

## Bond Length Alternation of Conjugated Oligomers: Wave Function and DFT Benchmarks

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Received November 12, 2010

**Abstract:** We have computed the bond length alternation (BLA) in a series of  $\pi$ -conjugated quasilinear chains containing from two to six unit cells. Several structures (eight oligomeric sets including three conformers of polyacetylene, polymethineimine, polysilaacetylene, etc.) have been considered to cover the possible evolutions of the BLA with increasing chain length. Three objectives have been tackled: (1) the computation of accurate reference values using the CCSD(T) theory; (2) an evaluation of the performances of other electron correlated wave function approaches (MP $n$ , SCS-MP2, CCSD, etc.); (3) the benchmarking of several DFT functionals, including global, range-separated, and double hybrids. It turns out that the SCS-MP2 approach is, on average, an efficient scheme in terms of its accuracy/cost ratio. Among the selected DFT approaches, no single functional emerges as uniformly accurate for all oligomeric series and chain lengths, but BHHLYP, M06-2X, and CAM-B3LYP could be reasonable choices for long oligomers.

### 1. Introduction

The bond length alternation (BLA) is a geometrical parameter calculated as the difference between the lengths of a single bond and the adjacent multiple (double or triple) bond in  $\pi$ -delocalized systems. For polyacetylene (PA, referred to as CC-II in the following), a polymer constituted of a sequence of sp<sup>2</sup> carbon atoms (see Figure 1), it is well-known that there is a close connection between the BLA and the electronic gap.<sup>1,2</sup> Indeed, in the one-electron approximation, there is a simple proportionality relationship between these two properties.<sup>3</sup> More generally, in  $\pi$ -conjugated compounds, the geometric and electronic structures are closely related, and an accurate description of the ground-state structures is an actual prerequisite for the determination of valid electronic properties.<sup>4,5</sup> The interested reader may find examples of the key role played by the BLA in several domains, including

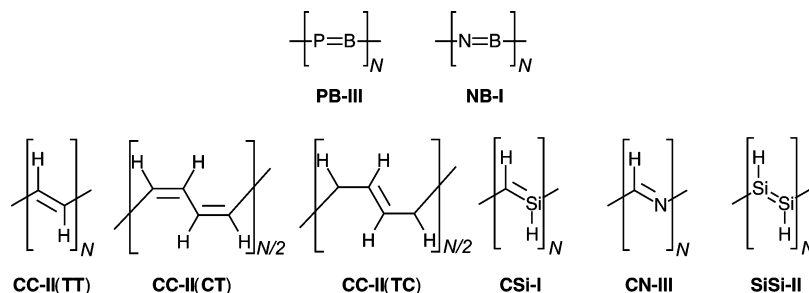
nonlinear optics,<sup>6–8</sup> two-photon absorption efficiencies,<sup>9–11</sup> transport properties,<sup>12</sup> and photochromic features.<sup>13,14</sup>

Straightforward experimental determinations of the BLA remain difficult, and the results may be relatively disappointing. First, gas-phase measurements are only possible on the shortest oligomers, as the intermolecular interaction energies tend to be substantial in  $\pi$  systems. This is unsatisfying, as the BLA evolves slowly with chain length; e.g., it is roughly divided by two when going from butadiene to infinitely long polyacetylene.<sup>3,15</sup> In other words, chain end effects cannot be neglected, as they span over more than five unit cells ( $N$ ).<sup>16</sup> Second, the available XRD data<sup>17</sup> suffer from the impact of environmental effects that are sizable for  $\pi$ -rich oligomers.<sup>18</sup> This statement can also be illustrated by comparisons between gas-phase and condensed-phase simulations that yield strongly dissimilar BLA in some cases.<sup>19</sup> Eventually, the experimental accuracy can also be a limiting parameter; e.g., two gas-phase experiments carried out on the simple and symmetric *trans*-butadiene yielded BLAs (double/single bond distances) of 0.118 Å (1.349/1.467 Å)<sup>20</sup>

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**Figure 1.** Representation of the oligomers considered in this work. All chains are capped by terminal hydrogen atoms.  $N$  is the number of unit cells.

and 0.130 Å (1.337/1.467 Å),<sup>21</sup> a 10% discrepancy. The same holds for solid-state measurements obtained through XRD<sup>22</sup> or NMR<sup>23</sup> techniques that allow for getting useful, yet not very accurate, estimates of the BLA of the polymeric PA:  $0.08 \pm 0.03$  Å.<sup>18</sup>

Due to these limitations, numerous efforts have been devoted to the computation of the BLA of conjugated chains with reliable theoretical models. For PA chains, the most intensively studied quasilinear oligomers, the first systematic study dates from 1997<sup>3</sup> and demonstrated that Hartree–Fock (HF) predicts BLA too large by a factor of 2, whereas a pure Density Functional Theory (DFT) scheme, namely BLYP,<sup>24,25</sup> leads the opposite error. On the contrary, the geometrical parameters obtained by the second-order Møller–Plesset (MP2) and the hybrid B3LYP functional<sup>26</sup> have been found in satisfying agreement with experimental measurements on short chains.<sup>3</sup> These conclusions were later confirmed by, on the one hand, simulations relying on more recent global hybrid functionals<sup>27</sup> and, on the other hand, self-interaction corrected DFT schemes.<sup>28</sup> However, during the past three years, it has been shown that CCSD(T) and MP2 BLAs are far from coinciding when the polyene chain lengthens.<sup>29–31</sup> Additionally, different authors have indicated that range-separated hybrids<sup>30,32,33</sup> as well as the spin-component scaled MP2 (SCS-MP2) approach<sup>31</sup> are in fact more accurate than conventional hybrids like B3LYP for PA. The difficulties encountered when modeling the BLA of polymethineimine (PMI, referred to as CN-III in Figure 1) are much more dramatic, though this polymer is isoelectronic to PA. Indeed, for PMI, global hybrids and MP2 already provide diverging results,<sup>34</sup> and the DFT estimates appear to decrease too rapidly with the chain length. This finding also holds, but to a smaller extent, for range-separated hybrids<sup>30</sup> and self-interaction corrected schemes:<sup>35</sup> no available DFT approach is able to completely cure the too sharp falloff, though the most recent functionals, combining range-separation and second-order perturbative corrections,<sup>36</sup> clearly attenuate the problem.<sup>33</sup>

Five years ago, we investigated several series of oligomers with MP2<sup>37</sup> and DFT<sup>38</sup> approaches. These works allowed for the definition of three phenomenological categories. In the first set (type I oligomers), the BLA exponentially decreases with the chain length and rapidly converges to zero. In the second category (type II), one finds symmetric oligomers that, due to the Peierls distortion, show nonzero BLA for all chain lengths. The last class (type III) is constituted of asymmetric compounds presenting significantly

different bond lengths even in very long oligomers. For type I, most *ab initio* models, including conventional hybrid functionals, give relatively accurate values,<sup>37,38</sup> whereas for type II, the *exact* exchange balance seems essential, as illustrated by the above discussion for PA. Eventually, for type III oligomers, no classic DFT functionals seem completely satisfying (see PMI above).<sup>38</sup> However, these previous works have been relying on MP2 references values<sup>38</sup> that are far from flawless. Additionally, other investigations performed with more refined wave function or DFT schemes have been limited to PA and PMI,<sup>3,27,28,30–35</sup> making any general conclusions difficult, if not impossible. In this paper, we treat several series (see Figure 1) of oligomers and go significantly beyond previous studies by (1) computing CCSD(T) BLA for small and medium oligomers of type I (NB-I and CSI-I), II (CC-II and SiSi-II), and type III (PB-III and CN-III) oligomeric series; (2) evaluating the performances of several electron correlated wave function schemes, including CCSD and SCS-MP2 approaches; and (3) assessing the efficiency of DFT functionals (pure as well as global, range-separated, and double hybrids).

## 2. Method

All calculations have been performed with the Gaussian 09 program,<sup>39</sup> except for the SCS-MP2<sup>40</sup> and B2PLYP<sup>41–43</sup> calculations, which have been achieved with the ORCA code.<sup>44</sup> We have systematically used a tightened SCF threshold ( $10^{-10}$  au) and geometry optimization criteria (rms force smaller than  $10^{-5}$  au). The 6-31G(d) basis set has been selected throughout (see next section). HF, MP2, MP4(SDQ), CCSD, MP4, and CCSD(T) calculations have been performed using analytic gradients, except for the two latter approaches, which relied on numerical differentiation. Consequently, the MP4 and CCSD(T) calculations have been the clear time-limiting steps in the present investigation (more than one year of CPU time for the hexamer of CN-III at the MP4 level). Several DFT functionals have also been used. First, we compared methods presenting a constant correlation functional (LYP): one GGA, BLYP;<sup>24,25</sup> two global hybrids, namely, B3LYP<sup>26</sup> and BHLYP;<sup>45</sup> two range-separated hybrids, LC-BLYP<sup>46</sup> and CAM-B3LYP;<sup>47</sup> as well as a double-hybrid, that is, B2PLYP.<sup>41–43</sup> For the record, note that the original damping parameter of 0.33 au for LC-BLYP has been applied to allow consistent comparisons with our previous work.<sup>30</sup> Second, we also considered four extra modern functionals: B97-D,<sup>48</sup> which is free of *exact ex-*

change; two members of the M06 family (M06 and M06-2X);<sup>49</sup> as well as a recent range-separated hybrid ( $\omega$ B97).<sup>50</sup> The optimizations have been performed by taking the symmetry into account but fully optimizing all nonredundant distances and valence angles (including the hydrogen-related bonds and angles). The only exceptions are CSI-I and CN-III, for which the valence angles of the skeleton have been set equal in order to enforce quasi-linearity of the molecules. Such a scheme has already been applied for the same two systems, and we refer the reader to these previous works for discussion.<sup>30,35,37,38</sup> For SCS-MP2 and B2PLYP, the skeleton valence angles have been fixed to their MP2 values for both CSI-I and CN-III. Test calculations have shown that this approximation has a negligible impact on the BLA. The BLAs reported in the following have been systematically measured at the center of the oligomers, as they represent a better approximation of the behavior obtained in longer chains. Note that all chains of Figure 1 are capped by terminal hydrogen atoms during our simulations.

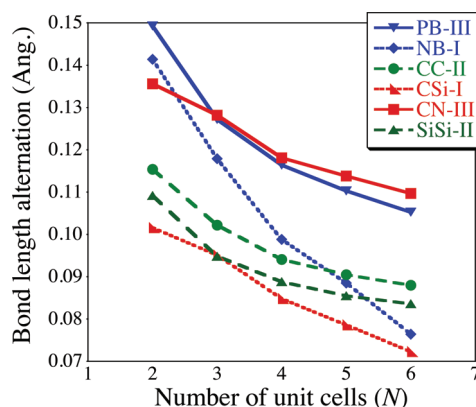
### 3. Results

**3.1. Reference CCSD(T) Values.** Before analyzing the results obtained for different oligomers, it is worth it to discuss the choice of the 6-31G(d) basis set. This selection of a relatively compact basis set is dictated by our consideration of the hexamer with numerical MP4 and CCSD(T) derivatives, but is clearly sound in view of several previous investigations on the topic. Indeed, for all-*trans* CC-II, the difference between the MP2/6-31G(d) and MP2/cc-pVDZ polymeric BLA is as small as 0.002 Å,<sup>18</sup> whereas for the octamer, the discrepancy between the MP2/6-31G(d) and MP2/6-311G(3df) BLA is only 0.003 Å.<sup>37</sup> For the dimer and tetramer of CC-II, the CCSD(T) differences between the 6-31G(d) and “best estimates” are both 0.003 Å according to the evaluations of Zhao and Truhlar.<sup>29</sup> For the CN-III dimer, the CCSD(T) BLA evolves only by +0.004 Å, when going from 6-31G(d) to 6-311G(3df).<sup>35</sup> It is also noticeable that, for the same system, the corresponding B3LYP (+0.005 Å), MP2 (+0.003 Å), and MP4 (+0.004 Å) basis set shifts are completely similar.<sup>35</sup> In addition, for the same system, the difference between the CCSD and CCSD(T) BLA systematically amounts to +0.007 Å with 6-31G(d), 6-311G(2d), and 6-311G(3df). For the trimer of PMI, the CCSD/CCSD(T) BLA difference is also nearly constant with 6-31G(d) at +0.007 Å and 6-311G(2d) at +0.008 Å. These remarkably stable results hint that the quite large errors of CCSD for type III chains (see below) are not basis-set related. In other words, while using much larger basis sets would imply small variations of the computed CCSD(T) values (ca.  $3 \times 10^{-3}$  Å), such a choice would not affect the conclusions regarding the relative accuracies of the different computational schemes nor the chemical trends noted below. The interested reader may find a detailed basis set study at the MP2 level in ref 37, as well as a complete coupled cluster investigation (including large Dunning’s basis set) for butadiene in ref 31, and both works allow for the conclusion that 6-31G(d) is indeed a very good compromise for the BLA.

**Table 1.** CCSD(T)/6-31G(d) BLA (Å) Computed for the Oligomers Sketched in Figure 1<sup>a</sup>

system	N = 2	N = 3	N = 4	N = 5	N = 6
PB-III	0.1493	0.1272	0.1164	0.1103	0.1053
NB-I	0.1414	0.1179	0.0988	0.0885	0.0764
CC-II (TT)	0.1154	0.1022	0.0941	0.0905	0.0880
CC-II (CT)	0.1154	0.1017	0.0951	0.0912	0.0893
CC-II (TC)	0.1284	0.1151	0.1060	0.1018	0.0992
CSI-I	0.1016	0.0951	0.0848	0.0786	0.0723
CN-III	0.1356	0.1282	0.1181	0.1138	0.1097
SiSi-II	0.1092	0.0948	0.0888	0.0855	0.0836

<sup>a</sup> See Figure 2 for a graphical representation of these data.



**Figure 2.** Evolution from the dimer to the hexamer of the CCSD(T) BLA. For CC-II, only the all-*trans* (TT) conformation has been represented.

The computed CCSD(T) values are collated in Table 1, and their evolutions with chain length are displayed in Figure 2. As expected, the BLA systematically decreases when the chain lengthens, as a result of the improved delocalization of the  $\pi$  electrons. Although the chains considered in this work are too short to allow direct extrapolation to the infinite oligomer limit,<sup>16</sup> one clearly sees that the BLA of NB-I and CSI-I rapidly declines, which is consistent with a type I evolution. Indeed, for the hexamer, they are the only two compounds with a central BLA smaller than 0.08 Å (see Table 1). This therefore qualitatively confirms a previous MP2 analysis.<sup>27</sup> From Figure 2, one clearly notes that the two type III oligomers, PB-III and CN-III, have significantly larger BLAs than the two type II derivatives, CC-II and SiSi-II. Nevertheless, the evolution of the BLA between the dimer and the hexamer remains similar for PA (−0.0274 Å) and PMI (−0.0259 Å). CC-II and SiSi-II also present BLA evolving at the same rate (−0.0256 Å for the latter), though their BLA tend to become slightly more alike as the chain lengthens. Eventually, from Table 1, one notes that going from the all-*trans* (TT) to the cis-*trans* (CT) conformer has a negligible impact on the BLA (ca.  $1 \times 10^{-3}$  Å), whereas the trans-*cis* (TC) oligomer possesses more dissimilar double and single bonds (BLA larger by ca.  $1 \times 10^{-2}$  Å).

**3.2. Wave Function Benchmarks.** The BLA computed with the HF, MP2, SCS-MP2, MP4(SDQ), MP4, and CCSD approaches can be found in the Supporting Information (SI), whereas the data obtained through a statistical analysis are given in Table 2. This table lists the mean signed errors (MSE) and mean absolute errors (MAE) obtained for different subsets, considering CCSD(T) as a reference. For



**Table 2.** Statistical Analysis of the Wavefunction Results<sup>a</sup>

set	mean signed error					
	HF	MP2	SCS-MP2	MP4(SDQ)	MP4	CCSD
$N = 2$	-293	4	-48	-79	21	-91
$N = 4$	-285	49	-39	-109	45	-122
$N = 6$	-271	80	-29	-97	61	-131
type I	-34	-3	-34	-51	-13	-43
type II	-385	56	-40	-115	28	-136
type III	-330	71	-43	-119	130	-153
full	-283	45	-39	-100	43	-117

set	mean absolute error					
	HF	MP2	SCS-MP2	MP4(SDQ)	MP4	CCSD
$N = 2$	293	30	48	79	34	91
$N = 4$	292	54	39	109	57	122
$N = 6$	313	80	29	111	68	131
type I	88	14	34	51	25	43
type II	385	66	40	121	31	136
type III	330	71	43	119	130	153
full	297	54	39	103	54	117

<sup>a</sup> CCSD(T) values have been used as references. Mean signed error [CCSD(T)-tested method] and mean absolute errors are given in  $10^{-4}$  Å. Type I corresponds to NB-I and CSI-I, type II to CC-II (three conformers) and SiSi-II, and type III to PB-III and CN-III. See text for more details.

the full set of 40 derivatives, it is clear that HF significantly overshoots the BLA. This behavior was expected, as it is well-known that HF tends to provide a too localized picture for most organic compounds.<sup>3,27</sup> The typical absolute errors brought by HF are on the order of  $3 \times 10^{-2}$  Å, and the only series for which HF could be viewed as a reasonable approximation corresponds to the easiest case, that is, type I oligomers. In short, HF is inadequate and should not be used to compute the BLA. Among electron-correlated approaches, the most accurate scheme is SCS-MP2, closely followed by MP2 and MP4, whereas MP4(SDQ) and CCSD produce significantly larger errors. This clearly indicates the importance of a balance between double, triple and quadruple contributions for the most refined approaches. Interestingly, MP4(SDQ) and CCSD both overshoot the BLA. Although this phenomena is less pronounced than for HF, the average errors ( $1 \times 10^{-2}$  Å) remain incompatible with accurate estimates.

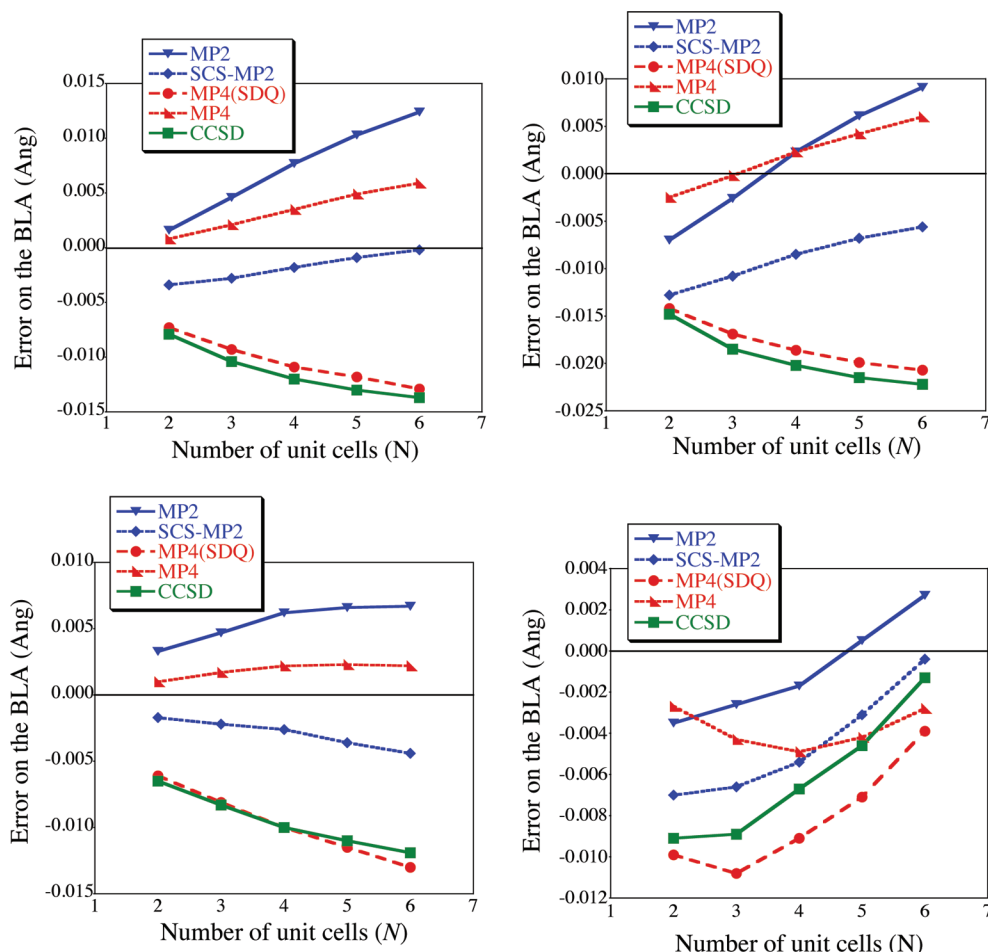
The evolution with chain length of the errors can be appreciated by comparing the average errors obtained for dimers ( $N = 2$ ), tetramers ( $N = 4$ ), and hexamers ( $N = 6$ ). It turns out that the discrepancies tend to slightly increase with chain length for all methods but SCS-MP2. For instance, the MAE doubles (almost triples) for MP4 (MP2) when going from  $N = 2$  to  $N = 6$ . This explains why the MP2 scheme was previously considered very accurate when CCSD(T) calculations were only technically possible for the shortest chains. Comparing the MSE and MAE obtained for different categories of compounds is also enlightening: the deviations obtained for type I are systematically small; any theoretical scheme seems satisfying. Additionally, for this series, the deviations tend to decrease with the chain length, as all approaches predict a zero BLA when  $N \rightarrow \infty$ . The errors obtained for types II and III are larger than for type I and are similar for the two series, but MP4 is extremely efficient for the former but apparently misses the target for

III. This phenomenon is associated with only one system, namely PB-III, as the MP4 errors for CN-III are very small (MSE and MAE of 0.0019 Å).

To obtain further insight, we have plotted in Figure 3 the evolutions with chain length of the errors for four selected derivatives, including examples of different types. For CC-II, extensive comparisons between MP2, SCS-MP2, and CCSD(T) values may also be found in ref 31. In all cases, the MP4(SDQ) and CCSD curves are almost coinciding. It is certainly striking that, for both CC-II and SiSi-II, two systems subject to Peierls distortion, the error patterns are similar and no wave function scheme possesses a flat curve; i.e., none of the tested approaches provides a constant error when the chain lengthens. Of course, in very long chains, this should become the case, but even for the hexamer, no convergence pattern clearly emerges for CC-II and SiSi-II. Nevertheless, one can predict, from the two top panels of Figure 3, that in long oligomers, SCS-MP2 is certainly more adequate than MP2 (and probably also than MP4). This finding backs the conclusions of Sancho-Garcia and Perez-Jimenez.<sup>31</sup> However, for infinitely long CC-II, SCS-MP2 probably slightly overestimates BLA, contrary to what is found in small polyenes. For CN-III, the MP2 and MP4 schemes provide nearly stabilized errors for  $N = 4, 5$ , and 6. If SCS-MP2 outperforms MP2 for short chains, the situation is hardly foreseeable for larger  $N$ . For CSI-I, all patterns are similar, the discrepancies remaining relatively small, as expected. Comparing the data in Table 2 to that in Figure 3 demonstrates that the nearly constant MSE and MAE with  $N$  noticed for SCS-MP2 are (in part) due to a compensation of errors between different series of oligomers. Eventually, the impact of changing the conformation is correctly predicted by all approaches; e.g., for the hexamer of CC-II, going from TT to CT (TC) induces a BLA increase of 0.0013 Å (0.0112 Å) at the CCSD(T) level, and MP2, SCS-MP2, MP4, and CCSD respectively deliver 0.0016 Å (0.0124 Å), 0.0010 Å (0.0137 Å), 0.0017 Å (0.0123 Å), and 0.0010 Å (0.0126 Å).

Overall, it seems that SCS-MP2 is an excellent compromise in terms of the accuracy/efficiency ratio, as it yields relatively small discrepancies that are quite uniformly distributed among the tested series and sizes. In fact, the MAE obtained with SCS-MP2 is on the order of the expected basis set error for the CCSD(T) reference values (see above). Nevertheless, SCS-MP2 tends to produce slightly too large of a BLA, and the error curves of Figure 3 are not flat. MP4 yields values close to the CCSD(T) reference, but in one specific case (PB-III). However, the computational effort associated with full MP4 (including contribution from the triples) is largely exceeding its SCS-MP2 counterpart. Indeed, the MP4 calculations involve resources similar to their CCSD(T) counterparts.

**3.3. Density Functional Theory Benchmarks.** As for the wave function results, the BLA computed with the selected six DFT functionals are given in the SI, whereas Table 3 collates the corresponding MSE and MAE. We have used a panel functional relying on the same correlation functional (LYP), to allow investigations of the impact of the exchange form, but we have additionally considered four



**Figure 3.** Evolution with the chain length of the errors obtained with wave function approaches for CC-II (top left), SiSi-II (top right), CN-III (bottom left), and CSI-I (bottom right). Note the different scales.

**Table 3.** Statistical Analysis of the DFT Results<sup>a</sup>

	mean signed error									
	BLYP	B3LYP	BHHLYP	LC-BLYP	CAM-B3LYP	B2PLYP	B97-D	M06	M06-2X	$\omega$ B97D
$N = 2$	102	11	-104	-151	-110	14	104	1	-96	-204
$N = 4$	259	116	-51	-146	-70	94	261	87	-58	-198
$N = 6$	337	170	-20	-142	-55	135	347	131	-38	-185
type I	213	117	43	-10	18	77	201	103	21	-20
type II	221	71	-116	-216	-134	60	231	58	-111	-277
type III	302	153	-35	-145	-54	137	301	118	-43	-214
full	239	103	-56	-147	-76	83	241	84	-61	-197

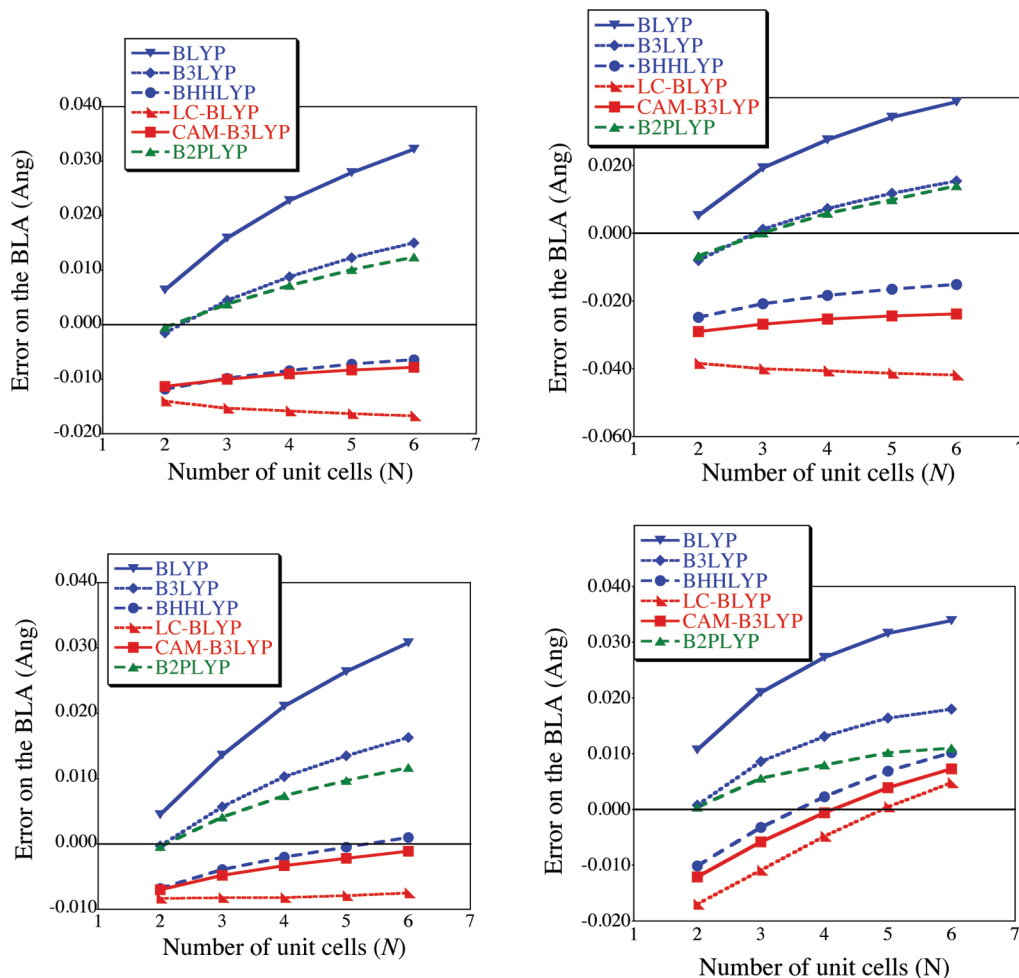
  

	mean absolute error									
	BLYP	B3LYP	BHHLYP	LC-BLYP	CAM-B3LYP	B2PLYP	B97-D	M06	M06-2X	$\omega$ B97D
$N = 2$	102	47	111	154	118	39	104	30	97	205
$N = 4$	259	116	76	155	86	94	261	87	72	204
$N = 6$	337	170	76	169	81	135	347	131	76	221
type I	213	117	70	55	55	77	200	108	49	67
type II	221	85	116	216	134	69	231	66	111	277
type III	302	153	37	145	54	137	301	119	43	214
full	239	110	85	158	94	88	241	90	79	209

<sup>a</sup> See caption of Table 2 for more details.

recently designed functionals (B97-D, M06, M06-2X, and  $\omega$ B97). BLYP and B97-D yield very similar figures, and both systematically underestimate the BLA. The discrepancies with respect to CCSD(T) rapidly increase with the chain length; e.g., they reach a factor of 2 for the hexamer of CSI-I. Therefore, this work confirms that pure functionals are

inadequate for estimating the geometry of medium and large  $\pi$ -conjugated chains. B3LYP and B2PLYP, respectively the most popular global and double hybrids, show similar patterns, an outcome already noticed for PA.<sup>31</sup> M06 follows alike trends but with errors systematically smaller than those of B3LYP. These three functionals predict BLAs that are



**Figure 4.** Evolution with chain length of the errors obtained with several DFT functionals for CC-II (top left), SiSi-II (top right), CN-III (bottom left), and CSI-I (bottom right). Note the different scales.

too small, with very small discrepancies for the dimers (for which they are the most accurate functionals, M06 providing the same performance as MP2), but their predictions tend to become less reliable with increasing chain length. For type II chains, they yield BLAs closer to the spot, but the errors nevertheless grow with  $N$ ; i.e., they cannot be considered completely satisfying even for symmetric polymers. LC-BLYP and  $\omega$ B97 enjoy relatively constant deviations with the chain length but significantly overshoot the BLA, especially the latter. Though the extent of this error is smaller than with HF (see previous section), the average absolute deviation still exceeds the  $1 \times 10^{-3}$  Å limit. Eventually, BHHLYP, CAM-B3LYP, and M06-2X deliver a more balanced description of the single and double bond lengths with stable MAEs for the tetramer and hexamer and good performances for the difficult case of type III oligomers. Overall, M06-2X is the most efficient functional, though as BHHLYP and CAM-B3LYP, it is not completely satisfying for type II chains, especially for SiSi-II. It is worth mentioning that CAM-B3LYP was already pinpointed as one of the most efficient functionals for the two prototype systems, PA<sup>30,32</sup> and PMI.<sup>30</sup>

In Figure 4, evolutions of the DFT (LYP correlation) error patterns are shown for four typical systems. The error ranges are significantly larger than in the corresponding Figure 3, and one notes that for all functionals and systems, the errors

tend to increase with  $N$ , so that the conclusions obtained with short oligomers do not pertain to longer chains. The only noticeable exception is LC-BLYP, which allows for relatively constant errors in three out of four cases: CC-II, CN-III, and SiSi-II. From Figure 4, it seems obvious that a large share of exact exchange is needed to grant reasonable estimates of the infinite chain limit, though no functional can be considered completely satisfying. Therefore, the use of BHHLYP, M06-2X or CAM-B3LYP, which yield very similar values for most oligomers, may be a good choice for medium and large conjugated chains in spite of the large errors obtained for the dimers. It is noticeable that, in the long range, the three functionals present a similar share of exact exchange (50% for BHHLYP, 56% for M06-2X, and 65% for CAM-B3LYP). This investigation illustrates how a simple structural parameter can be difficult to predict even with refined DFT schemes.

As noted above, the conformational CCSD(T) increase in the BLA noted for the hexamer of CC-II is 0.0013 Å (0.0112 Å) for CT (TC). The corresponding values are 0.0023 Å (0.0066 Å), 0.0024 Å (0.0094 Å), 0.0020 Å (0.0116 Å), 0.0007 Å (0.0107 Å), 0.0013 Å (0.0111 Å), and 0.0022 Å (0.0108 Å) for BLYP, B3LYP, BHHLYP, LC-BLYP, CAM-B3LYP, and B2PLYP, respectively. B97-D, M06, M06-2X, and  $\omega$ B97 respectively deliver 0.0034 Å (0.0054 Å), 0.0029 Å (0.0098 Å), 0.0017 Å (0.0118 Å), and 0.0011 Å (0.0111

Å), respectively. Therefore, BLYP and B97-D are again off target, whereas all other functionals give relatively accurate estimates of the impact of conformation.

#### 4. Conclusions

We have computed the central bond length alternation in eight oligomeric series of increasing size. Reference CCSD(T) values have been obtained in each case, allowing accurate comparisons for several chain lengths and atomic compositions of the unit cell. It turns out that the error patterns of the tested wave function and density functional approaches are significantly affected by the considered system. Nevertheless, several general trends have been identified. As expected, HF produces BLA that are too large with absolute deviations of ca.  $3 \times 10^{-2}$  Å. Both MP4(SDQ) and CCSD also overshoot the BLA, and though the errors are smaller than for HF, they remain sizable (ca.  $1 \times 10^{-2}$  Å). MP2, MP4, and SCS-MP2 generally yield accurate BLAs (average absolute deviations of ca.  $5 \times 10^{-3}$  Å), the two former (the latter) slightly underestimating (overestimating) the reference data. SCS-MP2 is, on average, the most efficient, although the discrepancies with respect to the CCSD(T) value evolve with the chain length, at least up to the hexamer. None of the selected functionals has a net edge for the full set of molecules. Indeed, for long oligomers, it is obvious that a global hybrid including a large share to exact exchange (BHHLYP or M06-2X) or a balanced range-separated hybrid (CAM-B3LYP) could be smart default choice to evaluate the BLA, whereas, for the smallest chains, B3LYP or B2PLYP are to be preferred.

**Acknowledgment.** D.J. is indebted to the Région des Pays de la Loire for financial support in the framework of a recrutement sur poste stratégique. This research used resources of the Interuniversity Scientific Computing Facility located at the University of Namur, Belgium, which is supported by the F.R.S.-FNRS under convention No. 2.4617.07.

**Supporting Information Available:** Tables listing the computed BLA for all oligomers and methods. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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CT1006532