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Effects of Chain Substitution on the Structures and Properties of Polyphosphinoborane

Denis Jacquemin,* Valérie Wathelet,† and Eric A. Perpète‡

Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix,rue de Bruxelles, 61, B-5000 Namur, Belgium

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ABSTRACT: The impact of side-group substitution on the three-dimensional structure and on the properties of the homologuous series of polyphosphinoborane oligomers has been investigated by using ab initio computational tools, taking into account dynamic electron correlation effects. This includes the evaluation of the following: geometries, conformations, rotational profiles, infrared spectra, vertical excitations energies, atomic charges, and dipole moments.

I. Introduction

PPB has recently been successfully synthesized with high molecular weight by Dorn, Manners, and coworkers,[1−3] and Denis, Gaumont, and co-workers.[4] In a recent contribution,[5] we have investigated the structures and properties of the unsubstituted ($R_1 \equiv R_2 \equiv H$ in Figure 1) polyphosphinoboranes (PPB, Figure 1), and it turns out that they can significantly be affected by the chain conformation.[5] In Dorn's experiment, the PPB chains are substituted by side groups: $R_1 \equiv$ Ph, ^{i}Bu, *p-n* BuC_6H_4, or *p*-dodecylC_6H_4, whereas $R_2 \equiv$ H. Obviously, the introduction of these side groups may affect the physicochemical characteristics of PPB. In this contribution, we investigate the properties of the substituted dimers ($R_1 \equiv$ Me and $R_2 \equiv$ H/$R_1 \equiv R_2 \equiv$ Me/$R_1 \equiv$ ^{i}Bu and $R_2 \equiv$ H/$R_1 \equiv$ Ph and $R_2 \equiv$ H, with $N = 2$ in Figure 1) in order to produce a semiquantitative estimation of the variations induced by the presence of side groups on the main PPB backbone.

II. Computational Details

As methodological results from our previous investigations,[5] we have selected the second-order Møller−Plesset (MP2) scheme (for most properties) and the hybrid-DFT B3LYP functional, together with Pople's polarized split-valence 6-31G* basis set to compute the vibrational and UV spectra (6-31+G* for the latest). This basis set gives a good agreement between the theoretical and the experimental PPB structures.[5] This is a slight downgrade from the 6-311G* basis set used in ref 5, but we demonstrate, in section III.A, that it should not significantly affect the amplitude of the property modifications induced by the substitution. The calculations have been performed with the Gaussian98[6] package of programs, following the procedure given below.

1. Geometry Optimization. The ground-state geometry has been determined for each oligomer by a full optimization of its structural parameters. The minimization steps have been carried out until the *rms* residual force was lower than 1 × 10^{-6} au (corresponding to a *very tight* threshold in Gaussian98) if the resulting geometries were to be used for vibrational spectra calculation, while the *tight* threshold (*rms* residual forces lower than 1 × 10^{-5} au) was selected when the Hessian matrix calculations can be skipped. The rotational profiles have subsequently been obtained by freezing one internal coordinate (the P−B−P−B backbone dihedral angle) and optimizing all the remaining parameters.

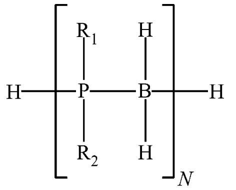

Figure 1. Illustration of the polyphosphinoborane (PPB) oligomers.

2. Vibrational Spectra. The vibrational circular frequencies and related intensities have been computed by performing, at the B3LYP level, a fully analytic determination of the Hessian-matrix. We have used an *ultrafine* integration grid (pruned (99 590) grid) during these calculations and the related preceding geometry optimizations. As discussed in the literature, a scaling factor of 0.97 has been used to reduce the residual discrepancy between the B3LYP results and the experimental frequencies.[5] Real-looking spectra have been drawn by convoluting the theoretical results, using a mixed Lorentzian(80%)/Gaussian(20%) function with two different full width at half-maximums (fwhm = 5 and 25 cm^{-1}).

3. Charges and Dipole Moment. We have used an electrostatic potential-derived formalism (Merz−Kollman charges,[7] usually abbreviated MK or ESP charges) for evaluating the partial atomic charges. This formalism is known to yield charges which are consistent with the experimental data.[8] The norm of the dipole moment ($|\mu|$) has been obtained on the basis of these ESP charges.

4. Excitation Energies. The singlet-state excitation energies have been computed with the B3LYP functional by using the time-dependent density functional theory (TFDFT)[9] as implemented in Gaussian98. This procedure provides excitation energies which are comparable with experimental results (see ref 10 and references therein).

From our previous investigation,[5] we are aware that the properties obtained for the dimers would weakly correspond to the *converged* (i.e., polymer) results. Indeed, the variations when successively going from the dimer ($N = 2$) to the tetramer ($N = 4$), the hexamer ($N = 6$), and the octamer ($N = 8$) could be large. However, the calculations on longer substituted chains using high-level ab initio approaches are currently not possible in practice. For this reason, this paper mainly deals with the semiquantitative amplitude of the property trends when substituting $R_1 \equiv$ H by $R_1 \equiv$ ^{i}Bu or Ph.

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* Corresponding author. E-mail: denis.jacquemin@fundp.ac.be. URL: http://www.fundp.ac.be/~jacquemd. Research Associate of the Belgian National Fund for Scientific Research.

† E-mail: valerie.wathelet@fundp.ac.be.

‡ E-mail: eric.perpete@fundp.ac.be. Research Associate of the Belgian National Fund for Scientific Research.

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Table 1. Relative Energy Per Unit Cell for the PPB Dimer as a Function of the Adopted Conformation/Configuration[a]

configuration	conformation	H	Me	Me_2	^{i}Bu	Ph
iso	TC(B)	0.00 (0.00)	+0.01 (+0.05)	0.00 (0.00)	+0.64	+0.37
	HEL(B+)	−0.28 (−0.29)	−0.34 (−0.31)	−0.57 (−0.63)	+0.13	−0.56
	HEL(B−)	−0.28 (−0.29)	−0.39 (−0.39)	−0.57 (−0.63)	?[b]	−0.47
	TT(A)	+2.52 (+2.53)	+3.40 (+3.34)	+3.91 (+3.74)	+4.48	+0.25
	HTT(A)	+2.52 (+2.53)	+3.26 (+3.19)[c]	+3.91 (+3.74)	+4.17	+0.25
syndio	TC(A)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00	0.00
	HEL(A+)	−0.28 (−0.29)	−0.15 (−0.15)	−0.57 (−0.63)	?[b]	−2.31
	HEL(A-)	−0.28 (−0.29)	−0.50 (−0.53)	−0.57 (−0.63)	−0.43	+0.10
	TT(B)	+2.52 (+2.53)	+2.96 (+2.91)	+3.91 (+3.74)	+2.90	+0.40
	HTT(B)	+2.52 (+2.53)	+2.96 (+2.91)	+3.91 (+3.74)	+2.81	+0.06

[a] All values have been obtained with the MP2/6-31G* approach (available MP2/6-311G* values are in brackets) and are given in kcal/mol. [b] It was not possible to optimize the geometry of the ^{i}Bu chain in the HEL(A+) and HEL(B−) conformations. [c] For the most stable HTT(A). See the text for more details.

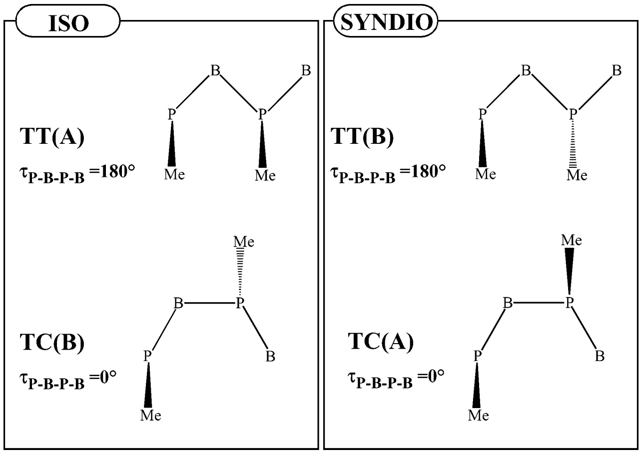

Figure 2. Structures of the different TC and TT dimers. HEL(A+) [HEL(A−)] corresponds to TC(A) with a positive [negative] $\tau_{P-B-P-B}$. HEL(B+) [HEL(B−)] corresponds to TC(B) with a positive [negative] $\tau_{P-B-P-B}$. A positive [negative] $\tau_{P-B-P-B}$ means that the terminal BH_3 is pointing into [out of] the plane.

III. Results

A. Conformations and Relative Energies. In addition to the intrinsic effect of the side groups, the substitution on the PPB phosphorus atom makes it a chiral center, consequently leading, on top of the different conformations, to different possible configurations. From the dimers, one can set an early comparison between the starting points of isotactic (iPPB) and syndiotactic (sPPB) chains[11] (see Figure 2). On the contrary to some other polymers, PPB tends to favor the trans−cisoid (TC) conformation over the trans−transoid (TT). In the TC conformation, the side groups of iPPB are on opposite sides of the backbone (for the TT-iPPB system, the substituting groups are on the same side). To circumvent possible confusion, we therefore use A when the groups are always on the same side, and B when the groups alternate on both sides of the backbone (see Figure 2). Of course, a 180° rotation around the backbone dihedral angle will change TT(A) into TC(B) for iPPB and change TT(B) into TC(A) for sPPB. In addition, for helical (HEL) structures (which are the most stable conformations for the unsubstituted PPB[5]) of chiral PPB, positive/negative $\tau_{P-B-P-B}$ lead to different minima, referred to as HEL(+)/HEL(−), respectively.

The rotational profiles for the P−B−P−B torsion ($\tau_{P-B-P-B}$) of the Me−iPPB and Me−sPPB ($R_1 \equiv$ Me, $R_2 \equiv$ H and $N = 2$ in Figure 1) chains are shown in Figure 3 and are compared to the profile of unsubstituted PPB. Among the planar conformations, the TC chains are more stable than the TT oligomers, and a small negative deviation from $\tau_{P-B-P-B} = 0$ leads to the global minimum [HEL(−)]. For sPPB/iPPB, it corresponds to a torsion of −32.1/−30.2°.[12] Another minimum [HEL(+)] can be found for dihedral angles of +28.0/+32.2°.[12]

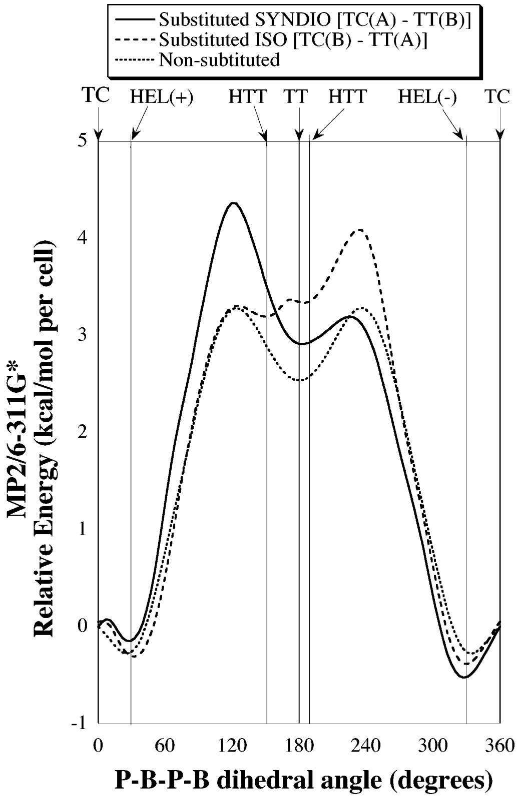

Figure 3. MP2/6-311G* rotational profile (kcal/mol per cell) for the PPB dimer ($N = 2$) substituted by Me groups (see Figure 2 for conventions). TT, HTT, HEL and TC stands for the trans−transoid, helical−trans−transoid, helicoidal, and trans−cisoid conformations. By convention, the relative energy of the latter has been set to zero. The rotational profile of the unsubstituted chain is reproduced for comparison purpose.

Although located in an energetic well, the TT compounds do not strictly correspond to a minimum in the rotational profile, contrary to what was found for the unsubstituted chains.[5] Indeed, due to the asymmetry, the minimum near the TT conformation (HTT[13]) presents a $\tau_{P-B-P-B}$ which slightly differs from +180.0°. For sPPB, $\tau_{P-B-P-B} = 182.6°$, whereas for iPPB there are two minima: the most (least) stable for $\tau_{P-B-P-B} = 149.7$ (184.4)°. Similarly, the TC chains are not exactly, but almost, positioned on the saddle point; that would identify them as transition states between the two

Table 2. Distance between the Two Phenyl Rings in $PH_2Ph-BH_2-PHPh-BH_3$ and the Estimated Type of Interaction between the Two Phenyl Rings[a]

configuration	conformation	d_{Ph-Ph}	interaction	RE
iso	TC(B)	7.5	none	+0.60
	HEL(B+)	7	none	−0.32
	HEL(B−)	6.5	weak quadrupolar (T-shape)	−0.30
	TT(A)	3.5	π-π	−0.75
	HTT(A)	3.5	π-π	−0.75
syndio	TC(A)	5.5	quadrupolar (T-shape)	0.00
	HEL(A+)	3.5	$\pi-\pi$	−3.27
	HEL(A−)	7.5	none	+0.61
	TT(B)	4.5	quadrupolar (staggered)	−0.17
	HTT(B)	4.5	quadrupolar (staggered)	−0.51

[a] The distances are in Å. MP2/6-31+G*//MP2/6-31G* relative energies (RE) per unit cell (kcal/mol) are also given.

Table 3. Bond Lengths of PPB Dimer Measured at the Chain Center[a]

	TC(A)	TC(B)	HEL(A+)	HEL(B+)	HEL(A-)	HEL(B−)	TT(A)	TT(B)	HTT(A)	HTT(B)
					$d_{BH_2-PX_{1,2}}$					
H	1.957	1.957	1.950	1.950	1.950	1.950	1.943	1.943	1.943	1.943
Me	1.956	1.956	1.946	1.945	1.945	1.946	1.940	1.940	1.948	1.940
Me_2	1.957	1.957	1.945	1.945	1.945	1.945	1.937	1.937	1.937	1.937
^{i}Bu	1.960	1.960	?[b]	1.949	1.952	?[b]	1.941	1.946	1.952	1.947
Ph	1.959	1.959	1.947	1.946	1.945	1.944	1.944	1.946	1.944	1.949
					$d_{PHX_{1,2}-BH_2}$					
H	1.948	1.948	1.946	1.946	1.946	1.946	1.938	1.938	1.938	1.938
Me	1.934	1.934	1.933	1.931	1.935	1.936	1.931	1.928	1.926	1.928
Me_2	1.925	1.925	1.926	1.926	1.926	1.926	1.924	1.924	1.924	1.924
^{i}Bu	1.937	1.940	?[b]	1.937	1.936	?[b]	1.938	1.932	1.928	1.930
Ph	1.937	1.938	1.933	1.931	1.947	1.948	1.932	1.933	1.933	1.933
					$d_{PX_{1,2}-BH_3}$					
H	1.955	1.955	1.953	1.953	1.953	1.953	1.962	1.962	1.962	1.962
Me	1.949	1.949	1.943	1.942	1.942	1.943	1.947	1.947	1.945	1.947
Me_2	1.943	1.943	1.938	1.938	1.938	1.938	1.938	1.938	1.938	1.938
^{i}Bu	1.955	1.952	?[b]	1.949	1.950	?[b]	1.950	1.951	1.953	1.951
Ph	1.948	1.949	1.945	1.945	1.943	1.942	1.951	1.952	1.951	1.951
					d_{P-H}					
H	1.407	1.407	1.407	1.407	1.407	1.407	1.413	1.413	1.413	1.413
Me	1.410	1.410	1.409	1.412	1.411	1.410	1.415	1.415	1.418	1.415
^{i}Bu	1.410	1.409	?[b]	1.411	1.412	?[b]	1.412	1.414	1.418	1.414
Ph	1.410	1.411	1.411	1.413	1.414	1.411	1.414	1.412	1.414	1.412
					d_{P-C}					
Me	1.834	1.834	1.836	1.833	1.833	1.835	1.841	1.840	1.838	1.840
Me_2	1.833	1.833	1.831	1.831	1.831	1.831	1.837	1.837	1.837	1.837
^{i}Bu	1.850	1.848	?[b]	1.844	1.850	?[b]	1.861	1.856	1.857	1.857
Ph	1.828	1.825	1.828	1.824	1.824	1.829	1.825	1.825	1.825	1.825

[a] $d_{BH_2-PX_{1,2}}$ is the length found for the central bond (even numbered) whereas $d_{PHX_{1,2}-BH_2}$ and $d_{PX_{1,2}-BH_3}$ are the lengths of the vicinal bonds (odd numbered). All values are in Å and have been obtained at the MP2/6-31G* level. For HEL, the reported P−H and P−C distances correspond to the shortest bonds at the center of the oligomers. [b] It was not possible to optimize the geometry of the ^{i}Bu chain in the HEL(A+) and HEL(B−) conformations.

helical structures. The vibrational analysis shows an imaginary frequency mode for TC structures of both iPPB and sPPB. Using Me−PPB, the rotational barrier is increased by ~1 kcal/mol per cell compared to the unsubstituted chains, and is estimated to be ~4−5 kcal/mol per cell. This barrier is also tuned for ^{i}Bu−PPB and Ph−PPB (see below).

Table 1 gives the relative conformational energies of the different dimers. First, we note that MP2/6-31G* and MP2/6-311G* values are in good agreement with each other, justifying the use of the former in our study. For alkyl−PPB, the relative stability of the TT conformers is increased when heavier side groups are used. For ^{i}Bu chains, the most stable nonplanar system is HEL(A−), which corresponds to a syndio configuration.[14] In addition, we predict from Table 1 that sPPB could have a smaller (by ~1 kcal/mol per cell) rotation barrier than iPPB (estimated barrier for iPPB ~5−6 kcal/mol per cell). Consequently, although the iso/syndio selection is probably imposed by the kinetics of the polymerization on the catalyst, the ^{i}Bu−sPPB should be more stable and probably more flexible (as flexible as Me−PPB) than ^{i}Bu−iPPB. The changes induced by using Ph substituents are even more discriminating. Indeed, the HEL(A+) conformation is strongly favored, whereas TC and TT chains present a similar energetic stability. This could be interpreted as a greater flexibility of Ph−PPB, especially in the isotactic configuration. It is striking to note that HEL(A+) was the least stable helical structure for Me−PPB.

To rationalize these changes, a study of the relative orientation of the Ph groups has been performed (Table 2). It turns out that the strong stabilization of HEL(A+) [sPPB] and TT(A) [iPPB] can be related to the π-π interactions occurring when the substituting phenyl groups are adjacent.[15] TC(A), HTT(B), and TT(B) present substantial quadrupolar (slip/staggered or T-shape) interactions while the other compounds display much weaker interactions between the Ph rings. To confirm the presence of these interactions, MP2/6-31+G* calculations have been performed on the MP2/6-31G* geometries (Table 2). Consistently with our analysis, it

Table 4. Selected Valence Angles of PPB Oligomers Taken at the Center of the Dimers

	TC(A)	TC(B)	HEL(A+)	HEL(B+)	HEL(A−)	HEL(B−)	TT(A)	TT(B)	HTT(A)	HTT(B)
					α_{B-P-B}					
H	114.8	114.8	113.8	113.8	113.8	113.8	117.6	117.6	117.6	117.6
Me	118.1	117.9	114.9	115.1	116.8	116.6	116.1	117.0	117.0	117.0
Me_2	121.4	121.4	118.6	118.6	118.6	118.6	114.3	114.3	114.3	114.3
^{i}Bu	118.6	116.8	?[b]	114.0	118.0	?[b]	115.7	117.4	112.9	117.1
Ph	116.6	116.3	114.1	114.3	117.0	115.3	115.9	118.0	115.9	117.3
					α_{P-B-P}					
H	108.0	108.0	107.1	107.1	107.1	107.1	110.9	110.9	110.9	110.9
Me	109.9	110.0	108.1	107.7	108.9	108.8	114.2	112.1	111.2	112.1
Me_2	112.5	112.5	110.8	110.8	110.8	110.8	118.6	118.6	118.6	118.6
^{i}Bu	109.7	107.4	?[b]	106.2	107.4	?[b]	114.5	111.7	110.5	111.5
Ph	108.5	107.8	105.1	106.2	109.5	106.3	111.9	107.7	112.0	108.9
					α_{H-B-H}					
H	113.4	113.4	113.9	113.9	113.9	113.9	114.2	114.2	114.2	114.2
Me	112.8	112.7	113.4	113.6	113.3	113.3	113.2	113.6	113.5	113.5
Me_2	112.1	112.1	112.8	112.8	112.8	112.8	112.2	112.2	112.2	112.2
^{i}Bu	112.6	113.1	?[b]	113.8	113.2	?[b]	113.2	113.0	113.6	113.0
Ph	112.9	113.0	114.1	113.7	113.7	114.0	113.2	113.9	113.2	113.6
					$\alpha_{X_1-P-X_2}$					
H	99.8	99.8	99.9	99.9	99.9	99.9	98.2	98.2	98.2	98.2
Me	102.0	102.0	102.0	102.1	102.2	102.2	100.7	100.8	100.9	100.8
Me_2	103.2	103.2	103.0	103.0	103.0	103.0	102.5	102.5	102.5	102.5
^{i}Bu	100.1	103.7	?[b]	103.0	100.9	?[b]	102.8	98.8	102.4	98.8
Ph	102.4	102.2	102.5	102.5	102.5	102.8	99.6	98.8	99.6	99.2

[a] All values are given in degrees and have been obtained at the MP2/6-31G* level. For $\alpha_{X_1-P-X_2}$, $X_{1,2}$ = H or C, depending on the system. [b] It was not possible to optimize the geometry of the ^{i}Bu chain in the HEL(A+) and HEL(B−) conformations.

Table 5. MP2/6-31G* Backbone Dihedral Angles of PPB Dimers[a]

	$\tau_{P-B-P-B}$					
	HEL(A+)	HEL(B+)	HEL(A−)	HEL(B−)	HTT(A)	HTT(B)
H	25.0	25.0	−25.0	−25.0	180.0	180.0
Me	27.8	31.0	−30.5	−29.1	151.3	181.3
Me_2	32.8	32.8	−32.8	−32.8	180.0	180.0
^{i}Bu	?[b]	30.1	−29.4	?[b]	145.7	170.3
Ph	45.9	36.6	−42.9	−55.0	181.6	162.5

[a] All values are given in degrees. [b] It was not possible to optimize the geometry of the ^{i}Bu chain in the HEL(A+) and HEL(B−) conformations.

turns out that the dimers with the strongest Ph interactions are estimated to be "more stabilized" when diffuse functions, which allow the modelization of more distant interaction, are added. From Ref. 5, we know that the difference between TC and TT tends to become smaller for longer oligomers, whereas the HEL chains are more stable for the tetramer than for the dimer. Therefore, it can reasonably be expected that Ph−sPPB strongly tends to form helical or coiled structures whereas Ph−iPPB prefers a HTT conformation. In addition, for Ph−iPPB, the $\tau_{P-B-P-B}$ corresponding to HTT(A) is very close to 180.0°: the nonplanarity of the backbone is negligible.

B. Geometries. The bond lengths, bond angles, and dihedral angles of the PPB conformers are listed in Tables 3−5, respectively. For each of the substitutions, the central bond lengths (the B−P bonds parallel to the longitudinal axis of PPB in the TC conformers) have the following ordering TC > HEL > TT, whereas the phosphorus terminal bonds (the P−B bonds, perpendicular to the longitudinal axis for TC chains) roughly order as TC ≈ HEL > TT. For the $PX_{1,2}-BH_3$ bonds, no general pattern has been found. HTT chains present a geometry very similar to TT (HEL), provided $\tau_{P-B-P-B}$ is very close to (or very far from) 180.0°. The results of Table 3 are consistent with the alternating-TC, slightly alternating-HEL and nonalternating-TT patterns found for unsubstituted PPB.[5] Central $BH_2-PX_{1,\ 2}$ bonds appear to be quite insensitive to the chemical substitution, whereas the terminal bonds are significantly shortened by the presence of side groups. This effect is especially strong for the Me_2 substitution.[16] The backbone's bond lengths are alike for ^{i}Bu and Ph. Consequently, the actually synthesized structures should present similar geometries for a given conformation. For each compound the P−H bond lengths are constant around 1.41 Å. The P−C bonds are, as foreseen, shorter for Ph (~ 1.825 Å) than for ^{i}Bu (~1.855 Å) or Me (~1.835 Å) chains. Finally, we note that the variations induced by the A/B configuration[17] or the HEL(+)/HEL(−) conformation are small, the largest differences being on the order of 0.005 Å. It is therefore expected that, for a given conformation, the tacticity of the chain and the sign of the dihedral angle would have a negligible impact on the backbone geometries.

For all the conformations, the B−P−B valence angle is more widely opened than the P−B−P angle, the differences getting larger when substituents are added. Indeed, it is ~ 5° for the unsubstituted chains, but ~ 8° or 9° for ^{i}Bu and Ph. Once again, ^{i}Bu and Ph induce similar geometry modifications wrt unsubstituted PPB. The H−B−H angles are quite insensitive to substitution, conformation and tacticity, the change being bounded by the 112.1/114.2° limits. On the other hand, the X−P−H angle is increased by ~ 3° for TC and HEL, when going from X = H to X = C.

Table 5 shows the optimal dihedral angles found for the HEL and HTT conformations. All $\tau_{P-B-P-B}$ of the

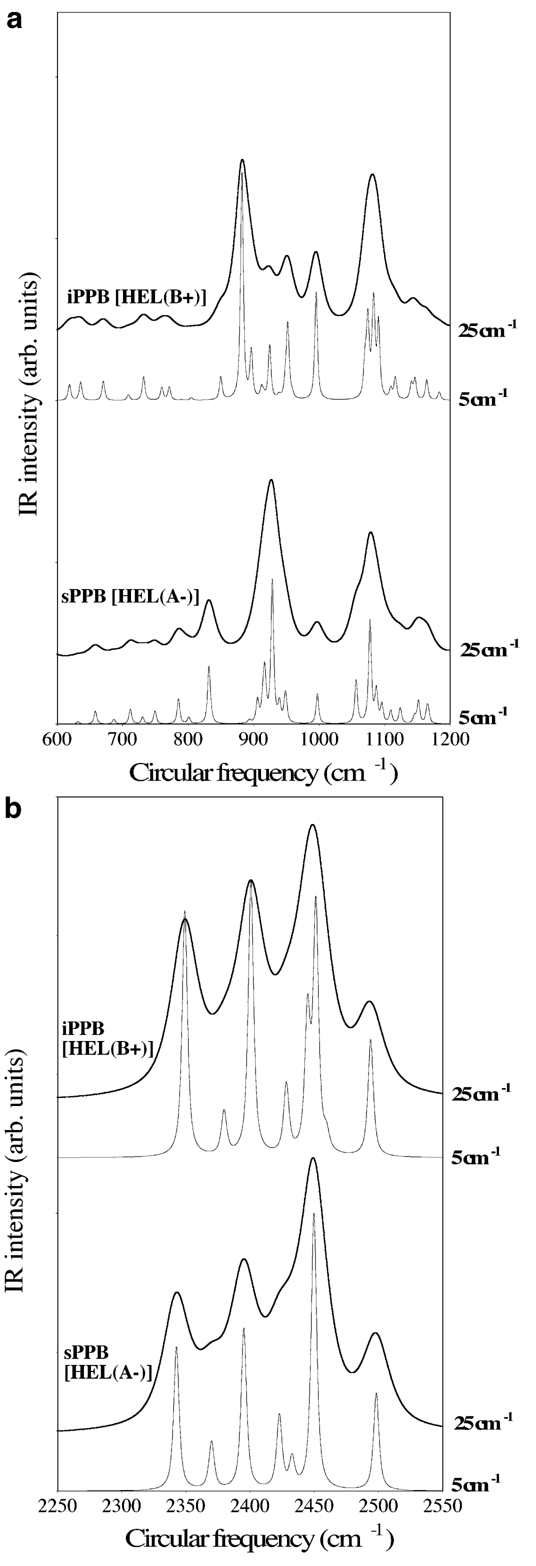

Figure 4. Offsets of the IR spectra for ^{i}Bu−PPB: the wagging (a) and stretching (b) regions. These results have been obtained at the B3LYP/6-31G* level. Frequencies have been scaled by a factor of 0.97. Two resolutions are presented: 5 and 25 cm^{-1}.

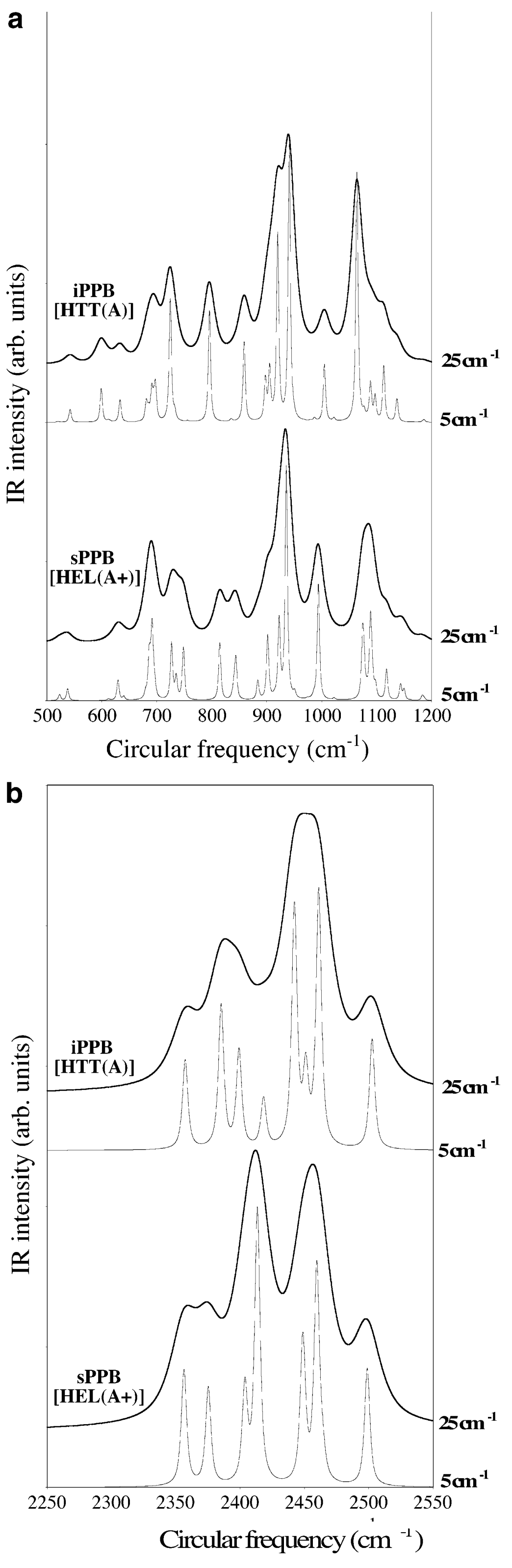

Figure 5. IR spectra of Ph−PPB: wagging (a) and stretching (b). See Figure 4 for more details.

HEL alkyl chains are in the range of ±30° whereas the deviations are larger for Ph-substituted chains: 45° in average. This is consistent with the results of Table 2: the interaction between Ph groups leads to strong deviations from planarity in order to bring the aromatic rings close enough to provide a maximal (stabilizing) interaction. The $\tau_{P-B-P-B}$ of the HTT system is either very close to 180.0° (Me−sPPB and Ph−iPPB) or differs from planarity by 10 (^{i}Bu−sPPB) to 35° (^{i}Bu−iPPB), and the impact of the configuration over $|\tau_{P-B-P-B}|$ is obviously larger than for HEL.

C. Vibrational Analysis. The dimers are too short to be able to estimate correctly the vibrational spectra of the polymer. For this reason, we present the spectra computed for the most stable species of the syndio and the iso dimers of ^{i}Bu−PPB and Ph−PPB. This should

Table 6. MP2/6-31G* Norm of the Dipole Moment (debye) and Charges of the Central Atoms of PPB Dimers (in $|e|$)

	TC(A)	TC(B)	HEL(A+)	HEL(B+)	HEL(A−)	HEL(B−)	TT(A)	TT(B)	HTT(A)	HTT(B)
					q_P					
H	0.35	0.35	0.31	0.31	0.31	0.31	0.37	0.37	0.37	0.37
Me	0.50	0.51	0.49	0.53	0.52	0.50	0.55	0.57	0.52	0.57
Me_2	0.77	0.77	0.75	0.75	0.75	0.75	0.76	0.76	0.76	0.76
^{i}Bu	0.45	0.51	?[a]	0.50	0.44	?[a]	0.48	0.46	0.45	0.45
Ph	0.31	0.37	0.38	0.38	0.34	0.32	0.33	0.29	0.35	0.37
					q_B					
H	−0.13	−0.13	−0.11	−0.11	−0.11	−0.11	−0.10	−0.10	−0.10	−0.10
Me	−0.25	−0.23	−0.23	−0.25	−0.24	−0.23	−0.26	−0.28	−0.26	−0.29
Me_2	−0.36	−0.36	−0.37	−0.37	−0.37	−0.37	−0.40	−0.40	−0.40	−0.40
^{i}Bu	−0.23	−0.29	?[a]	−0.34	−0.21	?[a]	−0.25	−0.24	−0.15	−0.24
Ph	−0.07	−0.07	−0.17	−0.13	−0.06	−0.10	−0.12	−0.11	−0.13	−0.15
					$\lvert\mu\rvert$					
H	4.8	4.8	5.0	5.0	5.0	5.0	10.1	10.1	10.1	10.1
Me	4.9	4.8	5.6	5.2	4.9	5.1	10.8	10.6	10.5	10.6
Me_2	4.9	4.9	5.2	5.2	5.2	5.2	11.2	11.2	11.2	11.2
^{i}Bu	4.8	4.5	?[a]	4.9	4.5	?[a]	11.3	10.8	10.7	10.9
Ph	5.2	4.8	6.7	5.5	5.1	6.0	11.0	10.8	11.0	10.9

[a] It was not possible to optimize the geometry of the ^{i}Bu chain in the HEL(A+) and HEL(B−) conformations.

Table 7. Singlet-State Excitation Energies in eV[a]

configuration	conformation	H	Me	Me_2	^{i}Bu	Ph
iso	TC(B)	6.0	5.8	5.6	6.0	5.0
	HEL(B+)	6.0	5.8	5.6	5.9	4.9
	HEL(B−)	6.0	5.8	5.6	?[b]	5.0
	TT(A)	5.6	5.3	5.1	5.6	4.3
	HTT(A)	5.6	5.3	5.1	5.6	4.3
syndio	TC(A)	6.0	5.8	5.6	6.0	4.9
	HEL(A+)	6.0	5.7	5.6	?[b]	4.7
	HEL(A−)	6.0	5.8	5.6	6.0	5.0
	TT(B)	5.6	5.3	5.1	5.5	4.3
	HTT(B)	5.6	5.3	5.1	5.5	4.3

[a] These values have been obtained with the B3LYP/6-31+G* scheme on the MP2/6-31G* geometries. The reported values are given for the first excited state (FES). [b] It was not possible to optimize the geometry of the ^{i}Bu chain in the HEL(A+) and HEL(B−) conformations.

help identifying the configuration/conformation adopted by PPB if the polymerization stops after the first step, just like for polyaminoborane, another BH_2-containing polymer.[18] Our spectra are depicted in Figures 4 and 5 for ^{i}Bu−PPB and Ph−PPB, respectively. Parts a (b) are offsets of the wagging (stretching) regions.

For ^{i}Bu−PPB, with a 25 cm^{-1} resolution, two peaks dominate the wagging region: 883 and 1082 cm^{-1} (iPPB); 928 and 1079 cm^{-1} (sPPB). In the stretching region, the are four peaks: 2349, 2401, 2449, and 2493 cm^{-1} (iPPB); 2343 cm^{-1}, 2395, 2449, and 2498 cm^{-1} (sPPB). As the relative intensity and position of the peaks in the stretching region are similar, the only way to distinguish the two conformers, HEL(B+) from HEL(A−), is the first wagging peak (45 cm^{-1} difference).

For Ph−PPB, the two peaks with the largest relative intensity in the wagging region have similar positions for both compounds: 940 and 1065 cm^{-1} (iPPB); 935 and 1086 cm^{-1} (sPPB) (25 cm^{-1} resolution). One broad peak at 2450 cm^{-1} dominates the total stretching region for iPPB, whereas there are two peaks of equal intensity (2415 and 2448 cm^{-1}) for sPPB. This last feature should help in discriminating HTT(A) from HEL(A+), provided a sufficient spectral resolution.

D. Charges and Dipole Moment. Table 6 lists the atomic charges on the central backbone atoms and the norm of the dipole moment for PPB dimers. It turns out that, from one system to the other, the variation of the charges is relatively insensitive to the conformation of the dimer. However, the charges on P and B are deeply affected by the side-group substitution. One has for the charge borne by the phosphorus atom (q_P):

$$\mathrm{H} \approx \mathrm{Ph}(0.3 \sim 0.4e) < {}^{i}\mathrm{Bu} \approx \mathrm{Me}(0.5e) < \mathrm{Me}_2(0.8e)$$

and for the boron atom ($|q_B|$):

$$\mathrm{H} \approx \mathrm{Ph}(-0.1e) < {}^{i}\mathrm{Bu} \approx \mathrm{Me}(-0.2 \sim -0.3e) < \mathrm{Me}_2(-0.4e)$$

Compared to the unsubstituted chains, Ph−PPB presents a similar charge distribution, whereas alkyl−PPB displays a stronger charge separation between P and B.

As mentioned,[5] the norm of the dipole moment is found to be much larger for TT and HTT than for TC and HEL whatever the substitution pattern. The dipole moment could nevertheless be tuned by the form adopted by HEL dimers. For instance, $|\mu|$ is 6.7 D for Ph[HEL(A+)] and 5.1 for Ph[HEL(A−)]. Such weak 1 D variations could also be obtained by changing the substituents; however the difference induced by replacing H by ^{i}Bu or Ph is modest and much less significant than the charge variations.

E. Excitation Energies. The vertical excitation energies are given in Table 7. Similar to those for the the unsubstituted PPB, the excitation energies are significantly lower for TT and HTT than for TC or HEL. Obviously, the determination of the *height* of the first excited state is not a reliable method to allow an accurate discrimination of the A/B substitution or the HEL(+)/HEL(−) structures. Nevertheless, for Ph−PPB, the differences between the most stable form[19] of iPPB-[HTT(A)] and sPPB[HEL(A+)] are on the order of 0.5 eV, a value that should be large enough to distinguish between the two systems. The ^{i}Bu chains present the same excitation energies as the unsubstituted compounds. On the contrary, Ph−PPB have smaller excitation energies than unsubstituted PPB (largest value: 5 eV). This can be understood as the first single-excited state of benzene lies about 5 eV above the ground state.[20−23] However, as the excitation energy of PPB decreases with chain length,[5] it is difficult to foresee if this 1 eV difference between Ph− and ^{i}Bu−PPB will perpetuate for longer chains.

IV. Conclusions

We have studied the structures and properties of substituted PPB dimers. It turns out that, for a given conformation, Ph− and ^{i}Bu−PPB present similar geometrical structures (except the dihedral angles) and dipole moments. However, they differ in the charge separation along the backbone (larger for ^{i}Bu−PPB) and the flexibility (larger for Ph−PPB). The configuration adopted by PPB has a small direct impact on the properties but it affects the most stabilized conformation, and will indirectly modify the properties. This is striking for Ph−PPB, for which we predict the isotactic chain to adopt a trans−transoid conformation, and the syndiotactic chain to adopt an helical (or coiled) conformation. This will consequently tune the dipole moment, excitation energy, etc. of PPB. We propose that the difference between Ph−iPPB and Ph−sPPB originates from the ∼ 3.5 Å distance between backbone phosphorus atoms which sterically allow significant stabilizing interactions between the substituting phenyl rings.

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(11) In the dimer, there is only one chiral center. Nevertheless, using the appropriate starting geometries, one can mimic the iso- and syndiotactic configurations.
(12) These values are based on MP2/6-311G* calculations.
(13) These minima are referred to as HTT in the following for helical-trans-transoid.
(14) As shown in Table 3, no ^{i}Bu−PPB chains with the HEL(A+) or HEL(B−) conformation could be obtained. Numerous procedures have been tested in order to optimize these compounds. However, in every case, the mnolecules *go back* to HEL(A−) or HEL(B+). Subsequently, no minimum in the potential energy surface corresponding to HEL(A+) and HEL(B−) could be identified.
(15) The distances between the Ph groups are close to 3.5 Å and the rings are almost perfectly parallel (deviation is only ∼10°), which is the frame of a typical $\pi-\pi$ interaction.
(16) However, as we consider dimers, this might be a chain-end effect.
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