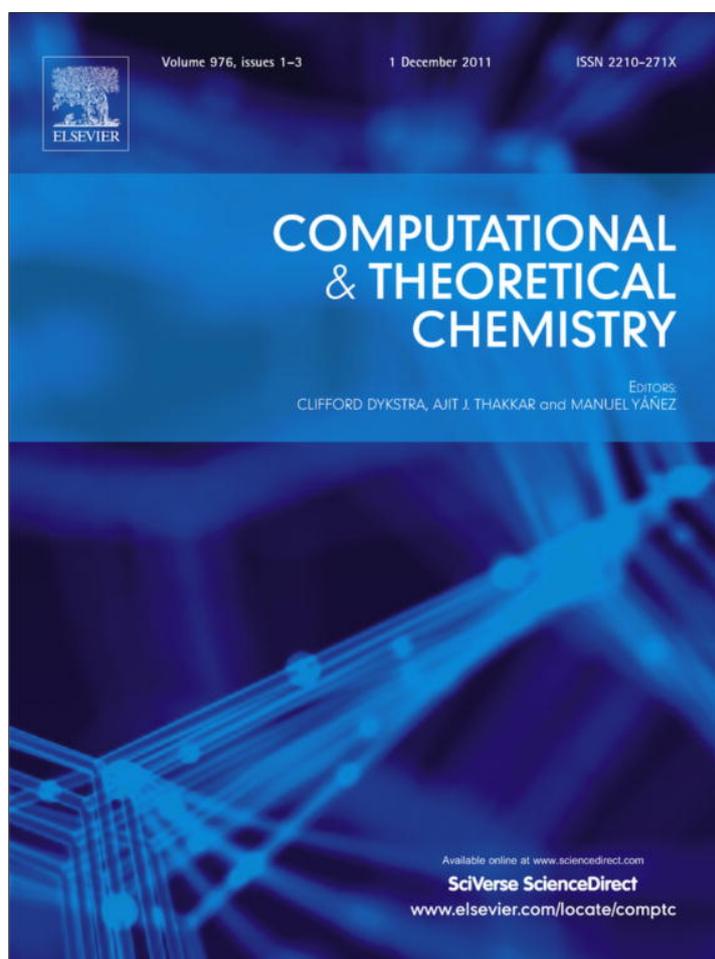


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

A comparison of density functional theory (DFT) methods for estimating the singlet–triplet (S_0 – T_1) excitation energies of benzene and polyacenes

Sierra Rayne^{a,*}, Kaya Forest^{b,c}^a Ecologica Research, PO Box 74, 318 Rose Street, Mortlach, Saskatchewan, Canada S0H 3E0^b Department of Chemistry, Okanagan College, 583 Duncan Avenue West, Penticton, British Columbia, Canada V2A 8E1^c Department of Environmental Engineering, Saskatchewan Institute of Applied Science and Technology, Palliser Campus, PO Box 1420, 600 6th Avenue NW, Moose Jaw, Saskatchewan, Canada S6H 4R4

ARTICLE INFO

Article history:

Received 16 July 2011

Received in revised form 7 August 2011

Accepted 8 August 2011

Available online 24 August 2011

Keywords:

Polyacenes

Singlet–triplet excitation energies

Density functional methods

Benchmarking

ABSTRACT

Singlet–triplet (S_0 – T_1) well-to-well (WWE_{S-T}) and adiabatic (AE_{S-T}) excitation energies of benzene and the linear polyacenes naphthalene through decacene were estimated using a range of density functional theory (DFT) methods and basis sets along with the assumption of a closed-shell singlet state. Via single exponential decay regression based extrapolations to the polymeric limit, significant variability in theoretically obtained WWE_{S-T}/AE_{S-T} predicted for longer polyacenes is evident that is primarily dependent on the model chemistry employed, with minor variations due to basis set incompleteness and zero-point energy (ZPE) corrections. With the exception of the B2PLYPD density functional (which, along with the mPW2PLYPD functional, combines exact HF exchange with an MP2-like correlation to the DFT calculation), all DFT methods investigated predict a negative WWE_{S-T}/AE_{S-T} (ground state triplet) at the polymer limit, with most functionals predicting a transition from a singlet to triplet ground state between octacene and decacene. Extrapolation of the B2PLYPD results predicts a vanishingly small singlet–triplet gap at the polymeric limit for an infinitely long homolog. Hartree–Fock calculations significantly underestimate the polyacene WWE_{S-T}/AE_{S-T} , whereas MPn methods overestimate the singlet–triplet gap but display a convergence toward experimental values with increasing truncation order and substitutions. The B2PLYPD and mPW2PLYPD functionals appear to balance the WWE_{S-T}/AE_{S-T} underestimating tendency of HF/DFT methods for longer polyacenes against the propensity for MPn methods to overestimate the WWE_{S-T}/AE_{S-T} for these compounds, and predict all acenes from benzene through decacene will be ground state singlets with positive singlet–triplet gaps.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The polyacenes (Fig. 1) are linearly annelated benzene units [1] that are of practical interest in materials science and nanotechnology [2], as well as of theoretical value in advancing our understanding of aromaticity [3–7] and in developing computational methods. While the shorter chain polyacenes (benzene through pentacene) are experimentally well-known, the difficult syntheses and long-term instabilities of hexacene and higher homologs remain a challenge, and only the members up to nonacene have been experimentally studied to a very limited degree [8–12]. The nature of the electronic ground state for the longer chain acenes, and the direction and magnitude of the singlet–triplet energy gap (E_{S-T}), are of substantial attention and debate [13]. Some groups have proposed triplet [14] (and/or higher multiplicities [15]) or open-shell singlet [10,16–26] di- and/or poly-radical ground states, and

in some cases, the difficulties in synthesizing these compounds and their instability following isolation have been attributed to the proposed radical character.

However, experimental evidence on nonacene by Tonshoff and Bettinger suggests that the longer polyacenes do not have triplet (or higher multiplicity) ground states [12], thereby appearing to narrow the ground state uncertainty to between closed and open-shell singlets. It is also important to note that where the E_{S-T} gap is on the order of several kcal/mol or less, a higher energy triplet state above a ground state closed-shell singlet should be thermally accessible, potentially allowing for thermal reactivity beyond that expected for a ground state closed-shell singlet. Recently, Hajgato et al. [27,28] have conducted two high-level theoretical studies that strongly suggest all linear polyacenes have a closed-shell singlet ground state and a singlet–triplet energy gap that approaches zero (but is never negative) at the polymeric limit. Their results are compelling due to the quality of the calculations, and findings that agree with experimental intuitions regarding the inherent closed-shell singlet ground states of small through mid-size hydrocarbons. In light of these controversies, it is of interest

* Corresponding author. Tel.: +1 306 690 0573.

E-mail address: rayne.sierra@gmail.com (S. Rayne).

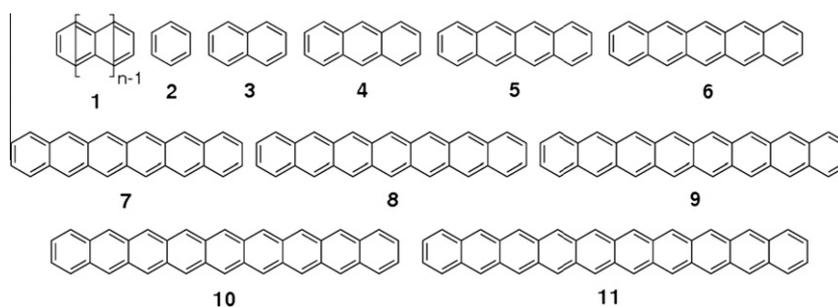


Fig. 1. General structure of the polyacenes (1) and the individual members from benzene (2; $n = 1$) through decacene (11; $n = 10$).

to investigate the performance of a broad range of density functionals for estimating the singlet–triplet energy gaps of polyacenes, and particularly the predicted singlet–triplet energy gaps at the polymer limit.

2. Computational details

Geometry optimizations, frequency calculations, and single point energy (SPE) calculations employed Gaussian 09 (G09) [29] with various combinations of the following model chemistries and basis sets: model chemistries, B1B95 [30], B1LYP [30–32], B2PLYPD [33], B3LYP [30–32,34], B3P86 [34,35], B3PW91 [34,36–38], B972 [39], B97D [40], B98 [41,42], BHandH [30–32,43–45], BHandHLYP [30–32,43–46], BMK [47], CAM-B3LYP [30–32,34,48], CCD [49,50], CCSD [49–53], CCSD(T) [49–54], HCTH/147 [55–57], HCTH/407 [55–57], HCTH/93 [55–57], HF [43–45], HFB [46], HFS [58–60], HSE03 [61–67], HSE06 [61–67], LC-wPBE [68–71], M06 [72], M062X [72], M06HF [73,74], M06L [75], MP2 [76–81], MP3 [76,82,83], MP4 (with DQ, SDQ, and SDTQ substitutions) [84,85], MP5 [86], mPW1LYP [30–32,87], mPW1PBE [87–89], mPW2PLYPD [90], mPW3PBE [87–89], O3LYP [30–32,91], PBE0 [88,89,92], PBEh1PBE [88,89,93], QCISD [54], tHCTH [94], tHCTHhyb [94], TPSSh [95], VSXC [96], wB97 [97], wB97X [97], wB97XD [98], and X3LYP [30–32,99]; basis sets, STO-3G [100,101], 6-21G** [102,103], 4-31G** [104–107], SV [108,109], 6-31G(d) [104–107,110,111], 6-31G(d,p) [104–107,110,111], TZVP [108,109], cc-pVDZ [112–115], and cc-pVTZ [112–115]. All singlet state calculations presented herein used a closed-shell consistent with the conclusions from Hajgato et al. [27,28]. Structures were confirmed as true minima absent imaginary frequencies. Geometry visualizations were conducted with Gabedit 2.2.12 [116]. KyPlot v.2.b.15 [117] was employed for all statistical analyses. The theoretical data presumably contains only systematic errors. The regression based error analyses as applied herein were designed for experimental data having only random errors, and should thus be taken as estimates for the uncertainty from extrapolating computationally derived datasets.

3. Results and discussion

The starting point for our investigations was a consideration of experimental singlet–triplet energy gap trends of polyacenes using the available dataset from $n = 1$ (benzene) through $n = 6$ (hexacene). Hajgato et al. [27] have compiled the experimental data in their work, and discussed how the different experimental conditions employed – almost entirely in condensed matrices – for the various compounds under study may result in intercomparability challenges within the experimental database and additional inherent differences when comparing the experimental values against gas-phase theoretical calculations. Fitting the experimental adiabatic singlet–triplet energy gap (AE_{S-T}) for the $n = 1$ –6 polyacenes

(and taking the average of the two datapoints for naphthalene [60.9 and 61.0 kcal/mol] and anthracene [42.6 and 43.1 kcal/mol]) to a single exponential decay function having a y -axis offset of the general form $y = ae^{-bx} + c$ (where a , b , and c are constants, x is the number of acene units, and y is the AE_{S-T}) yields an AE_{S-T} at the polymer limit of -9.8 kcal/mol ($r = 0.99998$; Fig. 2), and a y -intercept (i.e., crossover from positive to negative AE_{S-T}) at nonacene. Since Tonshoff and Bettinger [12] have experimental data on nonacene that indicates its ground state is not a triplet, this extrapolation appears to underestimate the AE_{S-T} of longer polyacenes.

The extrapolation of the experimental AE_{S-T} data is also highly sensitive to the AE_{S-T} value for hexacene (currently at 12.4 ± 1.2 kcal/mol). If an AE_{S-T} value of 16.4 kcal/mol is used instead for hexacene, the polymer limit AE_{S-T} is estimated at about zero (-0.2 ± 4.3 [SE; standard error]) via a regression equation of the form $y = ae^{-bx} + c$ with only a small loss in quality of fit ($r = 0.9992$). Similarly, fitting a single exponential decay function without x - or y -axis offsets (i.e., automatic convergence to an $AE_{S-T} \rightarrow 0$ as $n \rightarrow \infty$) of the form $y = ae^{-bx}$ to the original experimental data also yields a high quality fit ($r = 0.9990$). Consequently, the experimental AE_{S-T} dataset for the n -acenes ($n = 1$ –6) is ambiguous regarding the potential onset of negative AE_{S-T} for longer members of the series. The confidence in polymeric limit AE_{S-T} extrapolations from this dataset is limited owing to the regression sensitivity towards the single AE_{S-T} value reported for hexacene, as well as the varying matrices used among the experimental reports and the potential differences (currently not well defined) between gas and condensed phase AE_{S-T} values. Experimental AE_{S-T}

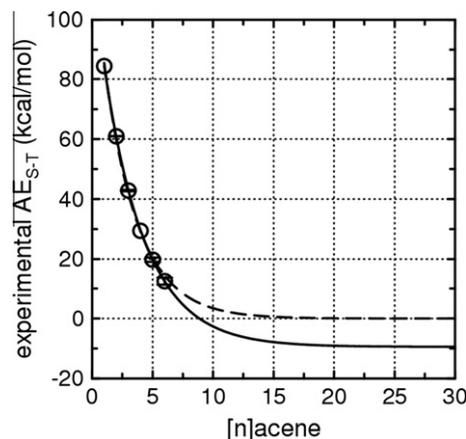


Fig. 2. Trend in experimental singlet–triplet energy gaps for benzene through hexacene and extrapolations to the polymeric limit using a single exponential decay function having a y -axis offset of the general form $y = ae^{-bx} + c$ (solid line; $a = 125.7 \pm 0.6$ [\pm SE], $b = 0.292 \pm 0.005$, $c = -9.4 \pm 0.9$; $r = 0.99998$) and a single exponential decay function without x - or y -axis offsets of the form $y = ae^{-bx}$ (dashed line; $a = 122.0 \pm 2.7$, $b = 0.357 \pm 0.010$; $r = 0.9990$). Experimental data are from Refs. [127–132] as compiled in Ref. [123]. Error bars represent the range of experimental reports.

datapoints for heptacene through nonacene are clearly needed to constrain polymeric limit extrapolations of the experimental dataset with high confidence.

In their early work, Hajgato et al. [27] reported the following benchmark quality AE_{S-T} for benzene through heptacene at the CCSD(T)/cc-pV ∞ Z level (values in kcal/mol): $n=1$ (benzene), 87.0; $n=2$ (naphthalene), 62.9; $n=3$ (anthracene), 46.2; $n=4$ (naphthacene), 32.2; $n=5$ (pentacene), 24.2; $n=6$ (hexacene), 16.8; and $n=7$ (heptacene), 12.6. When fit to a regression of the form $y = ae^{-bx} + c$, the data of Hajgato et al. [27] indicates an AE_{S-T} for linear acenes at the polymer limit of effectively zero (-0.3 ± 1.4 [SE] kcal/mol; 95% CL [confidence limit] range from -4.1 to $+3.5$ kcal/mol; $a = 120.5 \pm 1.0$, $b = 0.322 \pm 0.011$; $r = 0.9998$). An equally high quality fit ($r = 0.9998$) is obtained for the AE_{S-T} data of Hajgato et al. [27] using a regression of the form $y = ae^{-bx}$ ($a = 120.4 \pm 0.9$, $b = 0.324 \pm 0.003$) which yields an $AE_{S-T} \rightarrow 0$ as $n \rightarrow \infty$. Similarly, Hajgato et al. [27] reported the following benchmark quality well-to-well singlet–triplet energy gaps (WWE_{S-T}) for benzene through heptacene at the CCSD(T)/cc-pV ∞ Z level (values in kcal/mol): $n=1$ (benzene), 92.2; $n=2$ (naphthalene), 66.2; $n=3$ (anthracene), 48.5; $n=4$ (naphthacene), 34.0; $n=5$ (pentacene), 25.6; $n=6$ (hexacene), 18.0; and $n=7$ (heptacene), 13.6. When fit to a regression of the form $y = ae^{-bx} + c$, the data of Hajgato et al. [27] indicates a WWE_{S-T} for linear acenes at the polymer limit of about $+1$ kcal/mol (1.0 ± 1.2 [SE] kcal/mol; 95% CL range from -2.3 to $+4.4$ kcal/mol; $a = 127.1 \pm 1.0$, $b = 0.332 \pm 0.010$; $r = 0.99990$). An equally high quality fit ($r = 0.9990$) is obtained for the WWE_{S-T} data of Hajgato et al. [27] using a regression of the form $y = ae^{-bx}$ ($a = 127.3 \pm 0.9$, $b = 0.324 \pm 0.003$) which yields an $AE_{S-T} \rightarrow 0$ as $n \rightarrow \infty$. Thus, the data of Hajgato et al. [27] is unambiguous in predicting a vanishingly small singlet–triplet gap for the polyacenes at the polymeric limit.

In a recently published work, Hajgato et al. [28] have extended their high level E_{S-T} studies of the acenes out through undecacene. Using a focal point analysis approach applied to the results of a series of single-point and symmetry-restricted calculations employing correlation consistent cc-pVXZ basis sets ($X = D, T, Q, 5$) and single-reference methods [HF, MP2, MP3, MP4SDQ, CCSD, CCSD(T)] of improving quality, these authors have reported the following updated AE_{S-T} for benzene through undecacene at the CCSD(T)/cc-pV ∞ Z level (values in kcal/mol): benzene, 86.5; naphthalene, 62.5; anthracene, 45.9; naphthacene, 31.7; pentacene, 23.8; hexacene, 16.5; heptacene, 12.3; octacene, 8.2; nonacene, 6.0; decacene, 3.7; and undecacene, 2.6. The authors' own regression analysis of this data suggests an AE_{S-T} at the polymer limit of -1.1 kcal/mol. When we fit the data of Hajgato et al. [28] to a regression of the form $y = ae^{-bx} + c$, we obtain equivalent results with a projected AE_{S-T} for linear acenes at the polymer limit of

effectively zero (-1.0 ± 0.4 [SE] kcal/mol; 95% CL range from -2.1 to 0.0 kcal/mol; $a = 120.4 \pm 0.8$, $b = 0.318 \pm 0.005$; $r = 0.99990$). An equally high quality fit ($r = 0.9998$) is obtained for the AE_{S-T} data of Hajgato et al. [28] using a regression of the form $y = ae^{-bx}$ ($a = 120.8 \pm 1.0$, $b = 0.329 \pm 0.003$) which yields an $AE_{S-T} \rightarrow 0$ as $n \rightarrow \infty$.

Similarly, Hajgato et al. [28] reported the following updated WWE_{S-T} for benzene through undecacene at the CCSD(T)/cc-pV ∞ Z level (values in kcal/mol): benzene, 91.7; naphthalene, 65.8; anthracene, 48.2; naphthacene, 33.5; pentacene, 25.3; hexacene, 17.7; heptacene, 13.4; octacene, 9.2; nonacene, 7.0; decacene, 4.6; and undecacene, 3.6. The authors' own regression analysis of this data suggests an WWE_{S-T} at the polymer limit of $+0.2$ kcal/mol. When we fit the data of Hajgato et al. [28] to a regression of the form $y = ae^{-bx} + c$, we obtain equivalent results with a projected WWE_{S-T} for linear acenes at the polymer limit of effectively zero ($+0.2 \pm 0.4$ [SE] kcal/mol; 95% CL range from -0.8 to $+1.1$ kcal/mol; $a = 127.0 \pm 0.8$, $b = 0.328 \pm 0.005$; $r = 0.99990$). An equally high quality fit ($r = 0.99990$) is obtained for the AE_{S-T} data of Hajgato et al. [28] using a regression of the form $y = ae^{-bx}$ ($a = 127.0 \pm 0.7$, $b = 0.326 \pm 0.002$) which yields an $AE_{S-T} \rightarrow 0$ as $n \rightarrow \infty$. Thus, the data of both studies from Hajgato et al. [27,28] are collectively unambiguous in predicting a vanishingly small singlet–triplet gap for the polyacenes at the polymeric limit.

Other work by Bendikov et al. [17] calculated the AE_{S-T} for hexacene through decacene at the B3LYP/6-31G(d) level using both closed- and open-shell singlet state assumptions. The closed-shell singlet AE_{S-T} reported by these authors are in excellent agreement with our calculations at this level of theory (reported as current study/value from Ref. [17]; values are in kcal/mol; also see Table 1): hexacene, 9.6/9.5; heptacene, 4.5/4.4; octacene, 0.6/0.6; nonacene, $-2.3/-2.4$; and decacene, $-4.6/-4.7$. While ZPE corrections for the shorter acenes can be substantial (Hajgato et al. [27,28] reported ΔZPE at the B3LYP/cc-pVTZ of -5.2 , -3.3 , and -2.3 kcal/mol, respectively, for benzene, naphthalene, and anthracene), the corrections decline with increasing acene length and are $\sim 1-2$ kcal/mol for naphthacene through heptacene, converging on a polymeric limit ZPE correction of -1.0 for octacene and larger polyacenes. These corrections for longer polyacenes are within the inherent errors of the theoretical methods and the experimental AE_{S-T} data, indicating that WWE_{S-T} are approximately equal to AE_{S-T} for longer acenes.

With the exception of Hajgato et al. [27,28], who probed the WWE_{S-T}/AE_{S-T} using a range of model chemistries (HF, MP2, MP3, MP4(SDQ), CCSD, and CCSD(T)) and basis sets, the majority of computational studies on polyacene energetics employ sole use of the B3LYP functional (or other older functionals such as BLYP), despite the known problems with this method for calculating hydrocarbon energies (see, e.g., [118–126]). As is evident in our

Table 1

Experimental (where available) AE_{S-T} and theoretical WWE_{S-T}/AE_{S-T} for naphthacene through decacene using the B3LYP, B97D, M062X, and HF methods and the 6-31G(d) basis set. Values are in kcal/mol.

Compound	Expt. AE_{S-T} ^a	B3LYP		B97D		M062X		HF	
		AE_{S-T}	WWE_{S-T}	AE_{S-T}	WWE_{S-T}	AE_{S-T}	WWE_{S-T}	AE_{S-T}	WWE_{S-T}
Naphthacene	29.4 [127]	26.0	27.7	24.5	25.8	31.8	33.6	10.4	12.1
Pentacene	19.8 ± 0.7 [131]	16.5	17.9	15.5	16.6	21.5	23.0	-2.9	-0.8
Hexacene	12.4 ± 1.2 [132]	9.6	10.8	9.1	9.9	13.9	15.4	-13.5	-11.3
Heptacene	n/a ^b	4.5	5.6	4.3	5.1	8.3	9.8	-22.4	-20.1
Octacene	n/a	0.6	1.7	0.8	1.4	4.0	5.5	-30.1	-27.4
Nonacene	n/a	-2.3	-1.2	-2.0	-1.4	0.6	2.3	-36.9	-33.5
Decacene	n/a	-4.6	-3.5	-5.9	-3.6	n/c ^c	-0.3	n/c	-38.9

^a Experimental data taken from the compilation in Ref. [27].

^b Not available.

^c Frequency calculation did not converge.

Table 2
Experimental (where available) and theoretical AE_{S-T} for naphthacene through decacene using the B3LYP functional and various basis sets. Values are in kcal/mol.

Compound	Expt. AE_{S-T} ^a	STO-3G	6-21G**	4-31G**	SV	6-31G(d)
Naphthacene	29.4 [127]	28.3	26.6	26.3	26.2	26.0
Pentacene	19.8 ± 0.7 [131]	18.4	17.0	16.7	16.7	16.5
Hexacene	12.4 ± 1.2 [132]	11.4	10.1	9.8	9.8	9.6
Heptacene	n/a ^b	6.3	5.0	4.7	4.8	4.5
Octacene	n/a	2.5	1.1	0.9	1.0	0.6
Nonacene	n/a	-0.4	-1.8	-2.1	-1.9	-2.3
Decacene	n/a	-2.6	-4.2	-4.4	-4.1	-4.6

^a Experimental data taken from the compilation in Ref. [27].^b Not available.**Table 3**
Summary statistics of estimated WWE_{S-T} for benzene through decacene using a range of density functionals (see Table 4 for listing) obtained at the $x/6-31G(d)//B3LYP/6-31G(d)$ level of theory. Values are in kcal/mol.

Compound	Mean ± SD	Median	Range
Benzene	89.8 ± 3.6	89.3	79.2 (HFB) to 104.1 (M06HF)
Naphthalene	63.3 ± 3.7	62.6	54.5 (HFB) to 78.9 (M06HF)
Anthracene	42.1 ± 3.0	41.4	35.8 (HFB) to 54.8 (M06HF)
Naphthacene	27.9 ± 2.8	27.2	23.2 (HFB) to 39.9 (M06HF)
Pentacene	17.9 ± 2.4	17.4	14.5 (HFB) to 28.2 (M06HF)
Hexacene	10.7 ± 2.3	10.2	7.6 (BHandHLYP) to 19.9 (M06HF)
Heptacene	5.4 ± 2.3	5.0	1.5 (LC-wPBE) to 13.5 (M06HF)
Octacene	1.4 ± 2.4	1.1	-3.3 (LC-wPBE) to 8.6 (M06HF)
Nonacene	-1.6 ± 2.4	-1.9	-7.0 (LC-wPBE) to 5.4 (B2PLYPD)
Decacene	-3.9 ± 2.6	-4.2	-9.9 (LC-wPBE) to 3.6 (B2PLYPD)

AE_{S-T} calculations at the $x/6-31G(d)$ level and WWE_{S-T} calculations at the $x/6-31G(d)//B3LYP/6-31G(d)$ level with the B3LYP, B97D, M062X, and HF methods for naphthacene through decacene shown in Table 1, a relatively broad range of method dependent WWE_{S-T}/AE_{S-T} are obtained with variations of up to several kcal/mol among the DFT methods and clearly erroneous results from HF calculations. Of note is the method inconsistency in predicting the onset of a sign change in WWE_{S-T}/AE_{S-T} . The B3LYP and B97D methods predict a negative WWE_{S-T}/AE_{S-T} beginning at nonacene, whereas the M062X functional predicts this transition at decacene.

To consider the varying effects of differing low-level basis sets, geometry optimizations and frequency calculations were conducted on naphthacene through decacene using the B3LYP functional and the following basis sets (Table 2): STO-3G, 6-21G**, 4-31G**, and SV. AE_{S-T} generally decline with increasing basis set size, although the effect is modest and on the order of only 1–2 kcal/mol (i.e., within the coupled errors of the theoretical method and any experimental data being compared against). Consequently, when calculating the WWE_{S-T}/AE_{S-T} of longer polyacenes, ZPE and basis set size effects appear minor in comparison to the choice of model chemistry employed. Clearly, the inclusion of all relevant corrections and use of the largest basis set practical is desirable when estimating AE_{S-T} of large polyacenes via theoretical methods, but the decision regarding model chemistry is paramount.

To better understand how a range of density functionals perform for polyacene WWE_{S-T} estimates, we conducted SPE calculations at the $x/6-31G(d)//B3LYP/6-31G(d)$ level using a wide variety of methods for benzene through decacene (Supplementary information Table S6). A summary of the ranges of WWE_{S-T} obtained for each compound across all methods examined are provided in Table 3. There is little difference between the mean and median WWE_{S-T} for each compound, and WWE_{S-T} standard deviations for each compound range between about 2–4 kcal/mol. However, on average, DFT methods transition from significantly overestimating the WWE_{S-T} of short-chain acenes to significantly underestimating

Table 4

Regression analysis parameters using a single exponential decay function having a y-axis offset of the general form $y = ae^{-bx} + c$ ($x = n$, $y(x) = WWE_{S-T}$ in kcal/mol; $c = WWE_{S-T}$ at the polymeric limit) with estimated WWE_{S-T} for benzene ($n = 1$) through decacene ($n = 10$) obtained using a range of density functionals, as well as HF and MPn methods, at the $x/6-31G(d)//B3LYP/6-31G(d)$ level of theory.

Method	<i>a</i>	<i>b</i>	<i>c</i>	<i>r</i>
MP3 ^a	127.2	0.459	19.4	0.999
MP2	147.5	0.406	16.0	0.996
MP4(DQ) ^a	127.2	0.417	13.6	0.9992
MP4(SDQ) ^a	129.2	0.383	7.1	0.9998
B2PLYPD	135.1	0.357	0.0	0.99993
mPW2PLYPD	135.5	0.347	-1.9	0.99992
M062X	141.8	0.317	-6.0	0.9998
M06HF	148.5	0.291	-6.1	0.9997
HCTH/93	137.6	0.353	-6.5	0.9999
HCTH/147	136.7	0.353	-6.8	0.9999
HFS	136.4	0.355	-6.8	0.9999
B97D	133.7	0.350	-7.0	0.9999
HCTH/407	136.9	0.352	-7.0	0.9999
O3LYP	137.6	0.342	-7.0	0.99994
B1B95	141.1	0.332	-7.3	0.99993
wB97XD	136.4	0.320	-7.7	0.9998
tHCTHhyb	136.4	0.338	-7.7	0.99994
tHCTH	135.0	0.349	-7.8	0.99992
BMK	139.9	0.318	-7.9	0.9999
B98	136.8	0.331	-8.0	0.99993
B972	139.2	0.333	-8.0	0.99994
HFB	122.5	0.338	-8.1	0.99993
X3LYP	136.4	0.330	-8.4	0.99993
B3LYP	136.1	0.332	-8.6	0.99994
B3P86	137.4	0.331	-8.7	0.99993
M06L	139.4	0.343	-8.9	0.99992
B3PW91	136.3	0.330	-8.9	0.99992
VSXC	137.8	0.344	-8.9	0.99991
mPW3PBE	136.6	0.330	-8.9	0.99992
M06	136.3	0.330	-9.1	0.99996
TPSSH	135.1	0.333	-9.1	0.99993
mPW1LYP	135.7	0.325	-9.2	0.99992
B1LYP	135.5	0.323	-9.4	0.99992
PBE0	136.9	0.324	-10.1	0.9999
PBEh1PBE	136.4	0.323	-10.2	0.9999
mPW1PBE	136.3	0.322	-10.4	0.9999
CAM-B3LYP	136.9	0.307	-11.0	0.9998
HSE03	137.2	0.320	-11.2	0.99991
HSE06	137.2	0.320	-11.2	0.9999
wB97X	138.4	0.297	-12.5	0.9997
BHandH	144.5	0.300	-14.6	0.9998
wB97	139.5	0.281	-16.0	0.9997
BHandHLYP	138.5	0.287	-17.0	0.9997
LC-wPBE	138.8	0.272	-19.2	0.9995
HF	163.9	0.156	-74.3	0.998

^a Calculations completed for benzene through octacene.

the WWE_{S-T} of long-chain acenes. The M06HF method yields the largest WWE_{S-T} for benzene through octacene, with the B2PLYPD method having the highest WWE_{S-T} for the last two members of the series under consideration. The HFB method provides the lowest WWE_{S-T} for benzene through pentacene, followed by BHandHLYP for hexacene, and the long-range corrected version of

Table 5

Estimated WWE_{S-T} for benzene through anthracene using a range of Moller–Plesset perturbation theory (MP2, MP3, MP4(DQ), MP4(SDQ), MP4(SDTQ), and MP5), coupled cluster (CCD, CCSD, and CCSD(T)), and quadratic configuration interaction (QCISD) methods obtained at the $x/6-31G(d)//B3LYP/6-31G(d)$ level of theory. Values are in kcal/mol.

Method	Benzene	Naphthalene	Anthracene
MP2	112.8	84.4	57.6
MP3	98.9	72.4	49.8
MP4(DQ)	96.7	71.0	48.5
MP4(SDQ)	94.8	68.1	47.0
MP4(SDTQ)	102.9	74.6	52.0
MP5	96.7	n/a	n/a
CCD	96.4	71.4	49.1
CCSD	88.2	64.7	45.5
CCSD(T)	88.2	64.7	45.5
QCISD	87.5	64.0	45.1

wPBE (LC-wPBE) for heptacene through decacene. The range of WWE_{S-T} predicted for each compound generally declines with increasing acene length, from about 20 to 30 kcal/mol at short-through mid-chain lengths to about 10–15 kcal/mol for heptacene and longer homologs.

When the functional dependent WWE_{S-T} data are extrapolated via a single exponential decay function of the form $y = ae^{-bx} + c$, estimated WWE_{S-T} at the polymeric limit are provided in Table 4. In all cases, high-quality regression fits ($r \geq 0.9995$) are obtained. The predicted WWE_{S-T} for an infinitely large polyacene range from 0.0 kcal/mol (B2PLYPD) to -19.2 kcal/mol (LC-wPBE), although the large majority of functionals are clustered with WWE_{S-T} at the polymer limit ranging between about -6.0 to -11.0 kcal/mol (-9.0 ± 3.5 kcal/mol [mean \pm SD (standard deviation)]), in good agreement with the polymer limit AE_{S-T} (-9.8 kcal/mol) obtained by extrapolating the experimental data using the same regression function. Only the B2PLYPD (0.0 kcal/mol) and mPW2PLYPD (-1.9 kcal/mol) functionals have polymeric limit WWE_{S-T} greater than -6.0 kcal/mol, whereas only the wB97X (-12.5 kcal/mol), BHandH (-14.6 kcal/mol), wB97 (-16.0 kcal/mol), BHandHLYP (-17.0 kcal/mol), and LC-wPBE (-19.2 kcal/mol) have polymeric limit WWE_{S-T} less than -11.2 kcal/mol. Most functionals predict the onset of a negative WWE_{S-T} value at nonacene, with the exception of some functionals that predict this transition at octacene (LC-wPBE, BHandH, BHandLYP, wB97, HSE03, and HSE06) or decacene (M062X, wB97XD, and BMK), or at even longer acene chains (B2PLYPD [$n \rightarrow \infty$], mPW2PLYPD [$n = 13$], and M06HF [$n = 11$]).

The Hartree–Fock method greatly underestimates the WWE_{S-T} of all polyacenes, and the polymeric limit WWE_{S-T} of -74.3 kcal/mol at this level of theory is in gross error. By comparison, MPn methods (MP2, MP3, MP4(DQ), and MP4(SDQ)) overestimate WWE_{S-T} but tend to converge towards the experimental AE_{S-T} data with increasing truncation order and substitutions. Estimated WWE_{S-T} at the polymeric limit for the MPn methods are as follows (values in kcal/mol; MP3, MP4(DQ), and MP4(SDQ) estimates based on calculations for benzene through octacene): MP2, 16.0; MP3, 19.4; MP4(DQ), 13.6; and MP4(SDQ), 7.1. A comparison of estimated WWE_{S-T} for benzene, naphthalene, and anthracene among various Moller–Plesset perturbation theory (MP2, MP3, MP4(DQ), MP4(SDQ), MP4(SDTQ), and MP5), coupled cluster (CCD, CCSD, and CCSD(T)), and quadratic configuration interaction (QCISD) methods obtained at the $x/6-31G(d)//B3LYP/6-31G(d)$ level of theory (Table 5) supports the general trends discussed above, and illustrates progressive convergence towards experimental AE_{S-T} data with increasing level of theory.

Thus, the two double hybrid density functional methods which combine exact HF exchange with an MP2-like correlation to a DFT calculation (B2PLYPD and mPW2PLYPD) appear to balance the

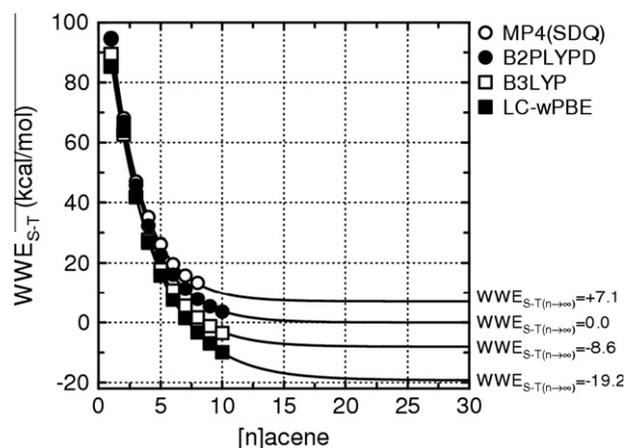


Fig. 3. Trends in calculated WWE_{S-T} for benzene through decacene at the $x/6-31G(d)//B3LYP/6-31G(d)$ level of theory ($x = MP4(SDQ)$, B2PLYPD, B3LYP, and LC-wPBE) and associated extrapolations to the polymeric limit using a single exponential decay function having a y -axis offset of the general form $y = ae^{-bx} + c$ (corresponding regression statistics given in Table 4). Regression estimated AE_{S-T} at the polymeric limit are provided along the right y -axis.

WWE_{S-T} underestimating tendency of HF/DFT methods for longer polyacenes against the propensity for MPn methods to overestimate the WWE_{S-T} for these compounds (Fig. 3). As Huenerbein et al. [123] have previously shown, double-hybrid functionals with dispersion corrections (i.e., B2PLYPD and mPW2PLYPD) offer superior performance compared to other functionals (particularly those without dispersion corrections) when calculating isomerization energies of large and complex molecules. A similar hierarchy of functional performance may also be evident for calculating the singlet–triplet energy gaps of large polyacenes. Progressively larger basis sets (6-31G(d), 6-31G(d,p), TZVP, cc-pVDZ, cc-pVTz) have minimal influence (<1 kcal/mol) on the estimated WWE_{S-T} using the B3LYP and B2PLYPD functional obtained via SPE calculations on B3LYP/6-31G(d) optimized geometries (Table 6).

One must also note the excellent agreement between the benchmark quality WWE_{S-T} obtained at the CCSD(T)/cc-pV ∞ Z level by Hajgato et al. [28] and our B2PLYPD/ $x/B3LYP/6-31G(d)$ WWE_{S-T} data (values in kcal/mol and reported as B2PLYPD/cc-pVDZ/B3LYP/6-31G(d) [CCSD(T)/cc-pV ∞ Z]): benzene, 93.4 [91.7]; naphthalene, 66.1 [65.8]; anthracene, 45.1 [48.2]; naphthalene, 31.8 [33.5]; pentacene, 22.2 [25.3]; hexacene, 15.6 [17.7]; heptacene, 10.9 [13.4]; octacene, 7.5 [9.2]; nonacene, 5.0 [7.0]; and decacene, 3.2 [4.6]. With discrepancies ranging only between 0.3 and 3.1 kcal/mol for these methods, the B2PLYPD functional (and its mPW2PLYPD counterpart) appears to be providing near benchmark quality WWE_{S-T} estimates for the polyacenes, in sharp contrast to what is likely the poor performance of all other major functionals.

Overall, we find substantial variability in the theoretically obtained singlet–triplet gaps predicted for longer polyacenes that is primarily dependent on the model chemistry employed, with minor variation due to basis set incompleteness and ZPE corrections. Assuming a closed-shell singlet state for polyacenes results in all density functionals considered (with the sole exception of the B2PLYPD method) predicting a negative singlet–triplet gap (i.e., ground state triplet) at the polymeric limit, and most functionals predicting a transition from a singlet to triplet ground state between octacene and decacene. The Hartree–Fock method significantly underestimates the WWE_{S-T} of the polyacenes, whereas MPn methods overestimate the singlet–triplet gap but display a convergence toward experimental values with increasing truncation order and substitutions. The two double hybrid methods

Table 6
Theoretical WWE_{S-T} for benzene through decacene using the B3LYP and B2PLYPD functionals and progressively larger basis sets obtained via SPE calculations on B3LYP/6-31G(d) optimized geometries. Values are in kcal/mol.

Compound	B3LYP				B2PLYPD				
	6-31G(d)	6-31G(d,p)	TZVP	cc-pVDZ	cc-pVTZ	6-31G(d)	6-31G(d,p)	TZVP	cc-pVDZ
Benzene	89.5	89.5	89.3	88.9	89.4	94.4	94.3	94.0	93.4
Naphthalene	62.6	62.6	62.7	62.2	62.7	66.9	66.9	66.8	66.1
Anthracene	41.8	41.8	42.1	41.5	41.9	45.7	45.7	46.0	45.1
Naphthacene	27.7	27.8	28.1	27.5	27.8	32.3	32.3	32.6	31.8
Pentacene	17.9	17.9	18.2	17.6	17.9	22.7	22.7	23.0	22.2
Hexacene	10.8	10.9	11.1	10.6	10.7	16.1	16.1	16.3	15.6
Heptacene	5.6	5.7	5.9	5.4	5.4	11.3	11.4	11.5	10.9
Octacene	1.7	1.8	1.9	1.5	1.4	7.9	8.0	8.1	7.5
Nonacene	-1.2	-1.1	-1.1	-1.5	-1.7	5.4	5.5	5.5	5.0
Decacene	-3.5	-3.4	-3.4	-3.8	-4.0	3.6	3.7	3.7	3.2

which combine exact HF exchange with an MP2-like correlation to a DFT calculation (B2PLYPD and mPW2PLYPD) balance the HF/MPn under/over-estimations and predict all acenes from benzene through decacene will be ground state singlets with positive singlet–triplet gaps. Extrapolation of the B2PLYPD results predict positive WWE_{S-T} for all polyacenes until a vanishingly small singlet–triplet gap is reached at the polymeric limit for an infinitely long homolog.

Acknowledgements

This work was made possible by the facilities of the Western Canada Research Grid (WestGrid: Project 100185), the Shared Hierarchical Academic Research Computing Network (SHARCNET: Project sn4612), and Compute/Calcul Canada.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.08.010.

References

- [1] E. Clar, Polycyclic Hydrocarbons, Academic Press, New York, 1964.
- [2] J.E. Anthony, Functionalized acenes and heteroacenes for organic electronics, Chem. Rev. 106 (2006) 5028–5048.
- [3] P.V.R. Schleyer, M. Manoharan, H. Jiao, F. Stahl, The acenes: is there a relationship between aromatic stabilization and reactivity?, Org. Lett. 3 (2001) 3643–3646.
- [4] G. Portella, J. Poater, J.M. Bofill, P. Alemany, M. Sola, Local aromaticity of [n]acenes, [n]phenacenes, and [n]helicenes ($n = 1-9$), J. Org. Chem. 70 (2005) 2509–2521.
- [5] J.I. Aihara, H. Kanno, Local aromaticities in large polyacene molecules, J. Phys. Chem. A 109 (2005) 3717–3721.
- [6] P. Bultinck, M. Rafat, R. Ponec, B.V. Gheluwe, R. Carbo-Dorca, P. Popelier, Electron delocalization and aromaticity in linear polyacenes: atoms in molecules multicenter delocalization index, J. Phys. Chem. A 110 (2006) 7642–7648.
- [7] N.H. Martin, B.W. Caldwell, K.P. Carlson, M.R. Teague, Ab initio calculation of through-space magnetic shielding of linear polycyclic aromatic hydrocarbons (acenes): extent of aromaticity, J. Mol. Graph. Model. 27 (2009) 689–692.
- [8] R. Mondal, C. Tonshoff, D. Khon, D.C. Neckers, H.F. Bettinger, Synthesis, stability, and photochemistry of pentacene, hexacene, and heptacene: a matrix isolation study, J. Am. Chem. Soc. 131 (2009) 14281–14289.
- [9] R. Mondal, R.M. Adhikari, B.K. Shah, D.C. Neckers, Revisiting the stability of hexacenes, Org. Lett. 9 (2007) 2505–2508.
- [10] R. Mondal, B.K. Shah, D.C. Neckers, Photogeneration of heptacene in a polymer matrix, J. Am. Chem. Soc. 128 (2006) 9612–9613.
- [11] H.F. Bettinger, R. Mondal, D.C. Neckers, Stable photoinduced charge separation in heptacene, Chem. Commun. (2007) 5209–5211.
- [12] C. Tonshoff, H.F. Bettinger, Photogeneration of octacene and nonacene, Angew. Chem. Int. Ed. 49 (2010) 4125–4128.
- [13] H.F. Bettinger, Electronic structure of higher acenes and polyacene: the perspective developed by theoretical analyses, Pure Appl. Chem. 82 (2010) 905–915.
- [14] K.N. Houk, P.S. Lee, M. Nendel, Polyacene and cyclacene geometries and electronic structures: bond equalization, vanishing band gaps, and triplet ground states contrast with polyacetylene, J. Org. Chem. 66 (2001) 5517–5521.
- [15] M.C. dos Santos, Electronic properties of acenes: oligomer to polymer structure, Phys. Rev. B 74 (2006) 045426.
- [16] J.C. Schug, B.H. Lengsfeld, D.A. Brewer, Open-shell ground state wave functions for linear polyacenes, J. Phys. Chem. 82 (1978) 1436–1438.
- [17] M. Bendikov, H. Duong, K. Starkey, K.N. Houk, E.A. Carter, F. Wudl, Oligoacenes: theoretical prediction of open-shell singlet diradical ground states, J. Am. Chem. Soc. 126 (2004) 7416–7417.
- [18] H. Gao, J.L. Hodgson, D. Jiang, S.B. Zhang, S. Nagase, G.P. Miller, Z. Chen, Open-shell singlet character of stable derivatives of nonacene, hexacene and teranthene, Org. Lett. 13 (2011) 3316–3319.
- [19] Z. Qu, D. Zhang, C. Liu, Y. Jiang, Open-shell ground state of polyacenes: a valence bond study, J. Phys. Chem. A 113 (2009) 7909–7914.
- [20] J.E. Norton, K.N. Houk, Electronic structures and properties of twisted polyacenes, J. Am. Chem. Soc. 127 (2005) 4162–4163.
- [21] J. Hachmann, J.J. Dorando, M. Aviles, G.K.L. Chan, The radical character of the acenes: a density matrix renormalization group study, J. Chem. Phys. 127 (2007) 134309.
- [22] D.E. Jiang, S. Dai, Electronic ground state of higher acenes, J. Phys. Chem. A 112 (2008) 332–335.
- [23] S.S. Zade, N. Zamoshchik, A.R. Reddy, G. Fridman-Marueli, D. Sheberla, M. Bendikov, Products and mechanism of acene dimerization. A computational study, J. Am. Chem. Soc. 133 (2011) 10803–10816.
- [24] S. Motomura, M. Nakano, H. Fukui, K. Yoneda, T. Kubo, R. Carion, B. Champagne, Size dependences of the diradical character and the second hyperpolarizabilities in dicyclopenta-fused acenes: relationships with their aromaticity/antiaromaticity, Phys. Chem. Chem. Phys. (2011), doi:10.1039/c1cp20773c.
- [25] K. Pelzer, L. Greenman, G. Gidofalvi, D.A. Mazziotti, Strong correlation in acene sheets from the active-space variational two-electron reduced density matrix method: effects of symmetry and size, J. Phys. Chem. A 115 (2011) 5632–5640.
- [26] C. Lambert, Towards polycyclic aromatic hydrocarbons with a singlet open-shell ground state, Angew. Chem. Int. Ed. 50 (2011) 1756–1758.
- [27] B. Hajtago, D. Szieberth, P. Geerlings, F. De Proft, M.S. Deleuze, A benchmark theoretical study of the electronic ground state and of the singlet–triplet split of benzene and linear acenes, J. Chem. Phys. 131 (2009) 224321.
- [28] B. Hajtago, M. Huzak, M.S. Deleuze, Focal point analysis of the singlet–triplet energy gap of octacene and larger acenes, J. Phys. Chem. A (2011), doi:10.1021/jp2043043.
- [29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, et al., Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- [30] A.D. Becke, Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing, J. Chem. Phys. 104 (1996) 1040–1046.
- [31] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789.
- [32] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr, Chem. Phys. Lett. 157 (1989) 200–206.
- [33] S. Grimme, Semiempirical hybrid density functional with perturbative second-order correlation, J. Chem. Phys. 124 (2006) 034108.
- [34] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.
- [35] J.P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, Phys. Rev. B 33 (1986) 8822–8824.
- [36] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation, Phys. Rev. B 46 (1992) 6671–6687.
- [37] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Erratum: atoms, molecules, solids, and surfaces: applications of the

- generalized gradient approximation for exchange and correlation, *Phys. Rev. B* 48 (1993) 4978.
- [38] J.P. Perdew, K. Burke, Y. Wang, Generalized gradient approximation for the exchange-correlation hole of a many-electron system, *Phys. Rev. B* 54 (1996) 16533–16539.
- [39] P.J. Wilson, T.J. Bradley, D.J. Tozer, Hybrid exchange-correlation functional determined from thermochemical data and ab initio potentials, *J. Chem. Phys.* 115 (2001) 9233–9242.
- [40] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (2006) 1787–1799.
- [41] A.D. Becke, Density-functional thermochemistry. V. Systematic optimization of exchange-correlation functionals, *J. Chem. Phys.* 107 (1997) 8554–8560.
- [42] H.L. Schmider, A.D. Becke, Optimized density functionals from the extended G2 test set, *J. Chem. Phys.* 108 (1998) 9624–9631.
- [43] C.C.J. Roothaan, New developments in molecular orbital theory, *Rev. Mod. Phys.* 23 (1951) 69.
- [44] J.A. Pople, R.K. Nesbet, Self-consistent orbitals for radicals, *J. Chem. Phys.* 22 (1954) 571–572.
- [45] R. McWeeny, G. Dierksen, Self-consistent perturbation theory. 2. Extension to open shells, *J. Chem. Phys.* 49 (1968) 4852.
- [46] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098–3100.
- [47] A.D. Boese, J.M.L. Martin, Development of density functionals for thermochemical kinetics, *J. Chem. Phys.* 121 (2004) 3405–3416.
- [48] T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chem. Phys. Lett.* 393 (2004) 51–57.
- [49] R.J. Bartlett, G.D. Purvis, Many-body perturbation-theory, coupled-pair many-electron theory, and importance of quadruple excitations for correlation problem, *Int. J. Quantum Chem.* 14 (1978) 561–581.
- [50] J.A. Pople, R. Krishnan, H.B. Schlegel, J.S. Binkley, Electron correlation theories and their application to the study of simple reaction potential surfaces, *Int. J. Quantum Chem.* 14 (1978) 545–560.
- [51] G.D. Purvis, R.J. Bartlett, A full coupled-cluster singles and doubles model: the inclusion of disconnected triples, *J. Chem. Phys.* 76 (1982) 1910–1918.
- [52] G.E. Scuseria, C.L. Janssen, H.F. Schaefer, An efficient reformulation of the closed-shell coupled cluster single and double excitation (CCSD) equations, *J. Chem. Phys.* 89 (1988) 7382–7387.
- [53] G.E. Scuseria, H.F. Schaefer, Is coupled cluster singles and doubles (CCSD) more computationally intensive than quadratic configuration-interaction (QCISD)?, *J. Chem. Phys.* 90 (1989) 3700–3703.
- [54] J.A. Pople, M. Head-Gordon, K. Raghavachari, Quadratic configuration interaction – a general technique for determining electron correlation energies, *J. Chem. Phys.* 87 (1987) 5968–5975.
- [55] F.A. Hamprecht, A.J. Cohen, D.J. Tozer, N.C. Handy, Development and assessment of new exchange-correlation functionals, *J. Chem. Phys.* 109 (1998) 6264–6271.
- [56] A.D. Boese, N.L. Doltsinis, N.C. Handy, M. Sprick, New generalized gradient approximation functionals, *J. Chem. Phys.* 112 (2000) 1670–1678.
- [57] A.D. Boese, N.C. Handy, A new parametrization of exchange-correlation generalized gradient approximation functionals, *J. Chem. Phys.* 114 (2001) 5497–5503.
- [58] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (1964) B864–B871.
- [59] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138.
- [60] J.C. Slater, *The Self-consistent Field for Molecular and Solids*, Quantum Theory of Molecular and Solids, vol. 4, McGraw-Hill, New York, 1974.
- [61] J. Heyd, G. Scuseria, Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional, *J. Chem. Phys.* 121 (2004) 1187–1192.
- [62] J. Heyd, G.E. Scuseria, Assessment and validation of a screened Coulomb hybrid density functional, *J. Chem. Phys.* 120 (2004) 7274.
- [63] J. Heyd, J.E. Peralta, G.E. Scuseria, R.L. Martin, Energy band gaps and lattice parameters evaluated with the Heyd–Scuseria–Ernzerhof screened hybrid functional, *J. Chem. Phys.* 123 (2005) 174101.
- [64] J. Heyd, G.E. Scuseria, M. Ernzerhof, Erratum: hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.* 124 (2006) 219906.
- [65] A.F. Izmaylov, G. Scuseria, M.J. Frisch, Efficient evaluation of short-range Hartree-Fock exchange in large molecules and periodic systems, *J. Chem. Phys.* 125 (2006) 104103.
- [66] A.V. Krukau, O.A. Vydrov, A.F. Izmaylov, G.E. Scuseria, Influence of the exchange screening parameter on the performance of screened hybrid functionals, *J. Chem. Phys.* 125 (2006) 224106.
- [67] T.M. Henderson, A.F. Izmaylov, G. Scalmani, G.E. Scuseria, Can short-range hybrids describe long-range-dependent properties?, *J. Chem. Phys.* 131 (2009) 044108.
- [68] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, A long-range-corrected time-dependent density functional theory, *J. Chem. Phys.* 120 (2004) 8425–8433.
- [69] O.A. Vydrov, J. Heyd, A.V. Krukau, G.E. Scuseria, Importance of short-range versus long-range Hartree-Fock exchange for the performance of hybrid density functionals, *J. Chem. Phys.* 125 (2006) 74106.
- [70] O.A. Vydrov, G.E. Scuseria, Assessment of a long-range corrected hybrid functional, *J. Chem. Phys.* 125 (2006) 234109.
- [71] O.A. Vydrov, G.E. Scuseria, J.P. Perdew, Tests of functionals for systems with fractional electron number, *J. Chem. Phys.* 126 (2007) 154109.
- [72] Y. Zhao, D. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* 120 (2008) 215–241.
- [73] Y. Zhao, D.G. Truhlar, Comparative DFT study of van der Waals complexes: Rare-gas dimers, alkaline-earth dimers, zinc dimer, and zinc-rare-gas dimers, *J. Phys. Chem. A* 110 (2006) 5121–5129.
- [74] Y. Zhao, D.G. Truhlar, Density functional for spectroscopy: no long-range self-interaction error, good performance for Rydberg and charge-transfer states, and better performance on average than B3LYP for ground states, *J. Phys. Chem. A* 110 (2006) 13126–13130.
- [75] Y. Zhao, D.G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, *J. Chem. Phys.* 125 (2006) 194101–194118.
- [76] C. Moller, M.S. Plesset, Note on an approximation treatment for many-electron systems, *Phys. Rev.* 46 (1934) 618–622.
- [77] M. Head-Gordon, J.A. Pople, M.J. Frisch, MP2 energy evaluation by direct methods, *Chem. Phys. Lett.* 153 (1988) 503–506.
- [78] S. Saebø, J. Almlof, Avoiding the integral storage bottleneck in LCAO calculations of electron correlation, *Chem. Phys. Lett.* 154 (1989) 83–89.
- [79] M.J. Frisch, M. Head-Gordon, J.A. Pople, Direct MP2 gradient method, *Chem. Phys. Lett.* 166 (1990) 275–280.
- [80] M.J. Frisch, M. Head-Gordon, J.A. Pople, Semi-direct algorithms for the MP2 energy and gradient, *Chem. Phys. Lett.* 166 (1990) 281–289.
- [81] M. Head-Gordon, T. Head-Gordon, Analytic MP2 frequencies without fifth order storage: theory and application to bifurcated hydrogen bonds in the water hexamer, *Chem. Phys. Lett.* 220 (1994) 122–128.
- [82] J.A. Pople, J.S. Binkley, R. Seeger, Theoretical models incorporating electron correlation, *Int. J. Quantum Chem.* 10 (Suppl. S10) (1976) 1–19.
- [83] J.A. Pople, R. Seeger, R. Krishnan, Variational configuration interaction methods and comparison with perturbation theory, *Int. J. Quantum Chem.* 12 (Suppl. S11) (1977) 149–163.
- [84] K. Raghavachari, J.A. Pople, Approximate 4th-order perturbation-theory of electron correlation energy, *Int. J. Quantum Chem.* 14 (1978) 91–100.
- [85] R. Krishnan, M.J. Frisch, J.A. Pople, Contribution of triple substitutions to the electron correlation energy in fourth-order perturbation theory, *J. Chem. Phys.* 72 (1980) 4244–4245.
- [86] K. Raghavachari, J.A. Pople, E.S. Replogle, M. Head-Gordon, Fifth order Moller-Plesset perturbation theory: comparison of existing correlation methods and implementation of new methods correct to fifth order, *J. Phys. Chem.* 94 (1990) 5579–5586.
- [87] C. Adamo, V. Barone, Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: the mPW and mPW1PW models, *J. Chem. Phys.* 108 (1998) 664–675.
- [88] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [89] J.P. Perdew, K. Burke, M. Ernzerhof, Errata: generalized gradient approximation made simple, *Phys. Rev. Lett.* 78 (1997) 1396.
- [90] T. Schwabe, S. Grimme, Towards chemical accuracy for the thermodynamics of large molecules: new hybrid density functionals including non-local correlation effects, *Phys. Chem. Chem. Phys.* 8 (2006) 4398.
- [91] A.J. Cohen, N.C. Handy, Dynamic correlation, *Mol. Phys.* 99 (2001) 607–615.
- [92] C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: the PBE0 model, *J. Chem. Phys.* 110 (1999) 6158–6169.
- [93] M. Ernzerhof, J.P. Perdew, Generalized gradient approximation to the angle- and system-averaged exchange hole, *J. Chem. Phys.* 109 (1998) 3313.
- [94] A.D. Boese, N.C. Handy, New exchange-correlation density functionals: the role of the kinetic-energy density, *J. Chem. Phys.* 116 (2002) 9559–9569.
- [95] J.M. Tao, J.P. Perdew, V.N. Staroverov, G.E. Scuseria, Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids, *Phys. Rev. Lett.* 91 (2003) 146401.
- [96] T. Van Voorhis, G.E. Scuseria, A novel form for the exchange-correlation energy functional, *J. Chem. Phys.* 109 (1998) 400–410.
- [97] J.D. Chai, M. Head-Gordon, Systematic optimization of long-range corrected hybrid density functionals, *J. Chem. Phys.* 128 (2008) 84106–84115.
- [98] J.D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections, *Phys. Chem. Chem. Phys.* 10 (2008) 6615–6620.
- [99] X. Xu, W.A. Goddard, The X3LYP extended density functional for accurate descriptions of nonbond interactions, spin states, and thermochemical properties, *Proc. Natl. Acad. Sci. USA* 101 (2004) 2673–2677.
- [100] J.B. Collins, P.V.R. Schleyer, J.S. Binkley, J.A. Pople, Self-consistent molecular orbital methods. XVII. Geometries and binding energies of second-row molecules. A comparison of three basis sets, *J. Chem. Phys.* 64 (1976) 5142–5151.
- [101] W.J. Hehre, R.F. Stewart, J.A. Pople, Self-consistent molecular-orbital methods. I. Use of Gaussian expansions of Slater-type atomic orbitals, *J. Chem. Phys.* 51 (1969) 2657–2664.
- [102] J.S. Binkley, J.A. Pople, W.J. Hehre, Self-consistent molecular orbital methods. 21. Small split-valence basis sets for first-row elements, *J. Am. Chem. Soc.* 102 (1980) 939–947.

- [103] M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro, W.J. Hehre, Self-consistent molecular-orbital methods. 22. Small split-valence basis sets for second-row elements, *J. Am. Chem. Soc.* 104 (1982) 2797–2803.
- [104] R. Ditchfield, W.J. Hehre, J.A. Pople, Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules, *J. Chem. Phys.* 54 (1971) 724–728.
- [105] W.J. Hehre, R. Ditchfield, J.A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules, *J. Chem. Phys.* 56 (1972) 2257–2261.
- [106] P.C. Hariharan, J.A. Pople, Accuracy of AH_n equilibrium geometries by single determinant molecular orbital theory, *Mol. Phys.* 27 (1974) 209–214.
- [107] M.S. Gordon, The isomers of silacyclopropane, *Chem. Phys. Lett.* 76 (1980) 163–168.
- [108] A. Schaefer, H. Horn, R. Ahlrichs, Fully optimized contracted Gaussian-basis sets for atoms Li to Kr, *J. Chem. Phys.* 97 (1992) 2571–2577.
- [109] A. Schaefer, C. Huber, R. Ahlrichs, Fully optimized contracted Gaussian-basis sets of triple zeta valence quality for atoms Li to Kr, *J. Chem. Phys.* 100 (1994) 5829–5835.
- [110] P.C. Hariharan, J.A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chem. Acc.* 28 (1973) 213–222.
- [111] M.M. Francl, Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements, *J. Chem. Phys.* 77 (1982) 3654–3665.
- [112] T.H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* 90 (1989) 1007–1023.
- [113] R.A. Kendall, T.H. Dunning, R.J. Harrison, Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, *J. Chem. Phys.* 96 (1992) 6796–6806.
- [114] D. Woon, T. Dunning, Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon, *J. Chem. Phys.* 98 (1993) 1358–1371.
- [115] K.A. Peterson, D.E. Woon, T.H. Dunning, Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the $H + H_2 \rightarrow H_2 + H$ reaction, *J. Chem. Phys.* 100 (1994) 7410–7415.
- [116] A.R. Allouche, Gabedit: a graphical user interface for computational chemistry softwares, *J. Comput. Chem.* 32 (2011) 174–182.
- [117] K. Yoshioka, KyPlot as a tool for graphical data analysis, in: W. Hardle, B. Ronz (Eds.), *Compstat – Proceedings in Computational Statistics: 15th Symposium Held in Berlin, Germany*, Springer, New York, 2002, pp. 37–46.
- [118] C.E. Check, T.M. Gilbert, Progressive systematic underestimation of reaction energies by the B3LYP model as the number of C–C bonds increases: why organic chemists should use multiple DFT models for calculations involving polycarbon hydrocarbons, *J. Org. Chem.* 70 (2005) 9828–9834.
- [119] M.D. Wodrich, C. Corminboeuf, P.V.R. Schleyer, Systematic errors in computed alkane energies using B3LYP and other popular DFT functionals, *Org. Lett.* 8 (2006) 3631–3634.
- [120] J. Tirado-Rives, W.L. Jorgensen, Performance of B3LYP density functional methods for a large set of organic molecules, *J. Chem. Theory Comput.* 4 (2008) 297–306.
- [121] S. Grimme, Seemingly simple stereoelectronic effects in alkane isomers and the implications for Kohn-Sham density functional theory, *Angew. Chem. Int. Ed.* 45 (2006) 4460–4464.
- [122] S. Grimme, M. Steinmetz, M. Korth, Stereoelectronic substituent effects in saturated main group molecules: severe problems of current Kohn-Sham density functional theory, *J. Chem. Theory Comput.* 3 (2007) 42–45.
- [123] R. Huenerbein, B. Schirmer, J. Moellmann, S. Grimme, Effects of London dispersion on the isomerization reactions of large organic molecules: a density functional benchmark study, *Phys. Chem. Chem. Phys.* 12 (2010) 6940–6948.
- [124] S. Grimme, M. Steinmetz, M. Korth, How to compute isomerization energies of organic molecules with quantum chemical methods, *J. Org. Chem.* 72 (2007) 2118–2126.
- [125] S. Rayne, K. Forest, Gas phase isomerization enthalpies of organic compounds: A semiempirical, density functional theory, and ab initio post-Hartree-Fock theoretical study, *J. Mol. Struct. (Theochem)* 948 (2010) 102–107.
- [126] Y. Zhao, D.G. Truhlar, A density functional that accounts for medium-range correlation energies in organic chemistry, *Org. Lett.* 8 (2006) 5753–5755.
- [127] W. Siebrand, Radiationless transitions in polyatomic molecules. II. Triplet-ground-state transitions in aromatic hydrocarbons, *J. Chem. Phys.* 47 (1967) 2411.
- [128] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
- [129] J.B. Birks, *Organic Molecular Photophysics*, Wiley, London, 1975.
- [130] J. Schiedt, R. Weinkauff, Photodetachment photoelectron spectroscopy of mass selected anions: anthracene and the anthracene- H_2O cluster, *Chem. Phys. Lett.* 266 (1997) 201–205.
- [131] J. Burgos, M. Pope, C.E. Swenberg, R.R. Alfano, Heterofission in pentacene-doped tetracene single crystals, *Phys. Status Solidi B* 83 (1977) 249–256.
- [132] H. Angliker, E. Rommel, J. Wirz, Electronic spectra of hexacene in solution (ground state, triplet state, dication and dianion), *Chem. Phys. Lett.* 87 (1982) 208–212.