Structures and Properties of Polyphosphinoborane: an Oligomeric Theoretical Study

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ABSTRACT: We have investigated the structures and properties of polyphosphinoborane oligomers by using ab initio computational tools, including electron correlation effects. The key data evaluated include geometries, conformations, rotational profiles, infrared spectra, vertical excitation energies, atomic charges, and dipole moments which can significantly depend on the conformation adopted by polyphosphinoborane.

I. Introduction

High molecular weight polyphosphinoboranes (PPB, Figure 1) have recently been synthesized with the help of rhodium catalysts by Dorn, Manners, and co-workers.[1−3] Similarly to other phosphorus containing polymer such as polyphosphazene (PP), the use of PPB as flame retardant material has been anticipated. PP presents a structure similar to PPB where the BH_2 groups have been replaced by nitrogen atoms. Probably due to the fact that the actually synthesized polymer is mainly amorphous, little is known about the properties of PPB. In this contribution, we have used theoretical tools to investigate the properties of unsubstituted PPB ($R_1 \equiv R_2 \equiv H$ in Figure 1), determining stable conformations, charges, excitation energies, vibrational spectra, etc. This allows, on one hand, to confirm/contradict some of the experimental assumptions and, on the other hand, to provide results that would help in the determination of the structure if the crystallinity of PPB is improved.

II. Computational Details

For our investigations we have selected the second-order Møller−Plesset (MP2) scheme if possible (from a cpu-time point of view) and, the hybrid B3LYP functional or the Hartree−Fock (HF) approximation, in the other cases. We have used Pople's polarized split-valence basis sets, 6-31G*, 6-31G**, and 6-311G*. As demonstrated in section IIIA, the agreement between MP2/6-311G* and X-ray structures is satisfactory for small PPB oligomers, whereas B3LYP/6-311G* provides slightly less accurate results and HF/6-31G* could only be used for qualitative purposes. The calculations have been performed for the unsubstituted chains (i.e., $R_1 \equiv R_2 \equiv H$ in Figure 1) with Gaussian 98[4] by using the following procedure.

1. Geometry Optimization. The ground-state geometry of each oligomer has been determined by a full optimization of its structural parameters. These minimizations have been performed until the rms residual force is lower than 1×10^{-6} a.u. (this corresponds to the *verytight* threshold in Gaussian 98) when the geometries are used for vibrational spectra calculation. In the other cases, the *tight* threshold (rms residual forces lower than 1×10^{-5} a.u.) has been used. The rotational profiles have been obtained by fixing one coordinate (the ad hoc dihedral angle) and optimizing all the other parameters.

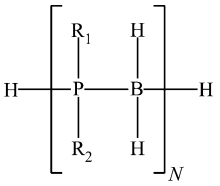

Figure 1. Illustration of the polyphosphinoborane oligomers.

2. Vibrational Spectra. The vibrational frequencies and related intensities have been obtained by a fully analytic determination of the Hessian. Real-looking spectra have been obtained by convoluting the theoretical results, using a mixed Lorentzian (80%)/Gaussian (20%) function with two different full width at half-maximum (fwhm = 5 and 25 cm^{-1}).[5] At the B3LYP level, the Hessian has been determined by using an *ultrafine* integration grid (pruned (99,590) grid[6]) during the Hessian calculations and the related geometry optimizations. Indeed, this grid is recommended to perform accurate geometry optimizations and to produce correct frequencies of all vibrational modes of molecules. Scaling factors have been used to reduce residual discrepancy between the computed frequencies and the experimental values.[7−10]

3. Charges and Dipole Moment. Among the several methods available to describe partial atomic charges in a molecule, we have selected an electrostatic potential-derived formalism that has proved to yield charges that are consistent with experimental data.[11] Our Merz−Kollman charges[12] (so-called MK or ESP charges) are obtained with virtually no CPU extra cost with respect to the Mulliken approximation. The norm of the dipole moment ($|\mu|$) has been obtained on the basis of these ESP charges. The $|\mu|$ obtained in this way are almost equivalent to the $|\mu|$ obtained by the standard expectation value formula.

4. Excitation Energies. We have computed the singlet-state excitation energies by using the time-dependent density functional theory (TFDFT),[13] as implemented in Gaussian 98, with the B3LYP functional. This procedure provides excitation energies that are comparable to experiment results (see ref 14 and references therein). Up to fifty states have been used during these calculations in order to reach an excited state significantly coupled with the ground state.

5. Ionization Potentials and Electroaffinities. These properties have been obtained by the outer-valence Green function (OVGF) method. OVGF provides values in excellent agreement with experimental measurements.[15,16]

III. Discussion

A. Choice of a Theoretical Approach. In 2000, Dorn et al. published the X-ray structure of the dimer-

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Table 1. Comparisons between the Theoretical and Experimental[2] Parameters of the Molecule Sketched in Figure 2 (and Figure 3 of Ref. 2)[a]

	experiment		HF			DFT (B3LYP)			MP2	
parameter	DRX	MNDO	6-31G*	6-31G**	6-311G*	6-31G*	6-31G**	6-311G*	6-31G*	6-311G*
d_{P1-B1}	1.924	2.004	1.995	1.994	1.986	1.951	1.951	1.943	1.939	1.932
d_{P1-H1P}	1.33	1.346	1.388	1.390	1.391	1.408	1.408	1.408	1.402	1.403
d_{P1-H2P}	1.33	1.346	1.390	1.393	1.395	1.414	1.414	1.413	1.409	1.407
d_{B1-H1B}	1.12	1.165	1.209	1.209	1.211	1.213	1.211	1.210	1.211	1.213
d_{B1-H2B}	1.10	1.165	1.208	1.207	1.209	1.211	1.209	1.208	1.209	1.211
d_{B1-H3B}	1.12	1.167	1.209	1.209	1.211	1.212	1.210	1.210	1.209	1.210
$\alpha_{H1P-P1-B1}$	112.9	113.4	114.9	114.9	114.9	116.0	115.9	115.7	117.0	116.6
$\alpha_{H2P-P1-B1}$	114.0	113.4	114.5	113.7	114.2	113.9	114.0	114.2	113.7	113.9
$\alpha_{H1B-B1-P1}$	106	100.4	104.1	104.8	105.1	104.0	104.0	104.0	105.2	105.4
$\alpha_{H2B-B1-P1}$	105	100.4	105.9	105.2	105.6	105.7	105.1	105.9	105.0	105.5
$\alpha_{H3B-B1-P1}$	103	98.2	104.9	103.9	103.6	105.0	104.9	105.2	104.7	104.9

[a] We have used the notation given in Ref. 2. Bond lengths are in Å, valence angles in degrees.

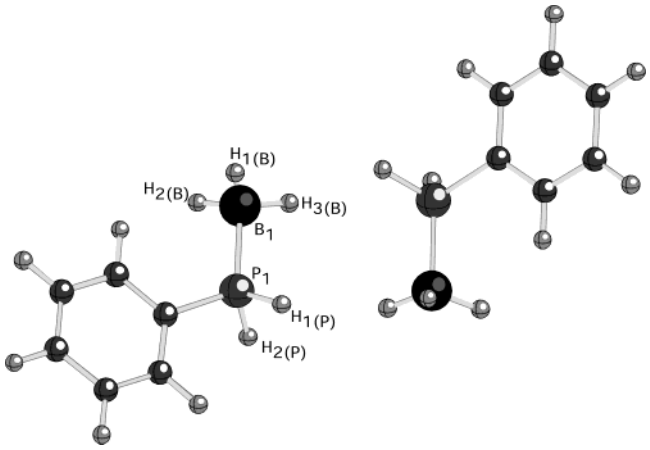

Figure 2. Structure of the $PhPH_2BH_3$ dimer studied in Table 1. We have used the notation given in ref 2.

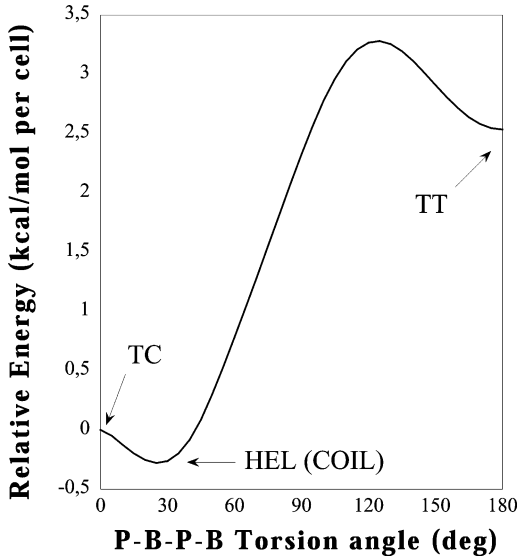

Figure 3. MP2/6-311G* rotational profile (kcal/mol per cell) for the PPB dimer ($N = 2$ and $R_1 \equiv R_2 \equiv H$ in Figure 1). TC, HEL (COIL), and TT indicates the positions of the trans-cisoid, helicoidal (coiled), and trans-transoid conformations. By convention, the relative energy of the latter has been set to zero. This profile is symmetric with respect to $\tau_{P-B-P-B} = 180$ degrees.

ized phenyl monomer (see Figure 2 of the present work or Figure 3 in ref 2). From Table 1, one could see that, with the exception of semiempirical MNDO, all the selected theoretical approaches produce longer BH and PH bonds than the experiment. However, as noted by Dorn, X-ray spectroscopy underestimates strongly the P−H and B−H bond lengths. Indeed, the geometrical parameters obtained by all ab initio approaches, (with the exception of MNDO) fit very well with the bond lengths measured by neutron diffraction and microwave spectroscopy (d_{B-H}: 1.21 Å; d_{P-H}: 1.40 Å, see ref 2). MNDO can straightforwardly be discarded as it leads to qualitatively incorrect bond lengths.

A significant bit of data for assessing the quality of a theoretical approach is the P−B bond length. HF P−B distance is far away from the X-ray results ($\Delta = 0.062-0.071$ Å) while B3LYP shortens the theory−experiment gap ($\Delta = 0.019-0.027$ Å) and MP2 is quite on the spot ($\Delta = 0.008-0.015$ Å). From Table 1 one can conclude that a triple-ζ atomic basis set is required to reach quantitative accuracy. The P−B bond lengths are shorter at the MP2 level than at the HF level. Although this may look surprising at a first glance, similar trends have been found for other polymers.[17] For valence angles, all schemes except MNDO, are within 2 degrees of the X-ray results, with the exception of $\alpha_{H1P-P1-B1}$, which is systematically overestimated, possibly due to some solid state (packing ?) effect. Our methodological ace would consequently be MP2/6-311G*, which provides the best theory/experiment agreement. Except when noted, it is the default level of approximation used in all the calculations described in the following. However, as the MP2/6-311G* approach is highly demanding, we also use B3LYP/6-311G* for vibrations or, when necessary, the more accessible HF/6-31G* approach for assessing the qualitative convergence speed with chain length of a property.

B. Conformation and Relative Energies. The rotational profile (around the P−B−P−B dihedral angle) of the dimer ($R_1 \equiv R_2 \equiv H$ and $N = 2$, see Figure 1) is shown in Figure 3. Among the planar conformations, the trans-cisoid (TC) chains are more stable than the trans-transoid (TT) oligomers. Moreover, a 25.7 degree deviation of the dihedral angle in the TC dimer leads to the global minimum, identified as the helicoidal (HEL) [or coiled (COIL), see below] chain. Although less energetically favored, the TT compounds correspond to a minimum in the rotational profile, whereas the TC chains are similar to a transition state between two helicoidal structures (one with a positive dihedral angle, one with a negative dihedral angle). This is confirmed by a vibrational analysis: all the frequencies of the TT dimer are real, whereas its TC counterpart presents one imaginary frequency. Nevertheless, TC conformation might be favored by a substitution of PPB by side groups, or by special experimental conditions as a quick cooling process.

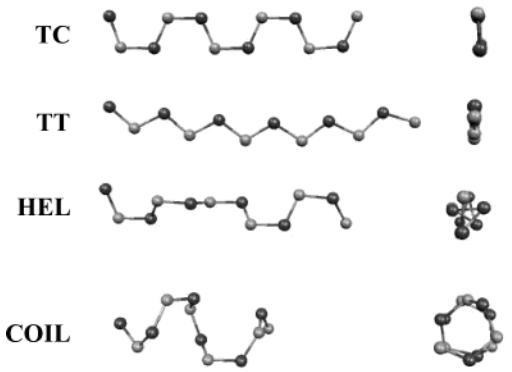

Figure 4. Side (left) and top (right) views of the MP2/6-311G* optimized structures of the PPB hexamer. From top to bottom: TC, TT, HEL, and COIL conformations. Phosphorus atoms are in dark-gray, boron nuclei in light-gray, hydrogens have been omitted for clarity.

Table 2. Relative Energy Per Unit Cell for the Four Conformers (TC energy is set to zero by convention)[a]

N	TC	TT	HEL	COIL
2	0.00	+2.53	−0.29	−0.29
4	0.00	+1.84	−0.74	−1.09
6	0.00	+1.30	−0.97	−0.97
8	0.00	+0.95		

[a] All values have been obtained with the MP2/6-311G* approach and are given in kcal/mol. *N* is the number of unit cell. For the dimer, HEL and COIL chains are the same.

For longer chains, there are numerous possible dihedral angles for the PPB backbone. To identify the most stable structures, two procedures have been used. (1) A distortion of the TC tetramer ($N = 4$) geometry along the three vibrational coordinates presenting imaginary frequencies. The resulting geometries are used as starting points for geometry optimizations, leading to the three hypothetical structures.[18] (2) Subsequent analysis of procedure 1 shows that the variations of the dihedral angles wrt the planar TC form are always ±30 degrees for dihedral P−B−P−B angles and ±10 degrees for B−P−B−P dihedral angles. By considering that some periodicity is desired for helicoidal chains, there are six nonequivalent possibilities (for the polymer) remaining.[19] We have used these six geometries as starting points for additional geometry optimizations.

Some of the stationary geometries determined by this second procedure are equivalent to those obtained via procedure 1. From procedures 1 and 2, it turns out that the most stable helicoidal tetramer has dihedral angles (from PH_3 end to BH_3 end) of 32.4, 176.6, 42.4, 178.0, 37.4 degrees. This structure is stable as confirmed by vibrational spectra analysis (no imaginary frequency). The TT, TC, and HEL systems have their spatial extension mainly in one direction (see Figure 4). However, as noted by Sun for PP,[20] phosphorus-containing polymers may form coiled structures.[21] We have tested this possibility by using the tetramer. It appears that (at least) one coil presents a stability similar to the helix.[22]

Table 2 gives the relative energies of increasingly long PPB oligomers in the four considered conformations (Figure 4). The differences reported in Table 2 are small: it is easy to modify the conformation of PPB. For comparison, in PP, which is considered very flexible, the rotation barrier between TT and TC is 5 kcal/mol per cell,[20] twice as much as for PPB. This larger flexibility of PPB is probably related to the pure single bond character of the backbone bonds (see next section). In PP, the character of the bonds is more mixed (single/double).[20] As a consequence of the significant flexibility of PPB, it is reasonable to think that the four conformations of PPB might coexist in the real-life experiment. At least, the results of Table 2 do not allow to disregard one particular conformation as being unstable. This is particularly true when chains lengthen as the energetic differences vanish.[23] Therefore, for the macromolecule, the four conformers are predicted as almost energetically equivalent even though off-planar systems (HEL and COIL) are very slightly favored (∼1 kcal/mol per cell).[23]

Table 3. Bond Lengths of PPB Oligomers Measured at the Chain Center

Planar

	TC				TT			
N	d_{B-P}	d_{P-B}	d_{P-H}	d_{B-H}	d_{B-P}	d_{P-B}	d_{P-H}	d_{B-H}
2	1.954	1.939	1.406	1.205	1.941	1.929	1.412	1.204
4	1.954	1.940	1.403	1.210	1.940	1.941	1.412	1.205
6	1.957	1.941	1.404	1.208	1.939	1.940	1.411	1.205
8	1.957	1.941	1.404	1.208	1.940	1.940	1.411	1.205

Nonplanar

	HEL				COIL			
N	d_{B-P}	d_{P-B}	d_{P-H}	d_{B-H}	d_{B-P}	d_{P-B}	d_{P-H}	d_{B-H}
2	1.947	1.937	1.406	1.204	1.947	1.937	1.406	1.204
4	1.940	1.937	1.404	1.208	1.947	1.944	1.404	1.206
6	1.941	1.938	1.405	1.207	1.959	1.955	1.405	1.203

[a] d_{B-P} is the length found for the central bond (even numbered) whereas d_{P-B} is the length of the previous bond (odd numbered). See Figure 5. All values are in Å and have been obtained at the MP2/6-311G* level. For HEL and COIL, the reported P−H and B−H distances correspond to the shortest bonds at the center of the oligomers.

Table 4. Selected Valence Angles of PPB Oligomers Taken at the Center of the Oligomers (see Figure 5)[a]

Planar

	TC				TT			
N	α_{B-P-B}	α_{P-B-P}	α_{H-P-H}	α_{H-B-H}	α_{B-P-B}	α_{P-B-P}	α_{H-P-H}	α_{H-B-H}
2	114.5	108.8	100.1	112.9	117.4	111.4	98.6	113.8
4	114.9	113.3	100.7	111.9	117.1	111.8	99.0	113.9
6	115.6	112.8	100.4	112.1	116.8	111.8	99.1	113.8
8	116.1	113.1	100.3	112.1	116.7	111.8	99.1	113.8

Non-Planar

	HEL				COIL			
N	α_{B-P-B}	α_{P-B-P}	α_{H-P-H}	α_{H-B-H}	α_{B-P-B}	α_{P-B-P}	α_{H-P-H}	α_{H-B-H}
2	113.6	107.5	100.1	113.6	113.6	107.5	100.1	113.6
4	114.0	110.8	100.8	112.7	125.0	116.8	100.8	111.4
6	114.6	110.4	100.5	113.0	119.9	111.3	100.3	111.9

[a] All values are given in degrees and have been obtained at the MP2/6-311G* level.

C. Geometries. The bond lengths and bond angles of the four PPB conformers are reported in Tables 3 and 4, respectively. Definitions of the parameters are given by Figure 5. Except for the COIL structures, the bond lengths become almost constant for $N = 6$ or $N = 8$.[24] In Table 3, the most striking feature is the amplitude of the bond length alternation (BLA) in the TC structure, whereas all bonds are equivalent in TT chains. For nonplanar chains, the BLA is predicted to be small in HEL and COIL. This means that the TC structure presents some longer bonds (the B−P, bonds parallel

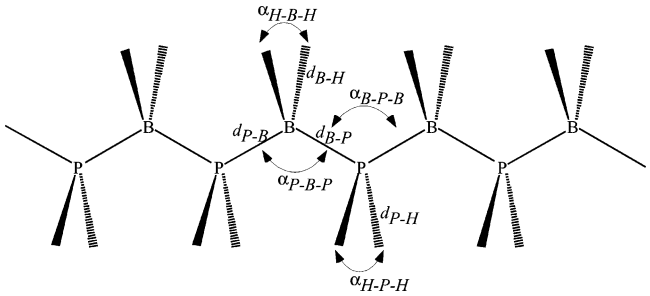

Figure 5. Illustration on the TT tetramer of the parameters reported in Tables 3 and 4.

to the longitudinal axis of PPB) and some shorter bonds (the P−B bonds, perpendicular to the longitudinal axis). However, according to a natural bond order (NBO) analysis,[25] these shorter bonds are purely single bonds and do not exhibit any significant double bond character, which is consistent with the experimental data.[2] The bond populations obtained by the NBO procedure are also in agreement with the alternance of bond lengths in the TC chains and nonalternance in the TT oligomers. For $N = 8$, the BLA of TC is 0.016 Å. Such a BLA is smaller than in polyphosphazene or polyacetylene: 0.024 Å[20] and 0.070 Å[26] for $N = 8$, respectively. The P−H and B−H bond lengths do not depend significantly on the oligomer length or on the conformation, the only exception being a slightly longer P−H bonds in the TT compounds. All the bond lengths reported in Table 3 do actually fit with experimental results (d_{B-H}: 1.21 Å; d_{P-H}: 1.40 Å; d_{P-B}: 1.92−1.96 Å, see ref 2).

The bond angles also converge rapidly with chain length. Indeed, at the HF/6-31G* level, it is found that the largest variations between $N = 8$ and $N = 20$ are of one degree only. For all the conformations, the B−P−B angle is larger (by ∼5 degrees) than the P−B−P angle; the largest differences between conformers being due to B−P−B. This 5 degree difference is in agreement with the X-ray spectra obtained by Dorn[2] for the dimer, $Ph_2PH-BH_2-PPh_2-BH_3$ (4 degrees), or the cyclic tetramer, $[Ph_2PH-BH_2]_4$ (6 degrees in average). The H−P−H angles are always smaller than the H−B−H angles by ∼10 degrees, and their variations are relatively limited when going from one conformation to the other. Eventually, Figure 4 shows the skeleton of the helical (coiled) hexamer with the successive optimized dihedral angle values: 33.5, 176.7, 43.0, 175.4, 43.5, 174.6, 45.0, 177.6, 39.6 (−42.7, −64.8, 56.3, −97.7, 12.5, −100.6, 60.6, −73.7, −45.6) degrees.

D. Vibrational Analysis. The IR spectra have been analytically computed at different levels of theory for the three stable conformers (TT, HEL, and COIL). Corresponding to a transition-state-like cell structure, the spectra of a TC N mer contains $N - 1$ imaginary frequencies and is therefore not meaningful.[27] For the hydrogen wagging, the different theoretical levels agree extremely well once scaled: the discrepancies arising on the 600−1200 cm^{-1} region are of 10 cm^{-1} order (Table 5 and Figure 6). On top of that, the spectra as well as the nuclear displacements corresponding to each peak are also similar for the HF, B3LYP, and MP2 approaches. Consequently, we are confident about the quality of these results. The mode dominating the total IR activity for HEL and TT presents a frequency that is stable with chain length, as listed in Table 5. It corresponds to the in-phase wagging of B−H and P−H bonds. Along the longitudinal axis of TT, the P−B−H angles are subject to modification during the vibration whereas the H−B−H or H−P−H angles remain almost unchanged. The relative intensity of this mode increases rapidly with chain length and dominates the IR spectra of TT and HEL conformers provided $N > 4$. For COIL, although the intensities of the wagging modes are also increasing with chain length (in comparison with the intensities of the stretching), this phenomenon is less effective than for TT or HEL. From Figure 6, one can predict that IR spectra measured around 700−800 cm^{-1} should help distinguish the conformation of PPB: the COIL chains present quite flat spectra, whereas the peak corresponding to the strongest absorption of TT (around 720 cm^{-1}) is predicted to be significantly far away from the one of HEL (around 810 cm^{-1}).

In the stretching region, the results obtained by ab initio techniques are less helpful for three reasons. (1) The variations obtained when upgrading from one theoretical level to another are larger than for the wagging modes. (2) The convergence with chain length is slow. Indeed, the chain end effects (especially due to modes related to the BH_3 terminal group) are still substantial for the hexamer. (3) Numerous modes with different character present a substantial IR intensity. Consequently, the spectra reported in Figure 7 should be considered cautiously. In TT chains, for which the

Table 5. Vibrational Frequencies of the Wagging Mode with Large IR Intensities[a]

	TT			HEL			COIL		
N	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
2	870	865	863	866	857	854	866	857	854
4	774	770		825	815		815	808	
6	747	745		802	793		780	777	
8	737			807					
10	731			807					
12	729								

[a] The values reported in this table have been scaled by a factor of 0.8953 (HF/6-31G*), 0.9427 (MP2/6-311G*), and 0.97 (B3LYP/6-311G*). All circular frequencies are in cm^{-1}.

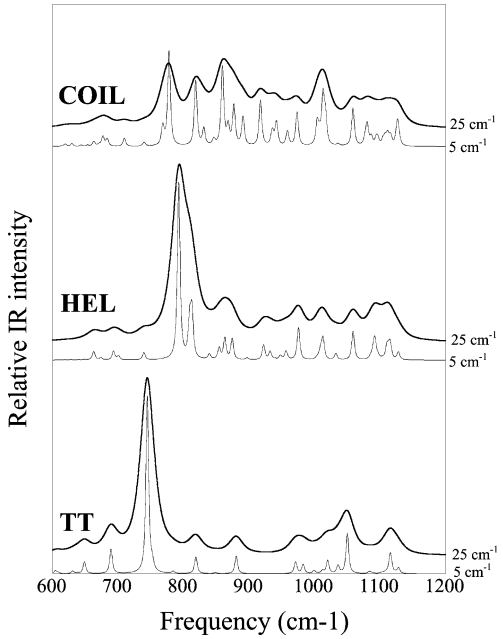

Figure 6. IR spectra: wagging region for three conformations of the hexamer. These results have been obtained at the B3LYP/6-311G* level. Frequencies have been scaled by a factor of 0.97. Two resolutions are presented: 5 and 25 cm^{-1}.

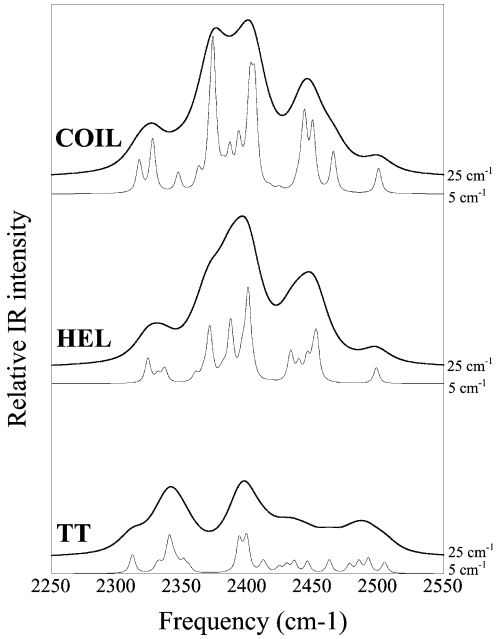

Figure 7. Offset of the hexamer IR spectra (three conformations): the stretching region. See Figure 6 for more details.

Table 6. Vibrational Frequencies of Stretching Modes with Substantial IR Intensities for the TT Oligomers[a]

N	Sym. stretch	Asym. stretch
6	2354−2371	2383−2415
8	2357−2362	2411−2417
10	2359−2362	2412−2417
12	2359	2413

[a] Numerous modes have a significant IR intensity and we report the low and high limits. The vibrational modes corresponding to vibrations taking place at the chain ends have not be considered as they are not significant in macromolecules. The values reported in this table have been obtained at the HF/6-31G* level and scaled by a factor of 0.8953. All circular frequencies are in cm^{-1}.

symmetry helps the analysis, one can identify two types of mode that develop significant contributions to the hydrogen stretching region (see Table 6): symmetric and asymmetric stretch. In the first, the two hydrogens attached to B or P are getting closer (or further) from B or P at the same time, whereas in the second, when one hydrogen is close to the heavy atom the other one is distant. In TT oligomers, the symmetric modes take place at the lowest frequencies (around 2360 cm^{-1}) and are dominated by B−H stretchings. The asymmetric modes appear around 2415 cm^{-1} and are constituted of both B−H and P−H displacements. For HEL and COIL, the symmetric/asymmetric separation is less pronounced and it appears that lower (higher) frequency stretching is dominated by B−H (P−H) movements. Overall, the contribution of P−H displacements is larger than in TT. The vibrational frequencies reported here (Figure 7 and Table 6) are fully compatible with the experimental results in which two peaks (2421 and 2381 cm^{-1}) have been identified for phenyl substituted chains. The theoretical results also confirm that it is not possible to separate the contributions of P−H and B−H stretching: each probably contributing to both the 2421 and 2381 cm^{-1} peaks.

E. Charges and Dipole Moment. Table 7 summarizes the charge on the central atoms and the norm of the dipole moment for increasingly long PPB chains. For the tetramer, the charges are mostly converged and

Table 7. MP2/6-311G* Norm of the Dipole Moment (Debye) and Charges of the Central Atoms of PPB Oligomers (in *e*)[a]

Planar

	TC					TT				
N	$\|\mu\|$	P	B	H(P)	H(B)	$\|\mu\|$	P	B	H(P)	H(B)
2	4.9	0.41	−0.14	−0.02	−0.10	10.3	0.43	−0.04	−0.06	−0.09
4	13.5	0.58	−0.39	−0.03	−0.06	24.2	0.42	−0.08	−0.06	−0.08
6	23.1	0.55	−0.33	−0.03	−0.08	39.2	0.43	−0.09	−0.06	−0.01
8	33.0	0.60	−0.38	−0.04	−0.08	54.2	0.43	−0.12	−0.06	−0.09

Non-Planar

	HEL					COIL				
N	$\|\mu\|$	P	B	H(P)	H(B)	$\|\mu\|$	P	B	H(P)	H(B)
2	5.2	0.37	−0.11	−0.03	−0.12	5.2	0.37	−0.11	−0.03	−0.12
4	13.9	0.40	−0.24	−0.00	−0.10	7.8	0.44	−0.21	−0.02	−0.09
6	23.4	0.44	−0.18	−0.02	−0.12	14.9	0.43	−0.29	−0.00	−0.10

[a] For nonplanar chains, the reported figures are given for the hydrogen bearing the largest charge.

are similar for the four conformations with the notable exception of TC chains for which stronger charge separation between P and B is observed. Indeed, the charges are $\sim +0.4$ *e* for phosphorus except for the TC conformation ($\sim +0.6$ *e*), ~ -0.20 *e* for boron (but TC: ~ -0.4 *e*), close to zero for the hydrogens attached to the phosphorus, and -0.1 *e* for the hydrogens bound to boron. Note that the charge separation in PPB is smaller than in PP in which P ($q = 0.94$ *e*) and N ($q = -1.07$ *e*) almost exchange one electron.[20] While these results are completely consistent with the differences of electronegativity between phosphorus, nitrogen, and boron elements, the zero charge on H(P) contradicts the assumed weak attractive intermolecular interaction suggested by Dorn[2] with the $P-H^{\delta+}...^{\delta-}H-B$ pattern. However, the $\delta+$ charge could be induced by stacking. For this reason we have computed the charges on the substituted dimer (Table 1). If the charges of some of the H(P) are positive, this is, nevertheless, an extremely weak effect (at most $+0.02$ *e*) and the average charge for H(P) is still 0.0 *e*, whereas the charge of H(B) remains unchanged at -0.1 *e*. As the charges on P and B are also mostly constant with respect to the isolated PPB chains ($+0.44$ *e* and -0.13 *e* for P and B of Table 1 structure), the interaction between chains is predicted to have a small effect on the charges. Consequently, the $P-H^{\delta+}...^{\delta-}H-B$ pattern assumption is not supported by our theoretical simulations.

The dipole moment per unit cell, $|\Delta\mu(N)| = 1/2|\mu(N)| - 1/2|\mu(N-2)|$, converges rapidly with chain length. It is almost constant for $N = 6$ and $N = 8$. Therefore, we predict polymeric values ($|\Delta\mu(\infty)|$) of 5 (TC and HEL), 7 (TT), and 3 (COIL) Debyes for the different conformers. These differences should be large enough to allow the discrimination of TT from COIL. One can rationalize this order by considering that each P−B bond brings a small contribution to $|\mu|$. Indeed, the bonds in coiled chains are pointing in a direction leading to a significant averaging of "bond dipole moments" and a weak total value; whereas TT chains have a perfect order of the bonds, leading to a large total norm. For comparison, TC PP has a $|\Delta\mu(8)|$ of 6.7 D,[28] i.e., larger than the corresponding PPB value. This difference can be related to the stronger charge separation in PP. Within this point of view, PPB has a significant dipole moment w.r.t. its limited atomic charges.

F. Excitation Energies. The vertical excitation energies of PPB are given in Table 8. For the hexamer

Table 8. Singlet-State Excitation Energies in eV[a]

	FES				FCES				FSCES			
N	TC	TT	HEL	COIL	TC	TT	HEL	COIL	TC	TT	HEL	COIL
2	6.4	6.0	6.5	6.5	6.4	6.0	6.5	6.5	8.6	6.4	9.0	9.0
4	5.5	4.6	5.4	5.9	5.6	4.6	6.5	6.7	>7.9	4.6	>8.0	>8.2
6	5.0	4.0	4.9	5.3	6.4	4.0	6.3	6.9	6.8	5.6		
8	4.8	3.7			6.4	5.0			>6.6	5.3		

[a] These values have been obtained with the B3LYP/6-311G* scheme on the MP2/6-311G* geometries. The reported values are the first excited state (FES), the first excited state that couples [oscillator strength > 0.01] with the ground state (FCES), and the first excited state that strongly couples [oscillator strength > 0.1] with the ground state (FSCES).

and the octamer, the first excited state (FES) lies 4 to 5 eV above the ground state. The excitation energy of the FES has not yet converged for this chain length. Therefore it is difficult to predict a polymeric value. Nevertheless, one can see that the excitation energies are lower for TT oligomers than for TC, HEL, and COIL chains. If one examines the states that couple with the ground state, the differences between the oligomers are of the same order of magnitude: the excitation energies of TT are roughly 1 eV smaller than these of TC, HEL, and COIL. This may be related to the planarity and absence of Peierls distortion in the TT conformer. Even for TT, the first strongly coupled excited state is 5 eV above the ground state, a large value if compared to conjugated systems, but small in comparison with polyethylene.[29,30]

The ionization potential and electroaffinity computed for the dimers at the OVGF/6-311G* level of approximation are of the order of 10 eV and −2 eV, respectively, and are almost independent of the conformation selected.

III. Conclusion

We have studied the structures and properties of increasingly long PPB oligomers. It turns out that different conformers present very similar stability (within 1 kcal/mol per cell). Furthermore, PPB is highly flexible, and shifting from one conformation to the other does not require a large amount of energy. Nevertheless, the four conformers present significantly different properties. Trans-transoid chains that present no bond length alternation have a larger dipole moment and a smaller vertical excitation energy than the other conformers. The IR spectrum of TT is dominated by a wagging mode around 720 cm^{-1}. The trans-cisoid and helicoidal chains have similar properties. The IR spectrum of the helicoidal compounds presents a strong absorption around 810 cm^{-1}. The coiled compounds have a small dipole moment and a more "flat" IR spectrum. It is our hope that such differences will help identify the structure of experimentally synthesized PPB.

The polymers actually synthesized by Dorn et al. are $R_1 \equiv$ Ph, ^{i}Bu, *p*-*n* BuC_6H_4, and *p*-dodecylC_6H_4 for one side group and $R_2 \equiv$ H for the other side group (Figure 1). We are currently studying the impact of substitution by Ph and ^{i}Bu on the properties and structures of PPB.

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(18) The three structures have the following skeleton torsional angles (in degrees, from PH_3 end to BH_3 end): Structure 1 27.7, 174.4, −37.2, −172.2, 32.4; Structure 2 −29.3, −176.1, 39.2, 178.0, 37.6; Structure 3 32.4, 176.6, 42.4, 178.0, 37.4. The relative energy per unit cell w.r.t. the trans-cisoid conformers are −0.58 kcal/mol, −0.67 kcal/mol, and −0.74 kcal/mol, respectively.
(19) These six possible sequences are (1) 30 190 30 190 30; (2) 30 190 30 170 30; (3) 30 170 30 170 30; (4) 30 190 −30 190 30; (5) 30 190 −30 170 30; (6) 30 170 −30 170 30 degrees.
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(22) Different coils have been considered for the tetramer, and the values reported are for the most stable structure found. However, due to the large number of possibilities, we cannot fully guarantee that another coiled structure would not have been slightly more stable.
(23) For long chains ($N = 14$ and beyond) HF/6-31G(d) calculations predict that TT and TC energies are within ∼0.1 kcal/mol

per cell of each other, whereas HEL is stablized by ~1 kcal/mol per cell.
(24) At HF/6-31G(d) level the variations of bond lengths between $N = 8$ and $N = 20$ are of the order of 0.001 ~ 0.004 Å for TT and TC chains.
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