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Second-Order Møller−Plesset Evaluation of the Bond Length Alternation of Several Series of Linear Oligomers

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We investigate, at the second-order Møller−Plesset level, the bond length alternation of 30 series of increasingly long linear oligomers for a total of more than 250 compounds, polyacetylene, polymethineimine, polyphosphinoborane, polyaminoborane, polyphosphazene, etc., for which, often for the first time, an accurate estimate of the polymeric bond length alternation is given. The variations induced either by chemical substitution of the backbone atoms or conformational modifications are discussed. Only three polymers present a large bond length alternation ($>$0.03 Å). Systematic basis set effects have been unravelled, i.e., MP2/6-311G(2d) always overshoots the bond length alternation. Best estimates of the bond length alternation are provided for more than a dozen of polymers.

I. 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 their ground-state geometry is often an essential prerequisite to the calculation of band gap, excited states, nonlinear optics (NLO) coefficients, conductivity parameters, etc. In conjugated chains, the main geometrical parameter is the bond length alternation (BLA, the difference between single, and double bond lengths). For instance, in PA the band gap is directly proportional to the BLA, within the one-electron approximation (see ref 2 and references therein). Many other properties related to excited states are therefore closely related to the BLA. Typical example are the NLO properties. Indeed, Marder and co-workers[3,4] established a parallel between the hyperpolarizabilities, 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 discredited later.[5] Nevertheless, the qualitative optimization of odd-order NLO properties by tuning the BLA, varying the solvent or changing the oligomeric length could be successfully performed.[6] Similar relationships were eventually established between the BLA and two-photon absorption phenomena.[7]

In PA, the BLA is nonzero due to the Peierls theorem:[2,8] alternating electron densities appear leading to different bond lengths and hindering an infinitely long nonalternating PA that would be a 1-D periodical metal. Although the Peierls theorem does not apply to asymmetric structures, polymethineimine (PMI, a polymer isolectronic to PA where half of the CH groups are replaced by nitrogen atoms) presents a nonzero BLA as well.[9−11] Therefore, even the presence of zero/nonzero BLA is difficult to determine on a simple basis. In this work, we investigate several series of linear oligomers of increasing size in order to quantitatively assess the BLA amplitude as a function of the chemical composition of the chains, the length of the oligomers, as well as their conformation. To our knowledge, with the exception of a density functional theory (DFT) study by Salzner and co-workers on series of ring-polymer (e.g., polythiophene, polypyrrole, etc.),[12] no systematic study of the BLA has been performed for a large number of compounds, although separate numerous individual investigations do coexist.

II. Methodology

Determinations of the BLA have been performed for the set of oligomers depicted in Figure 1.[13] Note that in our notation N represents the number of unit cells, i.e., N is equal to half of the number of backbone atoms. For the reader's comfort, we did use the following nomenclature: "AB−X D(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, 2 when the nuclei lie in a plane (as in PA or PMI), or 3 for structures such as polyethylene (PE). With these conventions, PA writes CC-2D, PMI becomes CN-2D, and PE is CC-3D. PPCC-2D stands for push−pull CC-2D. If the conformation of the chain is always "linear" for 1D molecules, it can be trans−transoïd (or all-trans, TT), cis−transoïd (CT), trans−cisoïd (TC), or helical (HEL) for 2D and 3D structures. For the macromolecules ($N \rightarrow \infty$), the CT and TC conformation can be distinguished only if the BLA differs from zero: the CT (TC) chains have the double bonds parallel (perpendicular) to the longitudinal axis. For instance, trans−cisoïd aminoborane will be BN-3D-(TC).

Each oligomer geometry has been determined by the optimization of its structural parameters with the Gaussian 98[14] package. These minimizations have been performed until the rms residual force is lower than 1×10^{-5} a.u. (tight threshold

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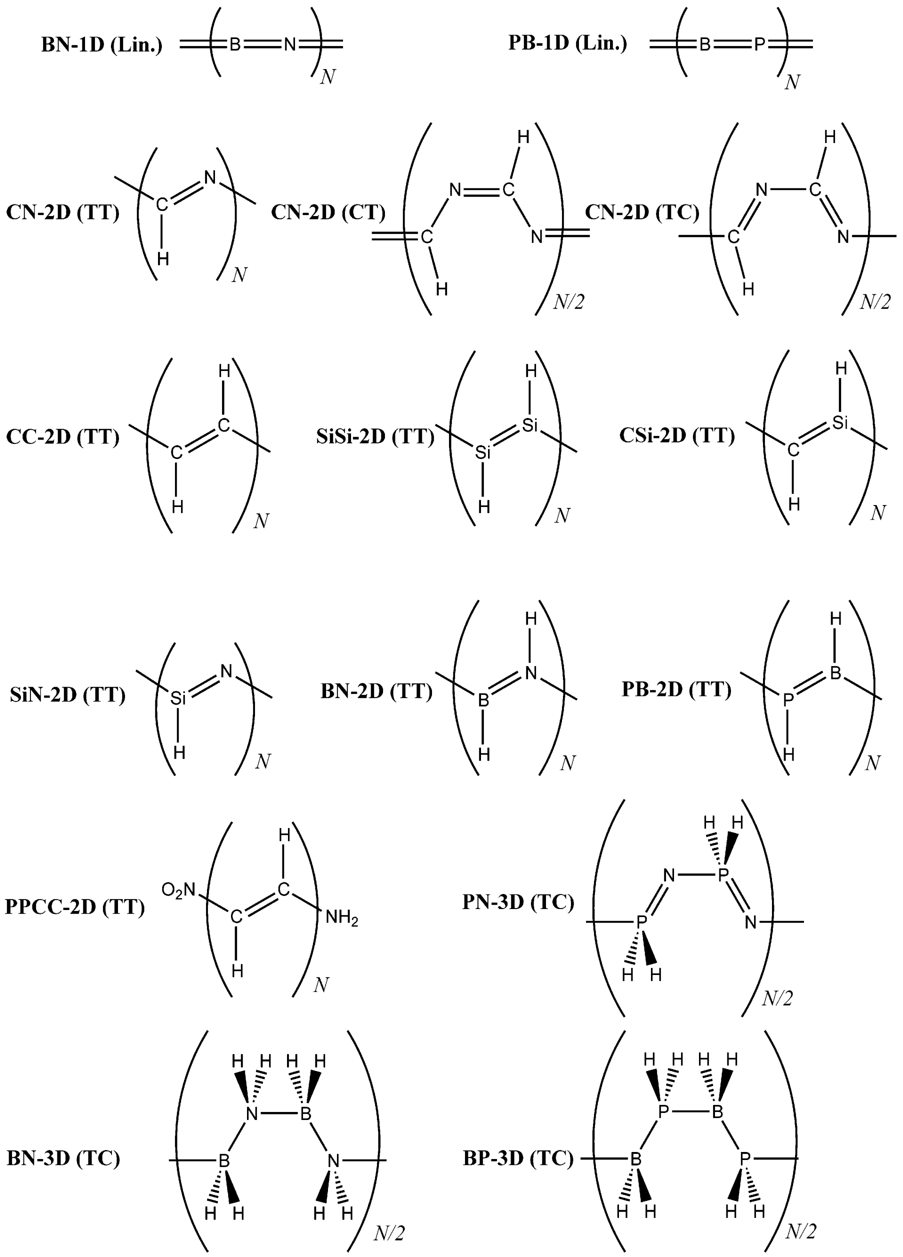

Figure 1. Sketch of the several compounds investigated.

in Gaussian 98). This corresponds to an accuracy of, at least, $\pm 1 \times 10^{-4}$ Å on BLA. In the present study, the backbone atoms have been constrained to be planar, except for BN-3D(HEL). For some polymers (for instance, PB-1D,[15] CN-2D,[16] and BP-3D[17]), other nonplanar conformations do exist, but a study of these oligomers is beyond the scope of the present paper. For BN-1D and PB-1D, the chosen conformation is linear, similar to the polyyne. For PN-3D[18] and BP-3D,[17] we have chosen the TC conformation because it leads to the most stable planar structures. For the computationaly less-demanding BN-3D, the TT, TC, and HEL conformers have been investigated.[19,20] Each 2D compound has been optimized in the three planar conformations (TT, CT, and TC). For SiN-2D, it was not possible to find a minimum corresponding to the CT conformation; that is, even in small chains CT and TC could not be distinguished. The asymmetric 2D systems (CN-2D, CSi-2D, SiN-2D, BN-2D, and BP-2D) tend to form bent, rather than linear, structures in the TT conformation. To avoid this bending effect, we have imposed all backbone valence angles to be equal in these oligomers. For CN-2D[21] and CSi-2d,[22] it has been demonstrated that this does not significantly affect the BLA.

To accurately describe the BLA, an efficient theoretical approach has to be selected. First, we note that we should exclude the Hartree−Fock (HF) approach which provides incorrect BLA in one of the simplest cases [CC-2D (TT)].[2] Indeed, HF overshoots the BLA of CC-2D (TT) by a factor of 2.[2] On the contrary, for the same compound, pure-DFT approaches strongly underestimate the BLA.[2] Therefore, the remaining available techniques are, on one hand, the hybrid-DFT schemes and, on the other hand, the dynamic electron correlated wave function approaches such as Møller−Plesset (MP), coupled-cluster (CC), etc. If the hybrid functionals such as the archetype B3LYP provide excellent results for CC-2D-(TT),[2] they are questionable for CN-2D(TT),[21] for which the difference wrt the second-order Møller−Plesset (MP2) results are ~0.03 Å for the longer chains. As the MP4 and CC schemes are not computationaly affordable for the extended systems treated here, we have selected the MP2 approach which should

TABLE 1: Basis Set Effects on the MP2 BLA of the Central Cell for Various Dimers ($N = 2$) and Tetramers ($N = 4$)[a]

	$N = 2$					$N = 4$				
basis	PB-1D (Lin.)	CN-2D (TT)	CC-2D (TT)	SiSi-2D (TT)	PN-3D (TC)	PB-1D[b] (Lin.)	CN-2D (TT)	CC-2D (TT)	SiSi-2D (TT)	PN-3D (TC)
6-31G	0.1432	0.1424	0.1168	0.1190	0.0387	0.1325	0.1218	0.0908	0.0935	0.0287
6-31G(d)	0.1328	0.1323	0.1138	0.1162	0.0585	0.1046	0.1119	0.0864	0.0865	0.0443
6-31G(2d)	0.1294	0.1347	0.1148	0.1143	0.0559	0.0999	0.1138	0.0864	0.0799	0.0435
6-31G(3d)	0.1281	0.1330	0.1121	0.1110	0.0553	0.0968	0.1116	0.0835	0.0773	0.0381
6-31G(3df)	0.1244	0.1320	0.1120	0.1124	0.0519	0.0924	0.1097	0.0831	0.0774	0.0391
6-31G(3df,p)	0.1239	0.1316	0.1120	0.1123	0.0533	0.0925	0.1098	0.0832	0.0775	0.0390
6-31+G	0.1400	0.1393	0.1139	0.1183	0.0325	0.1306	0.1202	0.0884	0.0930	0.0197
6-31+G(d)	0.1307	0.1293	0.1110	0.1150	0.0542		0.1099	0.0840	0.0846	0.0399
6-31++G(d)	0.1308	0.1292	0.1110	0.1149	0.0545		0.1099	0.0840	0.0847	0.0398
6-31+G(3df)	0.1227	0.1294	0.1094	0.1117	0.0505		0.1083	0.0811	0.0763	0.0379
6-311G	0.1414	0.1430	0.1182	0.1241	0.0422	0.1320	0.1238	0.0926	0.0995	0.0316
6-311G(d)	0.1290	0.1360	0.1147	0.1197	0.0581	0.0999	0.1152	0.0868	0.0891	0.0433
6-311G(2d)	0.1296	0.1383	0.1157	0.1182	0.0560	0.0981	0.1168	0.0865	0.0827	0.0437
6-311G(3d)	0.1256	0.1366	0.1133	0.1144	0.0569	0.0946	0.1147	0.0847	0.0797	0.0400
6-311G(3df)	0.1241	0.1353	0.1135	0.1135	0.0535	0.0918	0.1132	0.0848	0.0782	0.0404
6-311G(3df,p)	0.1237	0.1354	0.1140	0.1131	0.0542	0.0919	0.1132	0.0850	0.0782	0.0407
6-311+G	0.1436	0.1406	0.1164	0.1225	0.0346	0.1319	0.1214	0.0910	0.0969	0.0256
6-311+G(d)	0.1297	0.1332	0.1131	0.1185	0.0544		0.1134	0.0853	0.0877	0.0392
6-311++G(d)	0.1297	0.1333	0.1131	0.1185	0.0547		0.1134	0.0854	0.0876	0.0390
6-311+G(3df)	0.1237	0.1336	0.1122	0.1132	0.0521		0.1119	0.0838	0.0775	0.0391
cc-pVDZ	0.1264	0.1329	0.1111	0.1157	0.0572	0.0968	0.1119	0.0835	0.0820	0.0430
cc-pVTZ	0.1252	0.1344	0.1132	0.1142	0.0515	0.0936	0.1128	0.0845	0.0790	0.0399
cc-pVQZ	0.1247	0.1340	0.1130	0.1140	0.0505					
aug-cc-pVDZ	0.1221	0.1307	0.1080	0.1110	0.0506					
aug-cc-pVTZ	0.1234	0.1332	0.1116	0.1118	0.0491					

[a] All Values Are in Å. [b] For the PB tetramer most calculations with diffuse functions fail to converge.

provide an adequate balance between the CPU-time/memory requirements and the accuracy of ground-state geometries. As the HF BLA's are too large, and as the MP4 and CC results tend to be between the HF and the MP2 results (but much closer to MP2), the values presented in this paper should be viewed as minimal boundaries. All of the results presented in this paper have been obtained within the frozen-core approximation. For CN-2D(TT), the inclusion of the core electrons in the correlation process does not change the BLA.[21] An additional question is to determine a basis set (BS) which is sufficiently extended to obtain converged results. As we demonstrate in the next section, a selection of three basis sets, 6-31G(d), 6-311G(2d), and 6-311G(3df), offers a reasonable compromise between accuracy and computation speed.

III. Results

A. Basis Set Selection. Our goal is to determine a BS that provides an adequate size/accuracy balance for long oligomers. As no BS is totally satisfying (i.e., both small and accurately describing BLA), we have combined the results obtained with the most efficient in order to reach reliable estimates for the BLA of long chains. Table 1 presents the BLA obtained with various Pople's and Dunning's BS in order to assess which functions are actually needed to obtain a valid description of the ground-state geometry. This BS study has been carried out on five dimers and tetramers whose physicochemical characteristics cover our complete set (1D, 2D, and 3D; with/without permanent dipole moment; including second and/or third row atoms).

First, we note that the addition of polarization functions on the hydrogen atoms has a negligible impact on the BLA. Moreover this impact becomes smaller with increasing the chain length. For instance, the maximal absolute difference ($\Delta^{\max}$) between the 6-31[1]G(3df) and 6-31[1]G(3df,p) BLA is 14×10^{-4} Å for $N = 2$ but only 3×10^{-4} Å for $N = 4$. The same is true for diffuse functions with $\Delta^{\max}$ between 6-31[1]+G(d) and 6-31[1]++G(d) results limited to 3×10^{-4} Å for $N = 2$ and 2×10^{-4} Å for $N = 4$. This weak influence was expected because the BLA is not directly related to the position of the hydrogen atoms; a very accurate description of these side light atoms consequently appears unimportant for our purposes.

Except in one case (the PB-1D dimer), the addition of diffuse functions to a given BS systematically decreases the BLA for both Pople's and Dunning's BS. However, the amplitude of this effect falls down when the following occur:

1. The basis set size is increased. This is striking with Dunning's BS, where the changes brought by the aug- prefix are always smaller for cc-pVTZ than for cc-pVDZ. For all five dimers, the mean absolute deviation of BLA (Δ^{mad}) induced by diffuse functions is 42×10^{-4} Å for the cc-pVDZ but only 19×10^{-4} Å for cc-pVTZ. The same behavior is found for most of the BLA computed with Pople's split-valence BS.
2. Polarization functions are added. For instance, adding diffuse functions to 6-311G, 6-311G(d), and 6-311G(3df) produces Δ^{mad} of 29×10^{-4} Å, 20×10^{-4} Å, and 10×10^{-4} Å, respectively for $N = 2$. Similarly, we have for $N = 4$: 32×10^{-4} Å, 22×10^{-4} Å, and 11×10^{-4} Å, resepctively.[23]
3. The size of the system is increasing. For instance, the BLA variations induced by the addition of diffuse functions to 6-311G(3df) are -18×10^{-4} Å, -10×10^{-4} Å, and -8×10^{-4} Å, for the dimer, tetramer, and hexamer of CC-2D, respectively. For CN-2D [SiSi-2D], the corresponding values are -17 [-13] $\times 10^{-4}$ Å, -13 [-7] $\times 10^{-4}$ Å, and -10 [-6] $\times 10^{-4}$ Å, respectively.

On top of that, the addition of diffuse functions on extended systems often leads to quasilinear dependencies and impedes a proper convergence of the SCF process. Of course, this problem might be resolved by removing the basis set dimensions corresponding to too small eigenvalues of the metric matrix. However, this procedure may be problematic because it changes the fundamental characteristics of the initial BS and could break the symmetry of the density matrix.

At this stage, we only consider BS without diffuse functions and without extra polarization functions on the hydrogen atoms. First, we note that Δ^{mad} and Δ^{max} computed with cc-pVTZ wrt cc-pVQZ are very limited: 5×10^{-4} Å and 10×10^{-4} Å, respectively, cc-pVTZ provides converged results. On the contrary, cc-pVDZ provides quite poor results in regards of its size. Unfortunately, cc-pVTZ is still too large for our purposes: only Pople's basis sets are suitable for extended systems. For $N = 2$, Δ^{mad} is 43×10^{-4} Å, 43×10^{-4} Å, 21×10^{-4} Å, and 12×10^{-4} Å between cc-pVQZ and 6-311G(d), 6-311G(2d), 6-311G(3d), and 6-311G(3df), respectively. If the Δ^{mad} (w.r.t. cc-PVQZ) of 6-31G(3df) (13×10^{-4} Å) and 6-311G(3df) are similar, the errors on CC-2D, CN-2D, and SiSi-2D are almost multiplied by a factor of 2 compared to 6-311G(3df). For $N = 4$, Δ^{mad} is only 8×10^{-4} Å between cc-pVTZ and 6-311G(3df). Therefore, the 6-311G(3df) is chosen in order to obtain quantitative results on short oligomers. For a more qualitative approach, one could note that, once polarization functions are included, the differences between the smallest [6-31G(d)] and the largest [6-311G(3df), cc-pVTZ, and cc-pVQZ] BS are already small. Indeed, the Δ^{mad}'s between 6-31G(d) and 6-311G(3df) are 39×10^{-4} Å[24] and 56×10^{-4} Å, for $N = 2$ and $N = 4$, respectively. Actually 6-31G(d) appears to be satisfactorily balanced for qualitative purposes. Having selected a quantitative basis set [6-311G(3df)] and a more qualitative one [6-31G(d)], we have also added 6-311G(2d) to our computation list because (1) its size is intermediate; (2) for $N = 4$, it appears significantly more accurate than 6-311G(d);[25] (3) on the contrary to most BS, Δ^{mad} [wrt 6-311G(3df)] is decreasing when going from $N = 2$ to $N = 4$; and (4) for medium sized molecules (N=6 and N=8) 6-311G(2d) BLA's are consistent (systematic error) with 6-311G(3df) BLA's as we demonstrate in the following section.

To summarize, we have chosen three basis sets: 6-31G(d) for calculations on long chains (up to $N = 16$ or 20), 6-311G(2d) for intermediate chain lengths (up to $N = 8$, 10, or 12), and 6-311G(3df) for a quantitative evaluation on short oligomers (up to $N = 6$ or 8).

B. Short and Medium Chains. The MP2/6-311G(3df) and MP2/6-311G(2d) BLA's obtained for short and medium chains are reported in Tables 2 and 3, respectively. For short chains ($N = 2$, 4, and 6), the BLA is very often positive, meaning that the oligomers present a short/long/short rather than long/short/long bond pattern. The only exception is BN-3D (polyaminoborane), for which DRX experiments on the dimer also provide a negative BLA,[19] indicating the presence of strong chain-end effects for this system.[15] For BN-2D(CT), the BLA starts to be negative for $N = 8$, but the amplitude of this effect is quite small. For the 2D compound dimers, the BLA always significantly differs from zero and spans between 0.0484 Å [BN-2D(CT)] and 0.1570 Å [CN-2D(TC)]. No obvious relationship between the nature of the atoms and the BLAs could be unravelled for short chains. When going from $N = 2$ to $N = 6$, all BLA decrease (in magnitude) as expected for conjugated chains.[15,26] However, the speed of decrease is highly compound-dependent. For instance, in BN-2D(TT), BLA ($N = 6$) only amounts to 13% of the BLA ($N = 2$), whereas it is still 80% in CN-2D(CT). The conformation of the chain does affect the BLA as well as the speed of its evolution with chain length, but less significantly (typically 10%) than the nature of the nuclei. Often, the BLA of the TT chains are smaller than their TC counterparts, and the conformers ordering mainly remains unchanged when increasing chain length, at least up to $N = 8$.

TABLE 2: MP2/6-311G(3df) BLA of the Central Cell for Several Oligomers of Increasing Size[a]

compound	$N = 2$	$N = 4$	$N = 6$	$N = 8$
BN-1D (Lin.)	0.1310	0.0958	0.0716	0.0535
PB-1D (Lin.)	0.1241	0.0918	0.0812	0.0776
CC-2D (TT)	0.1135	0.0848	0.0729	0.0667
CC-2D (CT)	0.1135	0.0854	0.0745	0.0703
CC-2D (TC)	0.1289	0.1001	0.0870	0.0799
SiSi-2D (TT)	0.1135	0.0782	0.0630	0.0552
SiSi-2D (CT)	0.1135	0.0799	0.0681	0.0643
SiSi-2D (TC)	0.1236	0.0832	0.0651	0.0548
BN-2D (TT)	0.0487	0.0140	0.0064	0.0034
BN-2D (CT)	0.0484	0.0041	0.0000	−0.0007
BN-2D (TC)	0.0613	0.0230	0.0122	0.0074
CN-2D (TT)	0.1353	0.1132	0.1040	0.1004
CN-2D (CT)	0.1466	0.1250	0.1176	0.1150
CN-2D (TC)	0.1570	0.1319	0.1246	0.1197
CSi-2D (TT)	0.1075	0.0776	0.0569	0.0415
Csi-2D (CT)	0.1082	0.0743	0.0563	
CSi-2D (TC)	0.1144	0.0830	0.0578	
SiN-2D (TT)	0.0995	0.0625	0.0384	0.0252
SiN-2D (TC)	0.0899	0.0570	0.0330	
PB-2D (TT)	0.0623	0.0224	0.0119	0.0076
PB-2D (CT)	0.0628	0.0207	0.0113	
PB-2D (TC)	0.0712	0.0252	0.0101	
PPCC-2D (TT)	0.0860	0.0704		
CC-3D (TT)	0.0003	0.0002	0.0000	
SiSi-3D (TT)	0.0001	0.0002	0.0000	
PN-3D (TC)	0.0535	0.0404	0.0300	
BN-3D (TC)	−0.0410	−0.0185	−0.0033	
BN-3D (TT)	−0.1181	−0.0685	−0.0385	
BN-3D (HEL)	−0.0443	−0.0065	−0.0222	
PB-3D (TC)	0.0216	0.0156	0.0170	

[a] All Values Are in Å.

TABLE 3: MP2/6-311G(2d) BLA of the Central Cell for Several Oligomers of Increasing Size[a]

compound	$N = 2$	$N = 4$	$N = 6$	$N = 8$	$N = 10$	$N = 12$
BN-1D (Lin.)	0.1343	0.0994	0.0751	0.0566	0.0427	0.0325
PB-1D (Lin.)	0.1296	0.0981	0.0873	0.0838	0.0821	0.0807
CC-2D (TT)	0.1157	0.0865	0.0746	0.0683	0.0647	0.0627
CC-2D (CT)	0.1157	0.0876	0.0767	0.0725	0.0706	0.0698
CC-2D (TC)	0.1314	0.1013	0.0883	0.0814	0.0772	0.0747
SiSi-2D (TT)	0.1182	0.0827	0.0675	0.0599	0.0559	0.0539
SiSi-2D (CT)	0.1182	0.0825	0.0700	0.0649	0.0628	
SiSi-2D (TC)	0.1279	0.0890	0.0723	0.0634	0.0584	
BN-2D (TT)	0.0506	0.0157	0.0072	0.0039	0.0023	0.0015
BN-2D (CT)	0.0502	0.0048	0.0004	−0.0004	−0.0003	−0.0002
BN-2D (TC)	0.0636	0.0257	0.0136	0.0082	0.0051	0.0033
CN-2D (TT)	0.1383	0.1168	0.1073	0.1039	0.1019	0.1004
CN-2D (CT)	0.1503	0.1291	0.1223	0.1197	0.1178	0.1160
CN-2D (TC)	0.1620	0.1371	0.1298	0.1253	0.1218	0.1186
CSi-2D (TT)	0.1084	0.0804	0.0601	0.0445	0.0329	0.0245
Csi-2D (CT)	0.1087	0.0771	0.0597	0.0459	0.0357	
CSi-2D (TC)	0.1157	0.0868	0.0618	0.0433	0.0304	
SiN-2D (TT)	0.0965	0.0655	0.0406	0.0267	0.0182	0.0128
SiN-2D (TC)	0.0895	0.0602	0.0353	0.0215	0.0139	
PB-2D (TT)	0.0657	0.0242	0.0129	0.0082	0.0056	0.0039
PB-2D (CT)	0.0657	0.0208	0.0127	0.0111	0.0110	
PB-2D (TC)	0.0752	0.0280	0.0121	0.0043	−0.0005	
PPCC-2D (TT)	0.0871	0.0718	0.0667	0.0636		
CC-3D (TT)	0.0007	0.0002	0.0000	0.0000		
SiSi-3D (TT)	−0.0003	0.0002	0.0000	0.0000		
PN-3D (TC)	0.0560	0.0437	0.0320	0.0232		
BN-3D (TC)	−0.0417	−0.0188	−0.0031	0.0040		
BN-3D (TT)	−0.1209	−0.0697	−0.0391	−0.0239		
BN-3D (HEL)	−0.0453	−0.0257	−0.0120	−0.0056		
PB-3D (TC)	0.0190	0.0159	0.0174	0.0176		

[a] All Values Are in Å.

The amplitude of the MP2/6-311G(2d) BLA is all long too large. This is striking because even in BN-3D for which the BLA is negative, the absolute value of the MP2/6-311G(2d) BLA is too large, i.e., using the 6-311G(2d) BS always leads to an overshooting of the BLA. The only exceptions are the dimers of SiN-2D and SiSi-3D for which the differences between 6-311G(2d) and 6-311G(3df) results are negligible ($<4 \times 10^{-4}$ Å). For 2D chains, the largest BS-related difference is 9×10^{-3} Å for the octamer of SiSi-2D(TC), whereas its mean counterpart is remarkably constant from $N = 4$ to $N = 6$ (3×10^{-3} Å). These discrepancies are smaller than the differences between compounds, meaning that 6-311G(2d) gets, at least, the good ordering of the compounds. On top of that, for a given oligomeric series, the 6-311G(3df) and 6-311G(2d) BLA's differ by a constant or by a smoothly decreasing amount (provided $N \geq 4$). In the first category, one finds CN-2D, CC-2D, and SiSi-2D.[27] For instance, in CC-2D(CT)/SiSi-2D(TT), the corrections to the 6-311G(2d) values are $-2/-5 \times 10^{-3}$ Å for all oligomers. However, note that the corrections are conformation dependent, especially for SiSi-2D. BN-2D and PB-2D lie in the second category. For example for PB-2D(TT), the differences between the 6-311G(2d) and 6-311G(3df) BLA are $-3/-2/-1 \times 10^{-3}$ Å for $N = 2$, 4, and 6, respectively. This seems to indicate that the BLA is rapidly going to zero (see the next section). Figure 2 gives a plot of the evolution with chain length of the MP2/6-311G(2d) BLA for 2D compounds. It turns out that the ordering of the compounds remains unchanged from $N = 4$ to $N = 12$, except for PPCC-2D(TT). Indeed, for long push−pull chains, the central BLA becomes equivalent to that in the unsubstituted CC-2D(TT) chains, as could have been foreseen. From the graph of Figure 2, one can already identify two groups of compounds. In the first (CN, CC, SiSi, and PPCC), the BLA levels to a nonzero value, whereas in the second (CSi, BN, PB, and SiN), the BLA quickly decreases and looks like tending toward a small limit. By comparing panels a−c in Figure 2, one notes that the conformation does not strongly modify the decay speed nor the ordering of the different compounds. However, for long BN-2D(CT) and PB-2D(TC), the BLA becomes slightly smaller than zero; that was not found for TT chains. Except for boron systems which show a small (or zero) polymeric BLA, it is difficult to draw consistent conclusions about the nuclei substitution. Indeed, by changing C into N in CC-2D, one increases the BLA, whereas one strongly decreases it in SiSi-2D. At this stage, one can state that CN-2D and PB-1D are exceptional: they are the only asymmetric unit cell system presenting a large BLA.

C. Long Chains and Polymers. The MP2/6-31G(d) BLAs are reported in Table 4. Contrary to what has been observed with 6-311G(2d), the deviations between the 6-31G(d) and 6-311G(3df) (1) can be large ($\sim 1 \times 10^{-2}$ Å) especially for SiSi-2D, CSi-2D and PB-1D, (2) may significantly vary with chain and often tend to increase with N, and (3) are not systematic. For instance, the MP2/6-31G(d) BLA's are too small for CN-2D but too large for CC-2D. Nevertheless the qualitative ordering of the compounds is respected with the striking exception of SiSi-2D which is too close to CC-2D if 6-31G(d) is used.

The BLA evolution speed wrt N strongly differs from one compound to another. For instance, the BLA stands almost constant for CN-2D between $N = 8$ and $N = 16$, but it decreases by ∼75% for SiN-2D. The compounds with the fastest decrease (more than -1×10^{-2} Å from $N = 8$ to $N = 16$) tend to give very small BLAs. Figure 3 displays the evolution with chain length of the BLA for a selected series of compounds presenting typical shapes. CC-2D(TT) and SiN-2D(TT) have quite similar BLA for $N = 2$ and 4, but the latter shows a much more pronounced BLA decrease when the chain lengthens. If one uses boron instead of silicon, the fall-off is even faster and the BLA is almost zero, provided $N \geq 8$. However, the speed of decrease for the first oligomers does not indicate that the BLA of the polymer will be exactly zero, as one can check with both PB-2D conformers depicted in Figure 3. For the 3D systems, we

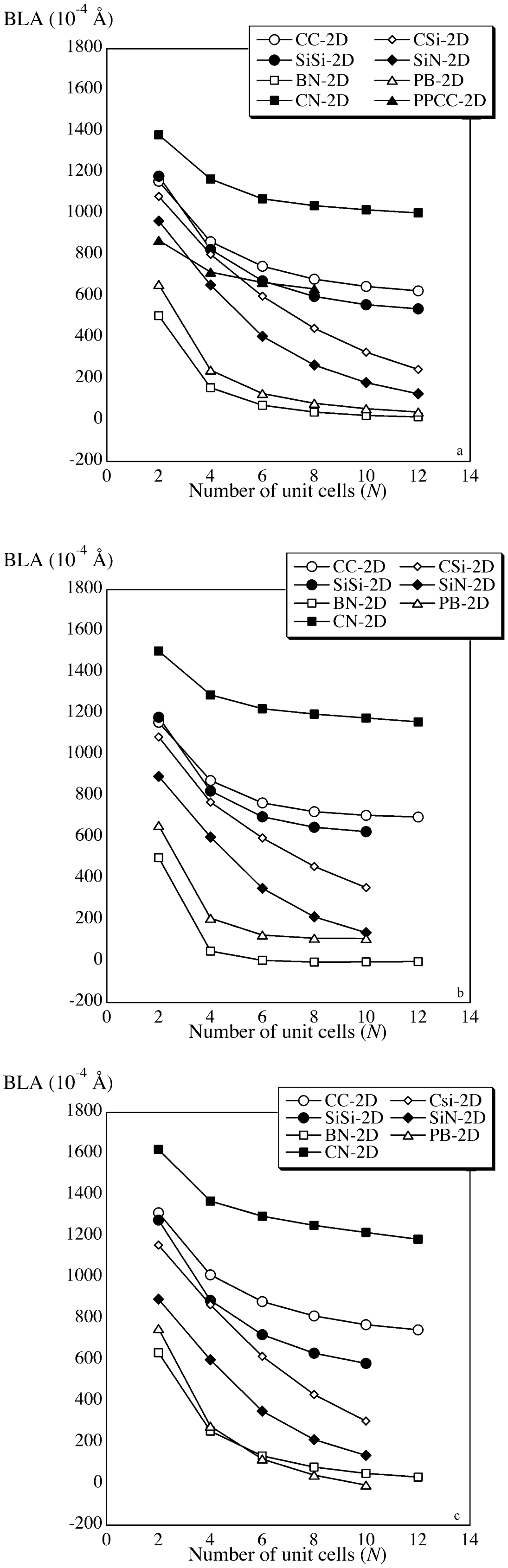

Figure 2. Evolution with chain length of the MP2/6-311G(2d) BLA of the various 2D structures. (a) TT conformers, (b) CT conformers, and (c) TC conformers.

TABLE 4: MP2/6-31G(d) BLA of the Central Cell for Several Oligomers of Increasing Size[a]

compound	$N = 2$	$N = 4$	$N = 6$	$N = 8$	$N = 10$	$N = 12$	$N = 14$	$N = 16$	$N = 18$	$N = 20$	$N = \infty$
BN-1D (Lin.)	0.1316	0.0987	0.0750	0.0568	0.0430	0.0328	0.0251	0.0196	0.0153	0.0121	0.000
PB-1D (Lin.)	0.1328	0.1046	0.0961	0.0938	0.0930	0.0923	0.0914	0.0899	0.0892	0.0880	[b]
CC-2D (TT)	0.1138	0.0864	0.0756	0.0700	0.0669	0.0652	0.0642	0.0636	0.0634	0.0633	0.061 ± 0.002
CC-2D (CT)	0.1138	0.0873	0.0772	0.0733	0.0714	0.0707	0.0703	0.0701	0.0701	0.0701	0.070
CC-2D (TC)	0.1274	0.0994	0.0880	0.0821	0.0787	0.0769	0.0759	0.0752	0.0748	0.0746	0.074 ± 0.001
SiSi-2D (TT)	0.1162	0.0865	0.0745	0.0688	0.0660	0.0647	0.0639	0.0637	0.0635	0.0634	0.062 ± 0.001
SiSi-2D (CT)	0.1162	0.0867	0.0764	0.0723	0.0705	0.0698	0.0695	0.0693			0.069
SiSi-2D (TC)	0.1232	0.0922	0.0803	0.0745	0.0717	0.0703	0.0695	0.0692			0.067 ± 0.001
BN-2D (TT)	0.0486	0.0155	0.0072	0.0038	0.0023	0.0014	0.0009	0.0006	0.0004	0.0003	0.000
BN-2D (CT)	0.0482	0.0045	0.0002	−0.0008	−0.0007	−0.0006	−0.0005	−0.0003	−0.0002	−0.0001	
BN-2D (TC)	0.0615	0.0257	0.0141	0.0086	0.0056	0.0037	0.0024	0.0015	0.0012	0.0008	≠0[d]
CN-2D (TT)	0.1323	0.1119	0.1030	0.1000	0.0985	0.0975	0.0967	0.0960	0.0954	0.0950	0.091 ± 0.003
CN-2D (CT)	0.1442	0.1245	0.1184	0.1165	0.1150	0.1137	0.1124	0.1112	0.1102	0.1091	0.095 ± 0.008
CN-2D (TC)	0.1519	0.1297	0.1236	0.1201	0.1173	0.1148	0.1127	0.1108	0.1091	0.1076	0.094 ± 0.005
CSi-2D (TT)	0.1116	0.0868	0.0692	0.0542	0.0418	0.0323	0.0251	0.0197	0.0156	0.0124	0.000
Csi-2D (CT)	0.1116	0.0832	0.0679	0.0543	0.0435	0.0350	0.0286	0.0236			≠0[d]
CSi-2D (TC)	0.1184	0.0943	0.0722	0.0534	0.0392	0.0286	0.0209	0.0152			≠0[d]
SiN-2D (TT)	0.1006	0.0718	0.0460	0.0308	0.0213	0.0151	0.0110	0.0082	0.0063	0.0050	0.000 ± 0.001
SiN-2D (TC)	0.0899	0.0662	0.0400	0.0245	0.0164	0.0103	0.0064	0.0039			0.000
PB-2D (TT)	0.0628	0.0226	0.0116	0.0071	0.0047	0.0032	0.0022	0.0016	0.0012	0.0009	0.000 ± 0.001
PB-2D (CT)	0.0628	0.0202	0.0116	0.0094	0.0087	0.0084	0.0084	0.0084			0.008
PB-2D (TC)	0.0704	0.0259	0.0113	0.0045	0.0005	−0.0021	−0.0038	−0.0052			−0.008 ± 0.005[e]
PPCC-2D (TT)	0.0854	0.0720	0.0682	0.0658	0.0645	0.0638	0.0634	0.0632			0.061 ± 0.002[c]
CC-3D (TT)	0.0005	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.000
SiSi-3D (TT)	0.0018	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.000
PN-3D (TC)	0.0585	0.0443	0.0339	0.0251	0.0197	0.0157	0.0131	0.0110			0.006 ± 0.004
BN-3D (TC)	−0.0436	−0.0189	−0.0024	0.0052	0.0103	0.0130	0.0152	0.0164			0.022 ± 0.005
BN-3D (TT)	−0.1314	−0.0710	−0.0386	−0.0231	−0.0148	−0.0101	−0.0072	−0.0053			0.000 ± 0.003
BN-3D (HEL)	−0.0480	−0.0097	−0.0209	−0.0065	−0.0030	−0.0011	−0.0032	0.0046			[b]
PB-3D (TC)	0.0089	0.0096	0.0127	0.0135	0.0143	0.0147	0.0150	0.0152			0.017 ± 0.002

[a] All values are in Å. At the right of the table, the values extrapolated for the polymer are given (see the text for more details). [b] The nonsmooth behavior prevents meaningful extrapolation. [c] The same as for PA(TT). [d] No proper extrapolation could be performed but the BLA, although small, is probably different from zero. [e] It seems likely that TC and CT PB-2D chains converge to the same limit.

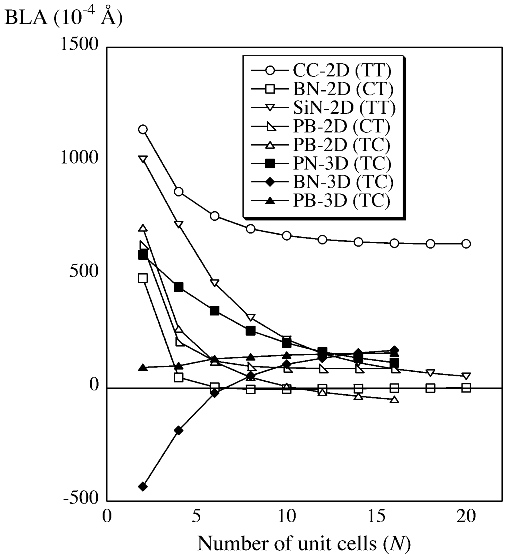

Figure 3. Evolution with chain length of the MP2/6-31G(d) BLA for a selected series of compounds.

have a variety of behaviors. Indeed, the PN-3D(TC) curve is like the CC-2D(TT) but displaced to smaller BLA; for PB-3D(TC), the BLA is increasing with chain length, whereas for BN-3D(TC), the BLA is first negative and passes through zero between $N = 6$ and $N = 8$. Eventually, all of these three present similar polymeric BLA.

To obtain an accurate estimate of the polymeric BLA, a 4-step procedure has been used:

1. A simple test was carried out to check if the MP2/6-31G(d) BLA tends to zero when $N \rightarrow \infty$. For this, we use a simple exponential fit on the whole set of points

$$\mathrm{BLA}(N) = a\mathrm{e}^{-bN} \tag{1}$$

If the regression coefficient (R) is larger than 0.999, we consider this exponential model to be satisfying, and the polymer BLA was set to zero.

2. When this first fit is not satisfying, we carry out extrapolations of the MP2/6-31G(d) BLA using three different fitting functions,[28,29] the first being a simple power series in $1/N$[30]

$$\mathrm{BLA}(N) = a + \frac{b}{N} + \frac{c}{N^2} \tag{2}$$

the second is an exponentially decreasing function[31,32]

$$\mathrm{BLA}(N) = a + b\mathrm{e}^{-cN} \tag{3}$$

whereas the third is the logistic function[33]

$$\mathrm{BLA}(N) = \frac{a}{1 + b\mathrm{e}^{-cN}} \tag{4}$$

In these three equations, the asymptotic BLA(∞) is given by a and is obtained from least-squares fits. The number of points included in each fit ranges from 4 to 8 in order to be statistically significant with respect to the number of parameters. We use several series of points to obtain the MP2/6-31G(d) BLA(∞) and an estimate of the extrapolation error. We refer the reader to ref 29 for more details on this procedure.

3. The MP2/6-31G(d) BLAs(∞) are corrected for basis set error by using the difference or the ratio (the fastest converging) between the MP2/6-311G(2d) and MP2/6-31G(d) BLAs for $N = 8$, 10, and 12. For chains with very fast BLA convergence, we have also extrapolated the MP2/6-311G(2d) BLA as described in steps 1 and 2.

4. The MP2/6-311G(2d) BLAs(∞) are corrected by using the differences between MP2/6-311G(2d) and MP2/6-311G(3df)

TABLE 5: Best Estimates of the Polymeric MP2/6-311G(3df) BLA[a]

compound	BLA(∞)	compound	BLA(∞)
CC-2D (TT)	0.056	CN-2D (CT)	0.090
CC-2D (CT)	0.067	CN-2D (TC)	0.095
CC-2D (TC)	0.066	PB-2D (CT)	0.010
SiSi-2D (TT)	0.045	PN-3D (TC)	0.002
SiSi-2D (CT)	0.059	BN-3D (TC)	0.020
SiSi-2D (TC)	0.041	BP-3D (TC)	0.018
CN-2D (TT)	0.091		

[a] All values are in Å. See the text for more detail on how these values have been obtained.

BLAs ($N = 6$ and $N = 8$), which is almost constant for all chain length as seen in section II.B.

The extrapolated 6-31G(d) BLAs are found at the right-hand-side of Table 4. For most macromolecules we could obtain a satisfying accuracy. We set up three categories: in the first the polymeric BLA significantly differs from zero (> 0.03 Å); in the second, the polymeric BLA is very small but non zero; in the third, the BLA is exactly zero. For the two first categories, our best (i.e., MP2/6-311G(3df)) BLA estimates are given in Table 5. In the first category, one finds CC-2D, SiSi-2D, and CN-2D (and probably PB-1D). For these three systems, the conformation of the chain significantly affects the polymeric BLA (especially for SiSi-2D) but the ordering of the different conformers cannot be foreseen on a simple basis. For instance the smallest BLA is obtained for TT in the case of CC-2D but TC for SiSi-2D and CT for CN-2D. In the second category, one finds PB-2D(CT) [which in the infinite chain limit probably becomes equivalent to PB-2D(TC)], PN-3D(TC), BN-3D(TC), and BP-3D(TC). The two latter correspond to transition-states-like structures[17,20] whereas PN-3D(TC) is a minimum at the MP2 level of theory.[34] To this list, one could add CSi-2D(CT and TC) and probably BN-2D(TC). These systems show nonzero first hyperpolarizabilities per unit cell for long chains[22,35] indicating non centro-symmetric polymers, i.e., a non zero BLA. It is striking to note that the corresponding TT macromolecules are centro-symmetric, indicating that TT conformers are more likely to display a zero BLA than CT or TC polymers. In addition to these TT chains, one finds in the third category the SiN-2D chains and, as expected, the saturated compounds CC-3D and SiSi-3D.

IV. Conclusion

We have studied with three atomic basis sets the bond length alternation of a bunch of increasingly long oligomers. For three compounds (CC-2D, SiSi-2D, and CN-2D), it can be predicted that the bond length alternation of the polymer significantly differs from zero for the three planar conformations used in this investigation. For the two first systems, this alternating structure is explained by the Peierls theorem but CN-2D appears to constitute an exception. Indeed, most macromolecules used in this study present a zero or very small BLA. The TT conformers are more likely to present a zero polymeric BLA.

For CN-2D, SiSi-2D, and CN-2D, one notes that the difference between BLA of the octamer and dimer is relatively small and that changing the BS modifies the BLA by a constant amount for every N. The reverse is found for the other compounds. Therefore calculations on relatively short oligomers already provide an indication of trends for longer chains.

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(13) In this figure, the different conformers have not been shown for all series of compounds.

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(23) For $N = 4$, the Δ^{mad}(BLA) is obtained with 4 rather than 5 compounds because most calculations including diffuse functions fail to converge for the tetramer of PB-1D.

(24) For $N = 2$, Δ^{mad}(BLA) between 6-31G(d) and cc-pVQZ is 42×10^{-4} Å.

(25) For $N = 4$, Δ^{mad}(BLA) between 6-311G(d)/6-311G(2d) and 6-311G-(3df) are $52/39 \times 10^{-4}$ Å. The corresponding Δ^{max}(BLA) are $62/109 \times 10^{-4}$ Å.

(26) The BN-3D(HEL) oligomers present a 4-cell rather than a 2-cell pattern, which explains the apparently nonsmooth evolution.

(27) The CT form looks like an exception for SiSi-2D.

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