Assessment of Several Hybrid DFT Functionals for the Evaluation of Bond Length Alternation of Increasingly Long Oligomers

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We have optimized the ground-state geometry of nine series of increasingly long oligomers, using six hybrid density functionals (O3LYP, B3LYP, B97-1, B98, PBE0, and BHHLYP) combined with three different atomic basis sets. In each case, the obtained bond length alternation (BLA) is compared to the corresponding MP2 values. Three phenomenological categories have been set up. In the first, the BLA exponentially decreases, in which case all the tested functionals give results in very good agreement with MP2. In the second category fall the symmetric oligomers that, due to the Peierls theorem, show large BLA. For these chains, BHHLYP tends to give too large and quickly converging BLA wrt chain length, while O3LYP often leads to the opposite misjudgments, and the remaining hybrids provide valuable results. In the third category, one finds asymmetric compounds presenting significantly unequal bond lengths, for which the divergence between DFT and wave function approaches can be dramatic. Indeed, all hybrids yield too small BLA values, especially for long chain lengths. We also study the effect of chain conformation on the BLA.

Introduction

In conjugated molecules and polymers, like the prototype polyacetylene (PA), the geometric and electronic structures are closely related.[1] For this reason, a very accurate description of the ground-state geometry is often an essential prerequisite to the calculation of electronic properties. In π-delocalized chains, the bond length alternation (BLA, the difference between single and double bond lengths) is actually the key geometrical parameter. Indeed, within the one-electron approximation, the band gap of PA is directly proportional to its BLA,[2] nicely illustrating the tight relationships between the structural and the electronic parameters in this family of macromolecules. Many other properties related to the excited states are therefore closely BLA-dependent. Typical examples are the nonlinear optics (NLO) coefficients, for which Marder, Brédas, and co-workers[3,4] established a parallel between the hyperpolarizability, the electric field amplitude, the donor−acceptor strength, and the BLA of push−pull compounds. As there is a hidden vibrational contribution in this simple model, it was later questioned by Kirtman and co-workers.[5] Nevertheless, the qualitative optimization of the odd-order NLO properties by tuning the BLA could be successfully performed.[6] Similar relationships were eventually established between the BLA and two-photon absorption phenomena.[7]

In many cases, experimental measurements of polymeric BLA happen to be difficult because most crystal structures are available only for (very) short chains, and the BLA tends to be highly chain-length dependent. Therefore, in order to accurately describe or, more essentially, predict the BLA, theoretical approaches are often required, and involve a careful choice of the model. For the prototype PA, the first systematic study of the geometry of long oligomers was performed in 1997.[2] It turned out that Hartree−Fock (HF) overshoots the BLA by a factor of 2, whereas the pure density functional theory (DFT) functional, BLYP,[8,9] leads to the opposite misjudgment. In contrast, the geometries obtained with the second-order Møller−Plesset (MP2) or the hybrid B3LYP[10] functional are both in good agreement, either with higher-order EC methods or with available experimental measurements on short compounds.[2] Consequently, hybrid functionals and, specifically, B3LYP are often selected to determine the ground-state geometries of conjugated compounds,[11−14] and the assumption *hybrid functionals predict reasonably accurate ground-state geometry for conjugated compounds* is commonly said to be true. Nevertheless we have shown in a recent study that hybrid DFT approaches dramatically fail to give the BLA of *all-trans* polymethineimine, [PMI, a polymer isoelectronic to PA where half of the CH groups are replaced by nitrogen atoms]. In that case, B3LYP,[10] PBE0,[15] and other functionals provide much too small BLA for long chains.[16] Consequently, there is at least one simple polymer for which the above-mentioned assumption remains unproven.

Although a few hybrids[15,17,18] have been designed on the basis of purely theoretical considerations[19] (originating in empirical observation,[20] but without fitting), the percentage of exact exchange (n^e) included in most hybrid functionals has been (semi-)empirically determined, i.e., using selected experimental data,[10,21−28] like heat of formation, ionization potential, elec-

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troaffinity, or total energy of small isolated molecules (G2, G3, or similar sets of compounds).[10,21,25,26] In some recent functional designs, such as in ref 27, properties such as the geometrical parameters, polarizability, and reaction barriers have been added to the training set. The obtained n^e is often lying in a 24 ± 4% region: 20% for B3LYP,[10] 21% for B97-1[21] and B97-2,[29] 21.8% for X3LYP,[26] 21.98% for B98,[22] 25% for *m*PW1PW91[17] and PBE0[15] (no fitting), 26.93% for B97-3,[27] and 28% in B1B95.[30] Nevertheless, three recently developed hybrid functionals, namely, TPSSh,[25] O3LYP,[23] and τ-HCTHh,[24] present significantly smaller n^e: 10%, 11.61%, and 15%, respectively. It has sometimes been argued that these smaller percentages are related to specific intrinsic qualities of the pure functional used in the mixing, but it mainly looks like the composition of the training set is the key to the small n^e deduced for "energy-optimized" functionals. For instance, the BMK[28] and MPWB1K[31] functionals specifically dedicated to reaction mechanics studies present much higher n^e (42% and 44%, respectively). The same trends can be found for B97-2[29] and B97-3,[27] with a significant increase of n^e when including geometries and reaction barriers in the fitting data (B97-3). The choice of experimental input for functional design is obviously governed (and restricted) by the twin requirements of highly accurate measurements and absence of environmental effects. Otherwise, one would need to include the surroundings in the theoretical computations, raising further difficulties. Following the same logic, a huge number of publications stating the pros and cons of the DFT functionals have appeared for a wide panel of properties, again for quite compact structures. To give a few selected examples, the efficiency of DFT for reaction barriers,[27−29,32−40] geometries or bonding properties,[23−27,29,33,35−37,39,41−46] harmonic vibrations,[25,27,28,37,42] NMR shielding or related properties,[27,29,37,47,48] dipole moments,[27,36,49] quadrupole moments,[27,49] and excitation energies,[27,43,50] has been tested. However, today, the majority of DFT calculations in the chemical physics field are focused on answering chemical questions of practical interest. Indeed, investigated molecules tend to be large (and often conjugated) and in crystalline, amorphous, or solvated states. Though sophisticated nonempirical (pure and/or hybrid) functionals could reasonably be expected to provide accurate results for a wide range of properties and molecules,[20,25] still the hybrids are designed/tested and used for different chemical targets. The overall success of hybrid-DFT is really astonishing, in spite of the surprisingly poor results that have been reported, often for specific properties of large or charged/polar systems,[51−59] as the conclusions drawn from training sets are probably not always transferable to extended molecules. For instance, in a recent study focused on the BLA of PA, we have shown that the *meta*-GGA functionals do not improve the too small BLA predicted by GGA, whereas hybrid functionals with n^e < 20% return relatively poor estimates,[60] in clear contrast with other results on smaller systems.[25] In particular, one can predict that OLYP will provide smaller BLA than both other "standard" GGA using the same correlation functional, and most *meta*-GGA. Consequently, the hybrid O3LYP functional, built with the OPTX exchange functional, coupled to the LYP correlation functional, would often provide smaller BLA than hybrids featuring another GGA. Indeed, the OPTX[61] exchange limit to zero (reduced) gradient is not the electron gas value, i.e., the Dirac exchange, but the Dirac exchange weighted by a (fitted) parameter which is greater than the theoretical 2/3 coefficient. This functional has been parametrized to reproduce Hartree−Fock exchange for atoms only. To take a better account of the static correlation effects, its local component, i.e., at zero (reduced) density gradient, is closer to the X-α functional which differs from the Dirac−Slater exchange (exact for electron gas) by a factor which has been taken either as an atomic parameter (in the early MS-α method)[62] or as a *global* constant equal to 0.7/(2/3) = 1.05. The standard coefficient 0.7 in the Slater exchange was the value retained for the so-called Hartree−Fock−Slater LCAO code and its variants such as the DVXα code.[63] The 2/3 value is the theoretical value in the electron uniform gas. For larger density gradients the OPTX exchange functional tends to be closer to other GGA (thanks to an enhancement factor similar to that of most GGA).

Assessments of functionals for determining ground-state geometrical parameters of large systems have recently appeared. For instance, the DFT performance when evaluating torsional potentials was judged towards highly accurate wave function schemes such as CCSD(T);[51,64] also the lattice constant, modulus, and electronic gaps of several inorganic crystals were studied by Scuseria and co-workers.[65−67]

In this paper, we evaluate the pros and cons of six widely available hybrid functionals (O3LYP, B3LYP, B97-1, B98, PBE0, and BHHLYP) for computing the BLA of increasingly long oligomeric chains of several polymers (Figure 1). Actually, we have been facing the problem of reference selection. Indeed, CCSD(T) or similar approaches are completely intractable for these large systems (up to sixty atoms) whereas experimental measurements are strongly affected by environmental effects and, often, quite inaccurate. Therefore, in this investigation we have used previous MP2 results as a landmark.[68] In ref 68, we show that, for most systems, the BLA rapidly decreases with chain length and only a few macromolecules would display BLA larger than 0.03 Å. Although these MP2 results are not fully quantitative, we demonstrate below that they can be trusted with (at the very least) a known sign of the error. Though comparisons in light of MP2 results might not be sufficient to formally answer questions such as *what is the best functional?*, they provide enough hints to detect large discrepancies, as was previously established for hyperpolarizabilities.[52,69] Therefore, in this contribution, we aim not only to gain an insight on which functionals look promising (or not) for predicting the BLA of long oligomers but also to determine topological criteria that can make one confident or cautious in using conventional DFT approaches rather than electron-correlated wave function techniques for ground-state optimization. By doing so, it is our hope that the first satisfying explanations of the difference between PA and PMI could be unraveled.

I. Methodology

Determination of the BLA has been performed for the set of oligomers depicted in Figure 1. As in our previous study,[68] the BLA reported in this investigation have been taken at the middle of the chain. Note that in our notation N represents the number of unit cells, i.e., N is the equal to half of the number of backbone atoms. For the reader's comfort, we are using the same nomenclature as in ref 68: AB-XD(conformation) where A and B are the two backbone atoms and X is the "dimensionality" of the molecule, i.e., 1 if all nuclei are collinear and 2 when all the nuclei lie in a plane (as in PA or PMI). Within these conventions, PA's label is CC-2D, and PMI's label is CN-2D. In the first part of this study, we have used the trans−transoid (or all-trans, TT) for 2D structures as the conformation is not the essential parameter governing the BLA.[68] Nevertheless, examples of cis−transoid (CT) and trans−cisoid (TC) conformers have been optimized in section II.D.

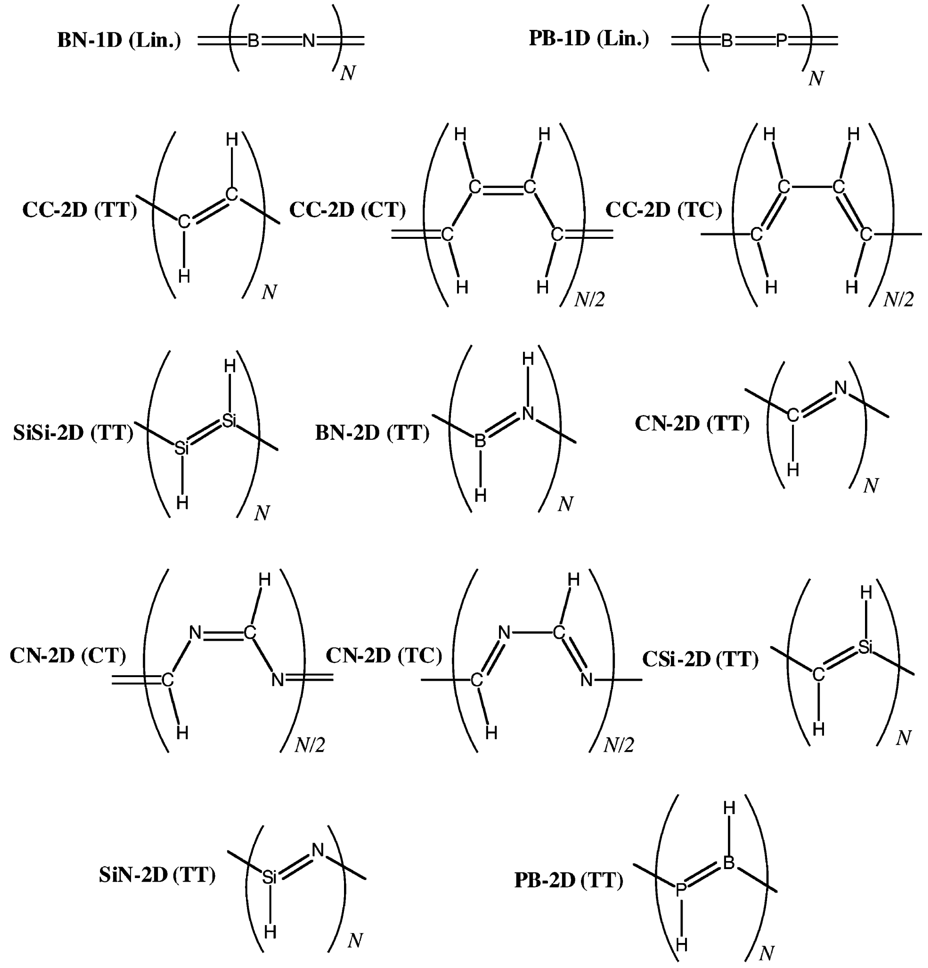

Figure 1. Sketch of the oligomers investigated in this work.

Each oligomer geometry has been determined by the optimization of its structural parameters with the Gaussian03[70] package. These minimizations have been performed until the rms residual force is lower than 1 × 10^{-5} au (*tight* threshold in Gaussian03) with the use of the best integration grid during all calculations [*ultrafine*, pruned (99 590) grid] and a tightened SCF threshold (at least 10^{-9} au). This corresponds to a minimal accuracy of ±1 × 10^{-4} Å on BLA. Consistently with our previous work,[68] the atomic backbones have been constrained to be planar. For some polymers,[71,72] other nonplanar conformations do exist, but a study of these oligomers is beyond the scope of the present paper. The five asymmetric TT chains (CN-2D, CSi-2D, SiN-2D, BN-2D, and BP-2D) tend to form bent, rather than linear, structures. To avoid this bending effect, we have imposed all the backbone valence angles to be equal in these oligomers. For CN-2D[16] and CSi-2D,[73] it has been demonstrated that this constraint does not significantly affect the BLA.

The functionals used in this contribution all come from the hybrid category. Indeed, as noted in the Introduction, pure functionals (that do not include a fraction of exact exchange) lead to poor results for both CC-2D(TT) and CN-2D(TT) and have consequently been discarded. Six hybrids have been selected: O3LYP, B3LYP, B91-1, B98, PBE0, and BHHLYP. In the 3-parameter B3LYP functional,[10] the exchange is a combination of 20% HF, Slater functional, and Becke's GGA[8] correction, whereas the correlation part combines local and LYP[9] functionals. O3LYP is based on the same model but uses the OPTX[61] exchange form and includes only 11.61% of exact exchange.[23,33] B97-1[21] and B98[22] contain 21% and 21.98% of Hartree–Fock exchange, respectively. In PBE0[15] the exchange is weighted (75% PBE[74]/25% HF) accordingly to theoretical considerations.[19] BHHLYP is the "historical" half-and-half functional where the HF exchange contribution amounts to 50%.

An essential computational parameter is the size of the atomic basis sets (BS). In the numerous DFT assessments available in the literature, one can find two different, yet complementary, points of view. On the one hand, it is sometimes advocated that small BS can be used for comparisons, as in practice, one is interested in reasonably accurate results for small computational costs.[36] On the other hand, fair statistical comparisons require BS converged values, as shown in the extensive study of Boese, Martin, and Handy.[75] Therefore, we compare DFT and MP2 results using both small and extended basis sets. In ref 68, it is shown that 6-311G(3df) offers BS-converged BLA at the MP2 level, i.e., further extension of the BS is not expected to give changes larger than 0.001 Å. Therefore, 6-311G(3df) has been used for quantitative calculations on small oligomers. Indeed, it is well-known that DFT (and HF) approaches are less sensitive to BS size than the electron-correlated wave function schemes: a BS providing MP2 structures close to the BS limit shall deliver (at least) the same accuracy for DFT and HF geometries. This was confirmed by a series of test calculations, and it is also quite obvious from the results discussed in section II.B. In addition, we have also used 6-311G(2d), which gives a valuable size/accuracy ratio, and 6-31G(d), which provides a correct qualitative evolution of the BLA with chain length.[68]

II. Results

A. MP2 Values. As we are using MP2 BLA as reference marks in this study, it is essential to assess the accuracy obtained

TABLE 1: Comparison between the 6-31G(d) BLA (10^{-4} Å) Obtained with HF and Electron-Correlated Approaches

oligomer	*N*	HF	MP2	MP4 (SDQ)	MP4	CCSD(T)
CC-2D(TT)[a]	2	1450	1138	1227	1146	1154
	4	1281	864	1050	906	941
	6	1239	756	1009		
SiSi-2D(TT)	2	1592	1162	1234		
	4	1418	865	1074		
	6	1383	745	1043		
CN-2D(TT)	2	1558	1322	1417	1346	1356
	4	1385	1119	1281	1159	1181
	6	1294	1030	1227		
SiN-2D(TT)	2	1039	1006	1003		
	4	625	718	721		
PB-2D(TT)	2	701	628	641	640	
	4	145	226	234		
	6	62	116	121		

[a] Taken from ref 60.

with this approach prior to any comparisons. Table 1 lists the 6-31G(d) BLA computed with several electron-correlated wave function approaches for a selected series of increasingly long oligomers of CC-2D, SiSi-2D, CN-2D, SiN-2D, and PB-2D. For the two latter, which present an exponentially decreasing BLA when *N* increases,[68] MP2 results perfectly match the BLA calculated with MP4(SDQ) and MP4 schemes, the typical discrepancy being smaller than 0.001 Å. For these systems, MP2 BLA are therefore to be fully trusted. For the remaining compounds, which possess nonzero polymeric BLA, conclusions can be drawn that parallel those of our previous study on CC-2D(TT):[60] (1) MP2 BLA are significantly smaller than MP4(SDQ) values, but only slightly undershoot the MP4 and CCSD(T) results. (2) MP4 and CCSD(T) BLA converge slightly faster with chain length than MP2 BLA. At this moment it is not possible to confirm these assertions on extended chains due to computational limits.

The results of Table 1 have been obtained with a relatively small basis set. Nevertheless, for CC-2D and CN-2D, it appears that the use of a larger basis set does not influence these conclusions. Indeed, for the dimer of the former, we found limited BS effects with a CCSD(T)/6-311G(3df) BLA of 0.1175 Å instead of 0.1154 Å with 6-31G(d). For the latter the MP4(SDQ)/6-311G(2d) BLA are 0.1487 and 0.1342 Å, for $N = 2$ and 4, respectively, to be compared to the corresponding 0.1383 Å and 0.1168 Å MP2/6-311G(2d) results. By comparing these BLA to their 6-31G(d) counterparts reported in Table 1, one finds that all are changed by 0.006 ± 0.001 Å. Therefore, it appears that the BS size does not modify the relative BLA: they are shifted by a nearly constant amount for the various electron-correlated wave function approaches. This is confirmed by 6-311G(3df) calculations for the CN-2D(TT) dimer: MP2 BLA = 0.1353 Å and CCSD(T) BLA = 0.1397 Å, respectively. That is 0.0030 and 0.0029 Å smaller than the corresponding 6-311G(2d) data. Therefore, for the polymers with BLA significantly larger than zero, the MP2 results can be regarded as minima, especially for long chains.

B. Classification of the Different Systems. The complete tables listing the BLA of all Figure 1 series for the three basis sets and the six functionals are provided as Supporting Information (Tables S1–S13). The MP2 BLA used as a reference in this study can be found in a previous investigation,[68] but have also been added in Supporting Information for the reader's comfort. In this study, we focus on medium and long chains as many studies already exist for the geometric parameters of smaller molecules (see Introduction). For most of the investigated systems, the BLA for these chain lengths are smoothly evolving wrt n^e, regardless of the form of the functional, the fraction of exact exchange being the essential parameter guiding the BLA. Of course, one could find exceptions to this rule, such as SiN-2D, but in that case the discrepancies between the various approaches are negligible. It is also worth noting that, for dimers and tetramers, such a simple relationship between BLA and n^e does not hold. The formalism of the pure functional(s) used as building block(s) of the hybrid strongly matters for small compounds, but not for longer ones.

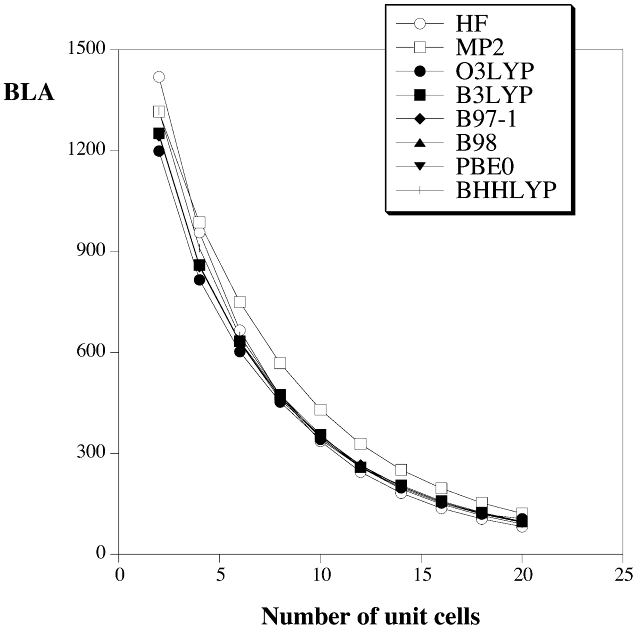

Figure 2. Variation with chain length (*N*) of the BLA of BN-1D(Lin) chains. The results are plotted in 10^{-4} Å and have been obtained with the 6-31G(d) basis set.

For oligomers presenting exponentially decreasing BLA when the chain length increases, i.e., for compounds with BLA tending to be (very close to) zero in the macromolecule, the results, on the one hand, are not strongly basis set dependent (especially for HF and DFT) and, on the other hand, show relatively similar qualitative and quantitative behavior for all eight theoretical schemes. A typical example, BN-1D(Lin), is displayed in Figure 2. All approaches clearly lead to similar BLA, with slightly larger (+0.006 Å for $N = 8$ compared to HF and DFT) MP2 figures, and negligible BS effects (but, as awaited, for MP2). For BN-1D(Lin) the falloff speed is also consistently foreseen by all approaches. Indeed, the 6-311G(2d) BLA is reduced by −0.04 Å when going from the hexamer to the dodecamer (Table S1) whatever the selected approach. CSi-2D(TT) behaves in the same fashion but with O3LYP BLA systematically and significantly smaller than the MP2 BLA, at all *N*. For this system, BHHLYP could be trusted but it provides no significant improvement over HF. For PB-2D(TT), HF BLA are too small and the results obtained with all hybrids are again in nice agreement with the MP2 values. For BN-2D(TT) and SiN-2D(TT), the DFT and MP2 results are extremely close, except for BHHLYP in the former and O3LYP in the latter. Therefore, for these polymers with rapidly vanishing BLA, all selected hybrids (but also HF) can be used without large (>0.01 Å) discrepancies, the "best" functionals presenting a n^e in between 20% and 25%.

Two chains undergoing the Peierls effect, namely, CC-2D(TT) and SiSi-2D(TT), have been investigated. For the former, we have already performed a thorough study,[60] and the results for the latter are available in Table S4 and displayed in Figure 3. For SiSi-2D(TT) the basis set effects are quite large at the

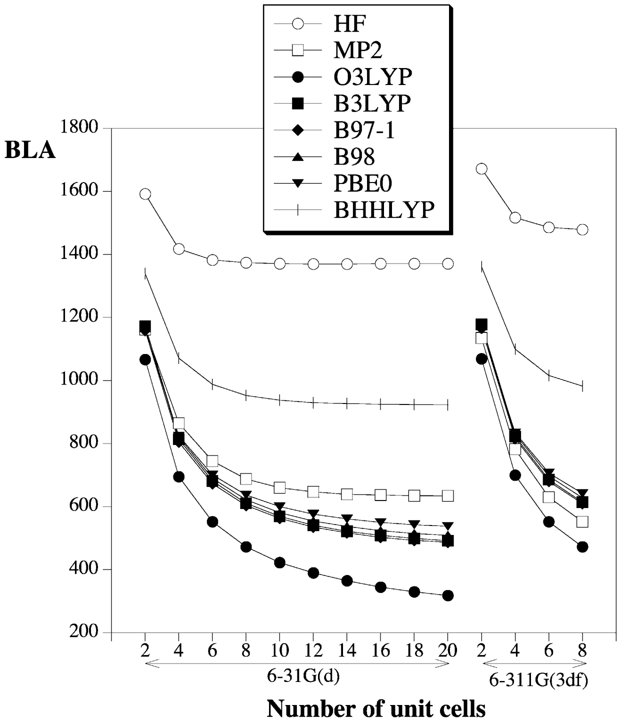

Figure 3. Comparison of the evolution with *N* of the 6-31G(d) (left) and 6-311G(3df) (right) BLA (in 10^{-4} Å) for SiSi-2D(TT) chains.

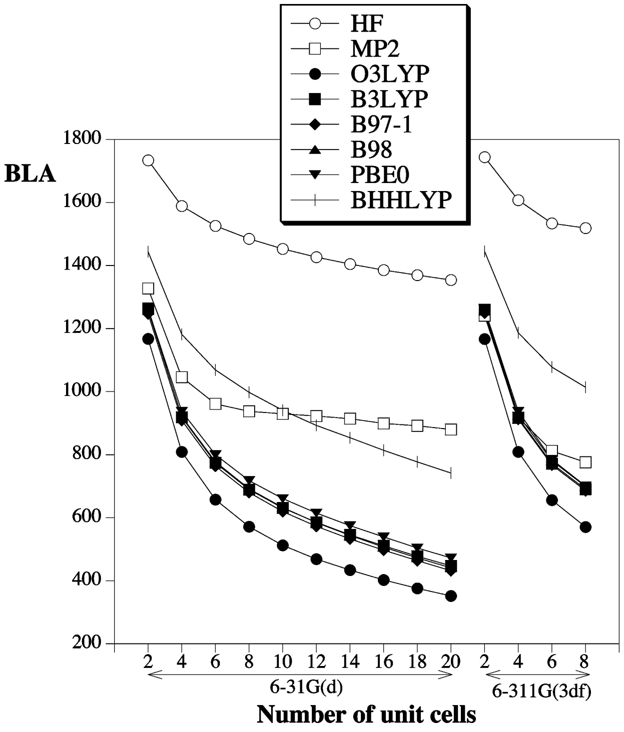

Figure 4. Comparison of the evolution with *N* of the 6-31G(d) (left) and 6-311G(3df) (right) BLA (in 10^{-4} Å) for PB-1D(Lin) chains.

MP2 level (but advantageously smaller with DFT), and 6-311G(3df) is required for quantitative comparisons. It clearly turns out that, for medium chain lengths, HF and BHHLYP BLA are too large, overshooting MP2 results by 0.09 and 0.04 Å, respectively. On the contrary, the O3LYP curves are below the MP2 ones, which should be viewed as minima, as we have shown in section II.A. Consequently, O3LYP has to be discarded, as was already the case for CC-2D(TT).[60] Once a sufficiently large basis set is selected, the other four hybrids predict BLA slightly larger than MP2 and are therefore exactly lying in the accuracy region. Note that the reverse effect would be incorrectly foreseen with 6-31G(d) due to overestimation of the MP2 BLA. The falloff of the MP2/6-311G(2d) BLA is −0.015 Å between $N = 6$ and $N = 12$, a value nicely reproduced by all other schemes (between −0.013 Å and −0.017 Å) but BHHLYP (−0.006 Å) and HF (−0.001 Å). These conclusions completely parallel the results for CC-2D(TT), i.e., BHHLYP gives too large and too rapidly converging BLA, whereas approaches with $n^e < 20\%$ underestimate the BLA.

In the last category, i.e., polymers built with asymmetric unit cells but presenting nonvanishing BLA, one finds PB-1D(Lin) and CN-2D(TT). For the latter, we refer the reader to a previous contribution,[16] where it was demonstrated that B3LYP and PBE0 provided much too small and too quickly decreasing BLA. Table S6 shows that O3LYP, B97-1, B98, and even BHHLYP (for long oligomers) present exactly the same problematic trends. Figure 4 provides a comparison of the evolution with chain length of HF, DFT, and MP2 BLA for PB-1D(Lin). Obviously, PB-1D(Lin) behaves like CN-2D(TT) but with much larger basis set effects. For 6-31G(d) results, it is striking that both HF and DFT BLA go down much too rapidly as *N* increases. Even the BHHLYP results break the MP2 line between $N = 10$ and 12. Subsequently, for long oligomers, all DFT approaches considerably undershoot the BLA (see Table S2). With 6-311G(3df), one gets a better agreement between B3LYP, B97-1, B98, PBE0, and MP2, but only up to $N = 6$. Indeed, the bond length equalization provoked by adding two unit cells to the hexamer is overrated with DFT (−0.008 Å with most hybrids) compared to MP2 (−0.004 Å). Nevertheless, contrary to CN-2D, HF values are much too large, at least up to $N = 20$, and there is a risk that one could incorrectly predict that error compensation would provide accurate geometries for PB-1D(Lin). Subsequently, for these asymmetric chains, we recommend the use of DFT approaches only after careful testing performed with sufficiently extended basis sets on large compounds (for instance, say $N = 6$ to $N = 12$).

C. Statistical Analysis. In Tables 2 and 3, we give the mean absolute error (MAE) and mean signed error (ME) for DFT/6-311G(3df) BLA. The median errors (DAE and DE) are reported as well. They have been determined using MP2/6-311G(3df) results as reference and the oligomers reported in Tables S1−S9, except when noted. The MAE of B3LYP, B97-1, B98, and PBE0 are really small (∼0.004 Å), relatively constant with chain length, and completely equivalent for the four functionals. The ME are slightly negative in all cases. DAE and DE are of the same order of magnitude as MAE and ME, respectively, and follow the same trends. On the contrary, HF MAE are at least five times larger (∼0.02 Å), confirming the well-known fact that electron correlation is required to accurately determine the structure of conjugated molecules. BHHLYP and O3LYP yield MAE and MDE systematically larger than the other hybrids but with signed differences in opposite directions, the former (latter) almost always overestimating (underestimating) the MP2 BLA. If one discards the only two problematic cases (CN-2D and PB-1D) from the set, there is no surprise that the errors tend to decrease, especially for HF, BHHLYP, and O3LYP. On the last line of Tables 2 and 3, we report the differences obtained when comparing the DFT/6-31G(d) BLA to the MP2/6-311G(3df) figures. It turns out that the MAE reported for B3LYP, B97-1, B98, and PBE0 are almost unaffected as could be foreseen from the small BS effects obtained with DFT results. This highlights the efficiency of these hybrids for oligomers belonging to categories 1 and 2 in section II.B: they provide accurate results with a small BS whereas, to reach a comparable

TABLE 2: Mean (and Median) absolute errors with respect to MP2/6-311G(3df) BLA (10^{-4} Å)[a]

N	HF	O3LYP	B3LYP	B97-1	B98	PBE0	BHHLYP
2	231 (194)	60 (66)	38 (43)	40 (44)	42 (45)	34 (29)	97 (65)
4	263 (60)	86 (82)	35 (26)	38 (30)	39 (40)	42 (38)	114 (58)
6	284 (69)	91 (89)	42 (40)	43 (44)	42 (39)	45 (29)	70 (178)
8	295 (81)	96 (86)	47 (44)	48 (41)	48 (39)	51 (33)	122 (34)
2−8	268 (95)	83 (81)	40 (40)	42 (38)	43 (41)	43 (33)	114 (62)
2−8[b]	214 (59)	65 (77)	37 (38)	39 (33)	41 (41)	40 (32)	100 (36)
2−8[c]	256 (128)	89 (83)	42 (37)	42 (37)	43 (38)	42 (31)	109 (59)

[a] The first six lines are obtained by using the 6-311G(3df) basis set. [b] 6-311G(3df) calculations without CN-2D(TT) and PB-1D(Lin). [c] HF and DFT 6-31G(d) calculations.

TABLE 3: Mean (and Median) Signed Errors with Respect to MP2/6-311G(3df) BLA (10^{-4} Å)[a]

N	HF	O3LYP	B3LYP	B97-1	B98	PBE0	BHHLYP
2	207 (194)	−60 (−66)	3 (−11)	−5 (−14)	1 (−16)	−8 (−17)	79 (65)
4	228 (60)	−86 (−82)	−20 (−11)	−23 (−17)	−17 (−14)	−21 (−24)	82 (−2)
6	243 (−8)	−90 (−89)	−22 (−22)	−25 (−25)	−18 (−23)	−22 (−21)	90 (−8)
8	255 (−11)	−95 (−86)	−27 (−13)	−29 (−15)	−22 (−14)	−24 (−12)	92 (−4)
2−8	233 (84)	−83 (−81)	−17 (−12)	−20 (−16)	−14 (−15)	−19 (−19)	86 (10)
2−8[b]	169 (−15)	−64 (−77)	−12 (−11)	−15 (−15)	−10 (−15)	−12 (−15)	64 (−13)
2−8[c]	232 (128)	−86 (−83)	−19 (−3)	−23 (−11)	−17 (−1)	−18 (−11)	85 (48)

[a] The first six lines are obtained by using the 6-311G(3df) basis set. [b] 6-311G(3df) calculations without CN-2D(TT) and PB-1D(Lin). [c] HF and DFT 6-31G(d) calculations.

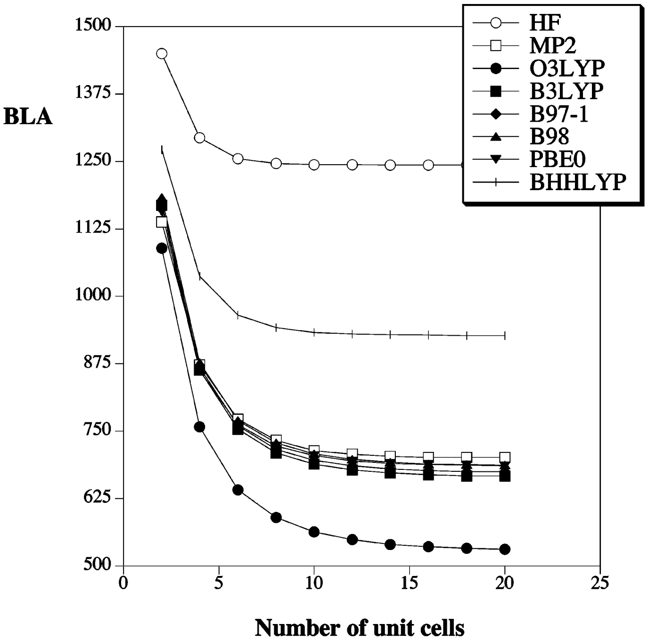

Figure 5. Comparison of the evolution with *N* of the 6-31G(d) BLA (in 10^{-4} Å) of CC-2D(CT) chains.

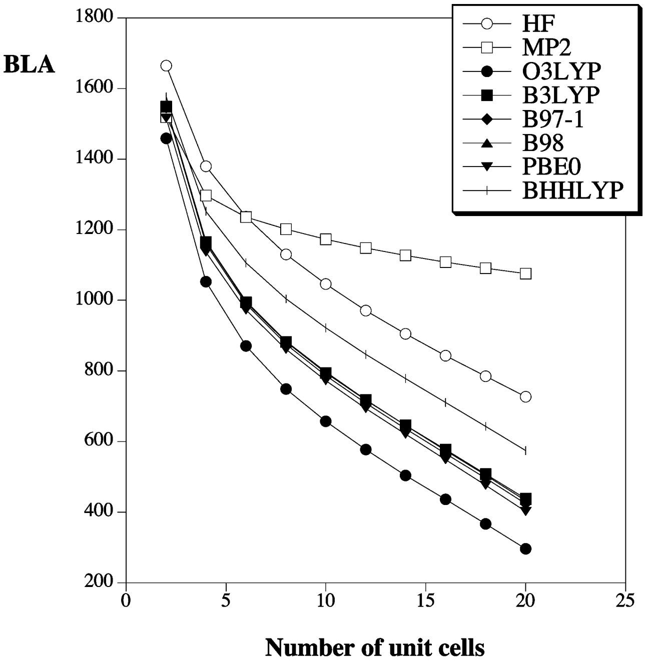

Figure 6. Comparison of the evolution with *N* of the 6-31G(d) HF, MP2, and DFT BLA (in 10^{-4} Å) for CN-2D(TC) chains.

accuracy, MP2 requires a (much) larger orbital flexibility, and hence computational effort. Tables S14 and S15 in the Supporting Information compare the MP2 and DFT 6-31G(d) results. One notes the larger MAE and ME (due to the non-BS-converged MP2 BLA) that are slowly increasing with chain length.

D. Effect of the Conformation. Tables S10 and S11 provide the BLA computed for cis−transoid and trans−cisoid CC-2D chains, respectively. For CN-2D, the corresponding information can be found in Tables S12 and S13. Figures 5 and 6 provide the evolution of the BLA for CC-2D(CT) and CN-2D(TC), respectively. For these chains, the BS effects are not dramatic, so only the 6-31G(d) BLA have been reported in these plots. For CC-2D(CT) we found qualitative and quantitative agreement between functionals with 20% ≤ n^e ≤ 25% and the MP2 results, especially with the triple-ζ BS. In addition, HF and BHHLYP (O3LYP) overestimate (underestimates) the BLA. Similar conclusions can be deduced for TT[60] or TC CC-2D chains. For CN-2D(TC), the DFT results are catastrophic. They are much too small (even for $N = 6$) and decrease quickly whereas MP2 foresees a fast saturation behavior. Interestingly, for CN-2D-(TC), the HF BLA also displays an incorrect evolution with chain length. Therefore, in this case, the lack of accuracy of hybrid DFT is understandable. Indeed, hybrid functionals generally work well due to error cancellation as one “averages” a too delocalized (DFT) scheme with a too localized (HF) approach. However, for CN-2D(TC) HF tends to go too far in bond length equalization, leading to too conjugated structure.

In short, the relative qualitative evolution of the HF, DFT, and MP2 BLA seems to be almost unaffected by the conformation of the chain. This conclusion probably holds as long as the bonding nature is not significantly altered by the conformation.

III. Conclusion and Outlook

We have calculated the BLA of increasingly long oligomers by using six hybrid functionals and the Hartree−Fock model. By comparing the DFT geometries with the MP2 electron-correlated wave function approach, we draw the following conclusions. (1) All methods lead to comparable results for systems in which the BLA is quickly decreasing with chain length. (2) For compounds for which the geometry is guided by the Peierls theorem, B3LYP, B97-1, B98, and PBE0 provide accurate results, whereas HF and BHHLYP yield too large, and O3LYP too small BLA. (3) For polymers with large BLA (though asymmetric), the values provided by DFT are too small and decrease much too rapidly when the chain lengthens. (4) For medium and long chains, the results are mainly guided by the percentage of exact exchange included in the functional, with B3LYP, B97-1, B98, and PBE0 providing comparable BLA values. (5) The basis set effects are much smaller with DFT than with MP2, especially for chains containing third-row atoms. (6) The conformation of the chain does not affect any of the conclusions 1 to 5. As a consequence, in the framework of geometry optimization of semiconducting polymers, one can probably recommend the use of any functional featuring around 25% of exact exchange, except for the systems mentioned in point 3, for which a careful testing is mandatory. Therefore, we predict that B97-3[27]/TPSSh[25] (for instance) would probably provide reasonable/relatively poor BLA for extended SiSi-2D-(TT) oligomers. For sure, the validity, quality, or interest in any functional could not be determined only on the basis of the calculation of a specific property for selected oligomers, but this study demonstrates that the transferability of the conclusions obtained for small gas-phase molecules to large conjugated systems is not obvious even for simple ground-state structures.

Of course, the functionals used in this study basically work on the principle of error compensation, i.e., one mixes a method that tends to equalize bond lengths (pure DFT) with a scheme displaying the opposite trends (HF). Therefore it is not surprising that the ratio of mixing guides the final results. Further improvements likely imply treating the exchange(-correlation) in a more “consistent” theoretical fashion. Several approaches have been proposed such as the inclusion of self-interaction corrections (SIC),[76−78] or a proper treatment of long-range effects,[79−82] or the use of “exact” exchange.[83] Our current research lines are following these procedures in order to check the accuracy obtained with these models. For CC-2D(TT), it has recently been shown that the inclusion of SIC dramatically improves the computed BLA (compared to pure-DFT) for medium chain lengths.[84]

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Supporting Information Available: Complete ref 70, complete (basis set/number of unit cells) BLA tables for each oligomer, and statistical analysis for the BLA computed at the 6-31G(d) level. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Brédas, J. L. *Adv. Mater.* **1995**, *7*, 263−274.

(2) Choi, C. H.; Kertesz, M.; Karpfen, A. *J. Chem. Phys.* **1997**, *107*, 6712−6721.

(3) Bourhill, G.; Brédas, J. L.; Cheng, L. T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc*. **1994**, *116*, 2619−2620.

(4) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703−10714.

(5) Kirtman, B.; Champagne, B.; Bishop, D. M. *J. Am. Chem. Soc.* **2000**, *122*, 8007−8012.

(6) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. *Chem. Eur. J* **1997**, *3*, 1091−1104.

(7) Bartkowiak, W.; Zalesny, R.; Leszczynski, J. *Chem. Phys.* **2003**, *287*, 103−112.

(8) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(11) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177−189.

(12) Hirata, S.; Iwata, S. *J. Chem. Phys.* **1997**, *107*, 10075−10084.

(13) Kudin, K. N.; Scuseria, G. E. *Phys. Rev. B* **2000**, *61*, 16440−16453.

(14) Pino, R.; Scuseria, G. *J. Chem. Phys.* **2004**, *121*, 8113−8119.

(15) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

(16) Jacquemin, D.; André, J. M.; Perpète, E. A. *J. Chem. Phys.* **2004**, *121*, 4389−4396.

(17) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664−675.

(18) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029−5036.

(19) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* **1996**, *105*, 9982−9985.

(20) Perdew, J. P.; Ruzsinsky, A.; Tao, J.; Staroverov, V. N.; Scuseria, G. E.; Csonka, G. I. *J. Chem. Phys.* **2005**, *123*, 062001.

(21) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264−6271.

(22) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, *108*, 9624−9631.

(23) Hoe, W. M.; Cohen, A. J.; Handy, N. C. *Chem. Phys. Lett.* **2001**, *341*, 319−328.

(24) Boese, A. D.; Handy, N. C. *J. Chem. Phys.* **2002**, *116*, 9559−9569.

(25) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129−12137.

(26) Xu, X.; Goddard, W. A., III. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 2673−2677.

(27) Keal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2005**, *123*, 121103.

(28) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405−3416.

(29) Wilson, P. J.; Bradley, T.; Tozer, D. *J. Chem. Phys.* **2001**, *115*, 9233−9242.

(30) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040−1046.

(31) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908−6918.

(32) Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *115*, 11040−11051.

(33) Baker, J.; Pulay, P. *J. Chem. Phys.* **2002**, *117*, 1441−1449.

(34) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 8996−8999.

(35) Li, Q. S.; Xu, X. D.; Zhang, S. *Chem. Phys. Lett.* **2004**, *384*, 20−24.

(36) Lynch, B. J.; Truhlar, D. G. *Theor. Chem. Acc.* **2004**, *111*, 335−344.

(37) Keal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2004**, *121*, 5654−5660.

(38) Andersson, S.; Grüning, M. *J. Phys. Chem. A* **2004**, *108*, 7621−7636.

(39) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2715−2719.

(40) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. M. *J. Phys. Chem. A* **2006**, *110*, 709−716.

(41) Swart, M.; Snijders, J. *Theor. Chem. Acc.* **2003**, *110*, 34−41.

(42) Teale, A. M.; Tozer, D. J. *J. Chem. Phys.* **2005**, *122*, 034101.

(43) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433−7447.

(44) Xu, X.; Zhang, Q.; Muller, R. P.; Goddard, W. A., III. *J. Chem. Phys.* **2005**, *122*, 014105.

(45) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673−676.

(46) Rubio-Pons, O.; Luo, Y. *J. Chem. Phys.* **2004**, *121*, 157−161.

(47) Watson, M. A.; C., H. N.; Cohen, A. J.; Helgaker, T. *J. Chem. Phys.* **2004**, *120*, 7252−7261.

(48) Filatov, M.; Cremer, D. *J. Chem. Phys.* **2005**, *123*, 124101.

(49) De Proft, F.; Tielens, F.; Geerlings, P. *J. Mol. Struct. (THEOCHEM)* **2000**, *506*, 1−8.

(50) Watson, M. A.; Handy, N. C.; Cohen, A. J. *J. Chem. Phys.* **2003**, *119*, 6475−6481.

(51) Sancho-García, J. C.; Brédas, J. L.; Cornil, J. *Chem. Phys. Lett.* **2003**, *377*, 63−68.

(52) Champagne, B.; Perpète, E. A.; Jacquemin, D.; van Gisbergen, S.; Baerends, E.; Soubra-Ghaoui, C.; Robins, K.; Kirtman, B. *J. Phys. Chem. A* **2000**, *104*, 4755−4763.

(53) Sancho-García, J. C.; Péréz-Jiménez, A. J.; Moscardó, F. *J. Phys. Chem. A* **2001**, *105*, 11541−11548.

(54) Tozer, D. J. *J. Chem. Phys.* **2003**, *119*, 12697−12699.

(55) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007−4016.

(56) Gruning, M.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Phys. Chem. A* **2001**, *105*, 9211−9218.

(57) Gilbert, T. M. *J. Phys. Chem. A* **2004**, *108*, 2550−2554.

(58) Gutierrez, F.; Rabbe, C.; Poteau, R.; Daudey, J. P. *J. Phys. Chem. A* **2005**, *109*, 4325−4330.

(59) LeTourneau, H. A.; Birsch, R. E.; Korbeck, G.; Radkiewicz-Poutsma, J. L. *J. Phys. Chem. A* **2005**, *109*, 12014−12019.

(60) Jacquemin, D.; Perpète, E. A.; Ciofini, I.; Adamo, C. *Chem. Phys. Lett.* **2005**, *405*, 376−381.

(61) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403−412.

(62) Chermette, H. *New J. Chem.* **1992**, *16*, 1081−1088.

(63) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51.

(64) Sancho-García, J. C.; Cornil, J. *J. Chem. Phys.* **2004**, *121*, 3096−3101.

(65) Heyd, J.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 1187−1192.

(66) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *Phys. Rev. B* **2004**, *69*, 075102.

(67) Heyd, J.; Peralta, J. E.; Scuseria, G. E.; Martin, R. L. *J. Chem. Phys.* **2005**, *123*, 174101.

(68) Jacquemin, D.; Femenias, A.; Chermette, H.; André, J. M.; Perpète, E. A. *J. Phys. Chem. A* **2005**, *109*, 5734−5741.

(69) Champagne, B.; Perpète, E. A.; van Gisbergen, S.; Baerends, E. J.; Snijders, J. G.; Soubra-Ghaoui, C.; Robins, K.; Kirtman, B. *J. Chem. Phys.* **1998**, *109*, 10489−10498.

(70) Frisch, M. J.; et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(71) Jacquemin, D.; Champagne, B.; André, J. M. *J. Chem. Phys.* **1998**, *108*, 1023−1030.

(72) Jacquemin, D.; Medved', M.; Perpète, E. A. *Int. J. Quantum Chem.* **2005**, *103*, 226−234.

(73) Jacquemin, D.; Perpète, E. A.; André, J. M. *J. Chem. Phys.* **2004**, *120*, 10317−10327.

(74) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(75) Boese, A. D.; Martin, J. M. L.; Handy, N. C. *J. Chem. Phys.* **2003**, *119*, 3005−3014.

(76) Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 8187−8193.

(77) Lundberg, L.; Siegbahn, P. E. M. *J. Chem. Phys.* **2005**, *122*, 224103.

(78) Ciofini, I.; Adamo, C.; Chermette, H. *Chem. Phys. Lett.* **2005**, *309*, 67−76.

(79) Gritsenko, O. V.; Baerends, E. J. *J. Chem. Phys.* **2004**, *121*, 655−660.

(80) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2004**, *120*, 8425−8433.

(81) Kamiya, M.; Sekino, H.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2005**, *122*, 234111.

(82) Maitra, N. T. *J. Chem. Phys.* **2005**, *122*, 234104.

(83) Bulat, F. A.; Toro-Labbé, A.; Champagne, B.; Kirtman, B.; Yang, W. *J. Chem. Phys.* **2005**, *123*, 014319.

(84) Ciofini, I.; Adamo, C.; Chermette, H. *J. Chem. Phys.* **2005**, *123*, 121102.