.452034	-1150.672292	-1303.890508	-1457.107222	n/c
mPW1LYP	-231.859694	-385.512802	-539.142954	-692.761204	-846.372691	-999.979979	-1153.584499	-1307.187102	-1460.788334	n/c
mPW1PBE	-231.837257	-385.476069	-539.092431	-692.696846	-846.294485	-999.887917	-1153.478582	-1307.067332	-1460.654709	n/c
mPW2PLYPD	-231.742260	-385.323593	-538.882938	-692.430523	-845.971343	-999.507981	-1153.041874	-1306.573891	-1460.104569	n/c
mPW3PBE	-231.817443	-385.442810	-539.045158	-692.635598	-846.219319	-999.798889	-1153.375739	-1306.950707	-1460.524330	n/c
O3LYP	-231.905542	-385.583745	-539.238101	-692.880561	-846.516373	-1000.148102	-1153.777168	-1307.404397	-1461.030320	n/c
OPBE	-231.883682	-385.552328	-539.196552	-692.828941	-846.454807	-1000.076706	-1153.696044	-1307.313614	-1460.929933	n/c
OTPSS	-231.885892	-385.556835	-539.203233	-692.837783	-846.465805	-1000.089857	-1153.711347	-1307.331069	-1460.949539	n/c
PBE0	-231.700303	-385.252743	-538.782644	-692.300597	-845.811774	-999.318747	-1152.822955	-1306.325249	-1459.826172	n/c
PDDG	0.380205	0.373788	0.386023	0.408507	0.437075	0.469476	0.504610	0.541535	0.579888	n/c

PM3	0.380013	0.371842	0.382552	0.403487	0.430475	0.461275	0.494770	0.530052	0.566720	n/c
PM6	0.374473	0.369356	0.380521	0.400468	0.425849	0.454765	0.486241	0.519435	0.553971	n/c
tHCTH	-231.921054	-385.601351	-539.257929	-692.902875	-846.541387	-1000.175969	-1153.808011	-1307.438291	-1461.067326	n/c
tHCTHhyb	-231.949223	-385.655396	-539.338086	-693.008991	-846.673281	-1000.333497	-1153.991052	-1307.646766	-1461.301168	n/c
TPSSh	-232.008999	-385.755221	-539.478196	-693.189374	-846.893937	-1000.594430	-1154.292262	-1307.988258	-1461.682942	n/c
VSXC	-232.095261	-385.903333	-539.687338	-693.459643	-847.225445	-1000.987268	-1154.746504	-1308.503956	-1462.260133	n/c
wB97	-231.929650	-385.623410	-539.297834	-692.960046	-846.615099	-1000.265543	-1153.912832	-1307.557940	-1461.201434	n/c
wB97X	-231.915640	-385.600233	-539.264505	-692.916494	-846.561360	-1000.201692	-1153.838948	-1307.474085	-1461.107667	n/c
wB97XD	-231.902046	-385.577417	-539.231143	-692.872664	-846.507194	-1000.137334	-1153.764538	-1307.389717	-1461.013427	n/c
X3LYP	-231.876747	-385.538857	-539.177711	-692.804674	-846.424907	-1000.040974	-1153.654303	-1307.265737	-1460.875817	n/c
XAlpha	-228.675173	-380.301790	-531.903543	-683.493488	-835.076942	-986.656431	-1138.233395	-1289.808581	-1441.382524	n/c

[a] calculation failed to converge.

Table S5. Molecular energies (298.15 K and 1 atm) of the anionic compounds at the optimized anionic geometries for the n=1-10 [n]acenes at the x/TZVP//B3LYP/6-31G(d) level of theory (note that semiempirical method energies are at the x//B3LYP/6-31G(d) level of theory).

	[n]acene									
model chemistry	1	2	3	4	5	6	7	8	9	10
AM1	0.040773	0.036239	0.048913	0.071207	0.099353	0.131388	0.166106	0.202746	0.240802	0.279941
B1B95	-232.143160	-385.808012	n/c[a]	-693.085691	-846.711337	-1000.332499	-1153.950691	-1307.566825	-1461.181481	-1614.795055
B1LYP	-232.132319	-385.782528	n/c	-693.032679	-846.644953	-1000.252853	-1153.857846	-1307.460822	-1461.062348	-1614.662805
B2PLYPD	-232.012420	-385.591359	-539.151297	-692.699542	-846.240864	-999.777859	-1153.312009	-1306.844208	-1460.375027	-1613.904838
B3LYP	-232.274206	-386.005854	-539.718000	-693.418442	-847.111985	-1000.801202	-1154.487555	-1308.171923	-1461.854868	-1615.536764
B3P86	-233.045654	-387.244981	-541.424534	-695.592181	-849.752827	-1003.909090	-1158.062454	-1312.213813	-1466.363732	-1620.512598
B3PW91	-232.178998	-385.850234	n/c	-693.141335	-846.773959	-1000.402209	-1154.027565	n/c	-1461.272840	-1614.893706
B97D	-232.090088	-385.703270	n/c	-692.878690	-846.454085	-1000.025401	-1153.594038	-1307.160829	-1460.726302	-1614.290800
B98	-232.169573	-385.837940	n/c	-693.123420	-846.753289	-1000.378792	-1154.001403	-1307.622011	-1461.241184	-1614.859294
BHandH	-230.438434	-383.010952	-535.564199	-688.105108	-840.638523	-993.167150	-1145.692567	-1298.215737	-1450.737275	-1603.257627
BHandHLYP	-232.111827	-385.747227	-539.363885	-692.968546	-846.565871	-1000.158488	-1153.747937	-1307.335162	-1460.920774	-1614.505192
BLYP	-232.160382	-385.830038	n/c	-693.118533	-846.750520	-1000.378450	-1154.003716	-1307.627146	-1461.249264	-1614.870410
BMK	-232.089608	-385.713878	-539.318416	-692.910874	-846.496092	-1000.076720	-1153.654284	-1307.229714	-1460.803610	-1614.376359
CAM-B3LYP	-232.129049	-385.770447	-539.392637	-693.002874	-846.605877	-1000.204270	-1153.799573	-1307.392714	-1460.984293	-1614.574717
HCTH/147	-232.252840	-385.963024	-539.652730	-693.330686	-847.001910	-1000.668981	-1154.333332	-1307.995813	-1461.656958	-1615.317122
HCTH/407	-232.246259	-385.949093	-539.631289	-693.301652	-846.965240	-1000.624653	-1154.281333	-1307.936135	-1461.589595	-1615.242075
HF	-230.685276	-383.413120	-536.125011	-688.825329	-841.517963	-994.205478	-1146.889435	-1299.570823	-1452.250300	-1604.928315
HFB	-230.749126	-383.525279	n/c	-689.029916	-841.770563	-994.507310	-1147.241486	-1299.973886	-1452.705021	-1605.435192
HFS	-227.412321	-378.068686	n/c	-679.331370	-829.950372	-980.565296	-1131.177544	-1281.787951	-1432.397035	n/c
HSE06	-232.001138	-385.565604	-539.110556	-692.643620	-846.169661	-999.691295	-1153.210009	-1306.726702	-1460.241945	-1613.756125
LC-wPBE	-232.089676	-385.696136	-539.283505	-692.858609	-846.426130	-999.988751	-1153.548049	-1307.105003	-1460.660248	-1614.214220
M05	-232.059250	-385.662181	-539.244810	-692.815553	-846.379270	-999.938570	-1153.494939	-1307.049272	-1460.602141	-1614.153932
M052X	-232.238094	-385.960618	n/c	-693.353279	-847.035932	-1000.713835	-1154.388562	-1308.061072	-1461.731984	-1615.401708
M06	-232.075801	-385.687469	n/c	-692.859398	-846.432517	-1000.001246	-1153.567059	-1307.130846	-1460.693174	-1614.254435
M062X	-232.158672	-385.829720	-539.480923	-693.119806	-846.751299	-1000.378094	-1154.001748	-1307.623211	-1461.243094	-1614.861804
M06HF	-232.206372	-385.907864	-539.590028	-693.259410	-846.920894	-1000.577254	-1154.230139	-1307.880571	-1461.529225	-1615.176534
M06L	-232.225711	-385.939021	-539.631772	-693.312665	-846.986688	-1000.656452	-1154.323419	-1307.988460	-1461.652124	-1615.314783
MP2	-231.515288	-384.784207	-538.034188	-691.271183	-844.500486	-997.724928	-1150.946073	-1304.164900	-1457.382053	-1610.597919
mPW1LYP	-232.130105	-385.780472	-539.411525	-693.030859	-846.643239	-1000.251240	-1153.856333	-1307.459408	-1461.061032	-1614.661586
mPW1PBE	-232.117506	-385.754968	-539.372759	-692.978587	-846.577337	-1000.171642	-1153.762999	-1307.352314	-1460.940161	-1614.526933
mPW2PLYPD	-232.013610	-385.593164	-539.153743	-692.702552	-846.244353	-999.781758	-1153.316261	-1306.848768	-1460.379858	-1613.909911
mPW3PBE	-232.101719	-385.725194	-539.328877	-692.920658	-846.505441	-1000.085845	-1153.663352	-1307.238856	-1460.812924	-1614.385937
O3LYP	-232.178576	-385.854262	n/c	-693.153349	-846.790069	-1000.422505	-1154.052123	-1307.679798	-1461.306085	-1614.931351
OPBE	-232.162100	-385.828743	n/c	-693.108243	-846.735143	-1000.357832	-1153.977772	-1307.595826	-1461.212537	-1614.828261
OTPSS	-232.165447	-385.834278	n/c	-693.118016	-846.747041	-1000.371861	-1153.993936	-1307.614128	-1461.232979	-1614.850845
PBE0	-231.980778	-385.531831	n/c	-692.582563	-846.094860	-999.602711	-1153.107613	-1306.610474	-1460.111867	-1613.612185
PDDG	0.041147	0.035394	0.047841	0.069970	0.097965	0.129811	0.164302	0.200677	0.238415	0.277225

PM3	0.041181	0.034636	0.045719	0.066409	0.092940	0.123327	0.156367	0.191303	0.227623	0.265014
PM6	0.038350	0.028561	0.037342	0.055365	0.079103	0.106635	0.136789	0.168827	0.202259	0.236777
tHCTH	-232.208015	-385.886280	-539.544210	-693.190437	-846.829943	-1000.465299	-1154.097935	-1307.728699	-1461.358126	-1614.986572
tHCTHhyb	-232.234018	-385.938021	n/c	-693.294288	-846.959632	-1000.620676	-1154.278883	-1307.935129	-1461.589973	-1615.243780
TPSSh	-232.283829	-386.027944	-539.752275	-693.464794	-847.170411	-1000.871725	-1154.570202	-1308.266720	-1461.961836	n/c
VSXC	-232.367523	-386.173863	-539.959928	-693.733967	-847.501084	-1001.263926	-1155.023964	-1308.782071	-1462.538797	-1616.294510
wB97	-232.208481	-385.903591	-539.579521	-693.243291	-846.899537	-1000.550918	-1154.199001	-1307.844756	-1461.488816	-1615.131605
wB97X	-232.194909	-385.879976	-539.545636	-693.199113	-846.845141	-1000.486391	-1154.124421	-1307.760190	-1461.394321	-1615.027232
wB97XD	-232.180270	-385.854962	-539.509987	-693.152918	-846.788571	-1000.419601	-1154.047540	-1307.673325	-1461.297555	-1614.920637
X3LYP	-232.154799	-385.814048	-539.453836	-693.081896	-846.703030	-1000.319814	-1153.933716	-1307.545620	-1461.156090	-1614.765503
XAlpha	-228.909604	-380.532433	n/c	-683.726642	-835.311108	-986.891404	-1138.468968	-1290.044654	-1441.618989	-1593.192355

[a] calculation failed to converge.

Table S6. Molecular energies (298.15 K and 1 atm) of the neutral compounds at the optimized neutral geometries for the n=1-10 [n]acenes at the B3LYP/y//B3LYP/6-31G(d) level of theory.

	[n]acene									
basis set	1	2	3	4	5	6	7	8	9	10
6-31G(d)	-232.248659	-385.892730	-539.530524	-693.165812	-846.799944	-1000.433489	-1154.066724	-1307.699787	-1461.332757	-1614.965672
6-311++G(d,p)	-232.311251	-385.988898	-539.660288	-693.329253	-846.996945	-1000.664088	-1154.330850	-1307.997475	n/c[a]	-1615.330385
6-311++G(2d,2p)	-232.320440	-386.003624	-539.680623	-693.355124	-847.028415	-1000.701094	-1154.373439	-1308.045594	-1461.717646	-1615.389643
SVP	-232.084562	-385.619041	-539.147373	-692.673251	-846.197987	-999.722142	-1153.245987	-1306.769666	-1460.293243	-1613.816774
TZV	-232.261006	-385.906810	n/c	-693.183462	-846.819346	-1000.454631	-1154.089595	-1307.724383	-1461.359079	-1614.993718
TZVP	-232.328219	-386.016675	-539.698972	-693.378770	-847.057382	-1000.735385	-1154.413064	-1308.090554	-1461.767954	-1615.445282
cc-pVDZ	-232.262815	-385.915685	-539.562359	-693.206530	-846.849535	-1000.491950	-1154.134049	-1307.775974	-1461.417799	-1615.059573
cc-pVTZ	-232.333067	-386.025123	-539.711016	-693.394406	-847.076603	n/c	-1154.439440	-1308.120500	-1461.801470	-1615.482363

[a] calculation failed to converge.

Table S7. Molecular energies (298.15 K and 1 atm) of the cationic compounds at the optimized neutral geometries for the n=1-10 [n]acenes at the B3LYP/y//B3LYP/6-31G(d) level of theory.

	[n]acene									
basis set	1	2	3	4	5	6	7	8	9	10
6-31G(d)	-231.917531	-385.610215	-539.277934	-692.933321	-846.581828	-1000.226111	-1153.867639	-1307.507246	-1461.145489	-1614.782723
6-311++G(d,p)	-231.970591	-385.696265	-539.397220	-693.086087	-846.768032	-1000.445851	-1154.120873	-1307.794037	n/c[a]	-1615.136548
6-311++G(2d,2p)	-231.980611	-385.711651	-539.418193	-693.112585	-846.800135	-1000.483492	-1154.164103	-1307.842799	-1461.520129	-1615.196459
SVP	-231.744669	-385.327878	-538.886092	-692.432033	-845.971126	-999.506015	-1153.038157	-1306.568391	-1460.097253	-1613.625116
TZV	-231.918701	-385.613852	-539.283617	-692.940914	-846.591252	-1000.237324	-1153.880614	-1307.521972	-1461.161960	-1614.800936
TZVP	-231.987818	-385.724466	-539.436393	-693.136116	-846.829005	-1000.517692	-1154.203638	-1307.887667	-1461.570342	-1615.251999
cc-pVDZ	-231.926091	-385.627292	-539.303716	-692.967884	-846.625207	-1000.278327	-1153.928702	-1307.577166	-1461.224263	-1614.870357
cc-pVTZ	-231.993999	-385.734181	-539.449731	-693.153080	-846.849582	n/c	-1154.231411	-1307.919024	-1461.605282	-1615.290512

[a] calculation failed to converge.

Table S8. Molecular energies (298.15 K and 1 atm) of the anionic compounds at the optimized neutral geometries for the n=1-10 [n]acenes at the B3LYP/y//B3LYP/6-31G(d) level of theory.

	[n]acene									
basis set	1	2	3	4	5	6	7	8	9	10
6-31G(d)	-232.164070	-385.859739	-539.530746	-693.188520	-846.838767	-1000.484356	-1154.126874	-1307.767321	-1461.406178	-1615.043956
6-311++G(d,p)	-232.289282	-385.977676	-539.678854	-693.368664	-847.051549	-1000.730141	-1154.405784	-1308.079495	-1461.751659	-1615.422759
6-311++G(2d,2p)	-232.298861	-385.992869	-539.699521	-693.394809	-847.083253	-1000.767363	-1154.448573	-1308.127809	-1461.805523	-1615.482205
SVP	-232.013682	-385.597780	-539.158511	-692.706447	-846.247039	-999.783066	-1153.316072	-1306.847043	-1460.376438	-1613.904776
TZV	-232.196855	-385.888917	-539.559673	-693.218182	-846.869528	-1000.516396	-1154.160294	-1307.802191	-1461.442551	-1615.081867
TZVP	-232.268556	-386.002221	-539.715294	-693.416356	-847.110350	-1000.797180	-1154.486519	-1308.171130	-1461.854212	-1615.536238
cc-pVDZ	-232.189687	-385.892197	-539.571342	-693.237645	-846.896571	-1000.550911	-1154.202217	-1307.851476	-1461.499155	-1615.145768
cc-pVTZ	-232.270315	-386.008871	-539.726053	-693.430974	-847.128726	-1000.821990	-1154.512277	-1308.200540	-1461.887264	-1615.572914

[a] calculation failed to converge.

Table S9. Molecular energies (298.15 K and 1 atm) of the cationic compounds at the optimized cationic geometries for the n=1-10 [n]acenes at the B3LYP/y//B3LYP/6-31G(d) level of theory.

	[n]acene									
basis set	1	2	3	4	5	6	7	8	9	10
6-31G(d)	-231.923065	-385.613632	-539.280491	-692.935395	-846.583570	-1000.227593	-1153.868899	-1307.508326	-1461.146414	n/a[a]
6-311++G(d,p)	-231.975768	-385.699432	-539.399570	-693.088027	-846.769684	-1000.447259	-1154.122054	-1307.795090	n/a	n/a
6-311++G(2d,2p)	-231.985547	-385.714608	-539.420433	-693.114467	-846.801778	-1000.484957	-1154.165385	-1307.843985	-1461.521197	n/a
SVP	-231.750117	-385.331376	-538.888692	-692.434106	-845.972824	-999.507410	-1153.039301	-1306.569321	-1460.098011	n/a
TZV	-231.924392	-385.617177	-539.286000	-692.942787	-846.592792	-1000.238617	-1153.881698	-1307.522892	-1461.162743	n/a
TZVP	-231.992816	-385.727402	-539.438624	-693.137978	-846.830629	-1000.519135	-1154.204921	-1307.888825	-1461.571385	n/a
cc-pVDZ	-231.931571	-385.630786	-539.306296	-692.969935	-846.626887	-1000.279711	-1153.929839	-1307.578097	-1461.225024	n/a
cc-pVTZ	-231.998898	-385.737066	-539.451954	-693.154959	-846.851242	-1000.543367	-1154.232756	-1307.920255	-1461.606402	n/a

[a] calculation failed to converge.

Table S10. Molecular energies (298.15 K and 1 atm) of the anionic compounds at the optimized anionic geometries for the n=1-10 [n]acenes at the B3LYP/y//B3LYP/6-31G(d) level of theory.

	[n]acene									
basis set	1	2	3	4	5	6	7	8	9	10
6-31G(d)	-232.171361	-385.864558	-539.534441	-693.191493	-846.841217	-1000.486408	-1154.128620	-1307.768779	-1461.407470	-1615.045079
6-311++G(d,p)	-232.263724	-385.981561	-539.681912	-693.371053	-847.053529	-1000.731732	-1154.407058	-1308.080557	-1461.752536	-1615.423516
6-311++G(2d,2p)	-232.273017	-385.996104	-539.702004	-693.396720	-847.084742	-1000.768517	-1154.449453	-1308.128471	-1461.806048	n/a[a]
SVP	-232.021525	-385.603268	-539.162864	-692.710050	-846.250085	-999.785680	-1153.318350	-1306.849003	-1460.378213	-1613.906357
TZV	-232.203567	-385.893315	-539.562982	-693.220798	-846.871657	-1000.518165	-1154.161797	-1307.803443	n/a	-1615.082841
TZVP	-232.274206	-386.005854	-539.718000	-693.418442	-847.111985	-1000.801202	-1154.487555	-1308.171923	-1461.854868	-1615.536764
cc-pVDZ	-232.197563	-385.897622	-539.575597	-693.241134	-846.899497	-1000.553404	-1154.204376	-1307.853321	-1461.500815	-1615.147238
cc-pVTZ	-232.275834	-386.012270	-539.728507	-693.432821	-847.130139	-1000.823079	-1154.513119	-1308.201152	-1461.887744	-1615.573274

[a] calculation failed to converge.

Table S11. Molecular enthalpies (298.15 K and 1 atm) of the neutral, cationic, and anionic n=1-10 [n]acenes at the B3LYP/y//B3LYP/6-31G(d) level of theory.

n	neutral	cationic	anionic
1	-232.205860	-231.872304	-232.073935
2	-385.737156	-385.458104	-385.714692
3	-539.325605	-539.075005	-539.334223
4	-692.911636	-692.680307	-692.941488
5	-846.496563	-846.279051	-846.541681
6	-1000.080942	-999.873751	-1000.137498
7	-1153.665034	-1153.465829	c/e[a]
8	-1307.248984	c/e	c/e
9	-1460.832841	c/e	c/e
10	-1614.416672	c/e	c/e

[a] calculation not completed due to computational expense.