Theoretical Study of Dehydrogenation Effects upon the First Hyperpolarizability of Polyphosphinoborane

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The longitudinal first hyperpolarizability of polyphosphinoborane oligomers, $-(PH_2-BH_2)_N-$, and their dehydrogenated derivatives $[-(PH-BH)_N-]$ are studied by using ab initio schemes taking explicitly into account dynamic electron correlation effects. The evolution with chain length of the geometries, charges, dipole moments, polarizabilities, and first hyperpolarizabilities is strongly modified when hydrogens are removed. $-(PH-BH)_N-$ chains possess mobile electrons and present larger hyperpolarizabilities than those of classical push−pull systems.

I. Introduction

In past decades, numerous works have been devoted to the theoretical characterization of the nonlinear optical (NLO) properties of organic materials.[1−3] From a microscopic point of view, the dipolar first hyperpolarizability (β) is the first term related to macroscopic NLO phenomena (second harmonic generation, dc-Pockels effect, optical rectification). To maximize β and, more precisely, β related to the size (β/N; N is the number of unit cells) or weight (β/W; W is the molecular weight) of the compound, electron delocalization and asymmetry have to be combined efficiently. Indeed, on one hand, it is known that the (hyper)polarizabilities of organic systems are often enhanced by the presence of mobile π electrons [the second hyperpolarizability is much larger for polyacetylene (PA) than for polyethylene (PE)], and, on the other hand, β is strictly zero for centrosymmetric molecules. (β corresponds to an odd term in the dipole moment expansion.) However, an efficient asymmetry/delocalization combination is difficult to reach. Indeed, in general, delocalization increases when asymmetry decreases and vice versa, but both are needed to obtain substantial β values. As a simple illustration, PA, one of the most delocalizable segments, is perfectly symmetric. To bypass this problem, different molecular species have been investigated,[4−11] but the most intensively studied class of compounds remains push−pull systems. These systems consist of a symmetric delocalizable chain capped at its extremities by an electroacceptor group on one side and a electrodonor group on the other side. The end groups are responsible for the asymmetry whereas the conjugated linker provides the mobile π electrons. To maximize β/N, one can increase the strength of the donor/acceptor pair or/and use more polarizable chains. Even without considering practical limitations (medium effects, stability of the compounds, ...), both strategies are limited. Indeed, it is difficult to obtain push/pull groups significantly stronger than NO_2/NMe_2. In addition, once a conjugated segment has been selected, the only way to improve its delocalization is to increase its length (i.e., to use more unit cells). Nevertheless, for large N, the end groups do not interact anymore, leading to the

stabilization of β as well as a sharp falloff of β/N.[12−15] As a consequence, the graph of β/N versus N presents a maximum. This could be rationalized in terms of balance between asymmetry and delocalization: the electron mobility is too weak in short chains whereas long oligomers are too symmetric. The maximal β/N could be large,[15] but these push−pull systems present a major practical drawback: opposing to even-order (hyper)polarizabilities, the optimal response is not obtained for the polymer ($N \rightarrow \infty$) (i.e., to reach the highest efficiency a given oligomer length has to be synthesized). For this reason, we have shown interest in compounds in which each unit is both asymmetric and presents π electrons: the so-called AB systems $[-(A = B)_N-]$. Different AB compounds have been studied previously, and,depending on the nuclei and bonds, very different macromolecular responses ($[\beta/N]_{N \rightarrow \infty}$) have been predicted. In linear boron nitride chains, $=(B=N)_N=$, $[\beta/N]_{N \rightarrow \infty}$ is close to zero for the macromolecule because of a nearly zero bond-length alternation ($\Delta r = d_{B-A} - d_{A=B}$) found in long chains[16] (i.e., the polymer is too symmetric). In polymethine-imine [PMI, $-(CH=N)_N-$], $[\beta/N]_{N \rightarrow \infty}$ is as large as in the best α,ω-nitro,amino-PA chains[15,17] and larger than in most of the compounds synthesized up to now. For example, the β/N of PMI is 1 order of magnitude larger than the β/N reported for 3-methyl-4-nitroaniline (MNA)[18] and N-(4-nitrophenyl)−(L)-prolinol (NPP).[19]

To complete our understanding of the interplay between delocalization and asymmetry, we have selected two inorganic polymers—polyphosphinoborane [PPB, $-(PH_2-BH_2)_N-$], which has been recently synthesized with high molecular weight,[20−22] and its conjugated parent [DHPPB, $-(PH-BH)_N-$] (see Figure 1) [similar to the polyethylene−polyacetylene series], which has not been synthesized yet although it is known that PPB easily undergoes reduction.[23]

II. Computational Details

The calculations have been performed by using the following procedure:

1. The ground-state geometry of each oligomer has been determined by the optimization of its structural parameters with the Gaussian 98 program.[24] The only constraint was the use of the planar trans−cisoïd conformation (Figure 1). Test calcula-

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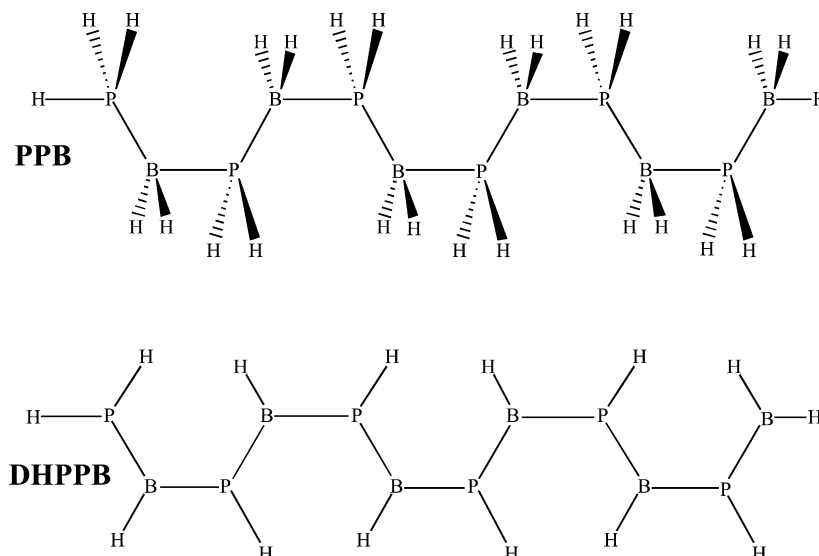*J. Phys. Chem. A, Vol. 108, No. 3, 2004* **501**

Figure 1. Schematic representation of PPB and DHPPB.

tions carried out at the MP2/6-31G(d) level reveal that this conformation is the most stable planar structure for PPB, as it is the case for other AB systems such as polyphosphazene (PP)[25] or PMI.[26,27] These optimizations have been performed within the Hartree−Fock (HF) and second-order Møller−Plesset (MP2) levels of approximation using the 6-31G(d) basis set.[28] After the geometry optimization, each oligomer has been oriented in the Cartesian frame so that the longitudinal axis passes through the center of the first and last PB bonds.

2. In addition to longitudinal dipole moments (μ_L), charges have been computed on the optimized geometries using the Mulliken approximation within the MP2/6-31G(d) approach. However, because Mulliken charges are generally unreliable, we have also selected an electrostatic potential-derived type formalism for evaluating the charges (so-called Merz−Kollman or ESP charges[29]). Contrary to Mulliken charges, it has been proven that the ESP scheme yields charges that are consistent with experimental data.[30]

3. Polarizabilities (α) and first hyperpolarizabilities (β) have been calculated on the optimized geometries with two ab initio methods (HF/6-31G(d) and MP2/6-31G(d)). In quasilinear chains, the longitudinal components of α and β tensors (α_L and β_L) dominate the total responses for sufficiently long chains. For example, for $N = 20$ the β_L of DHPPB evaluated at the HF/6-31G(d)//HF/6-31G(d) level[31] is 10 times larger than the next larger component. For this reason, we focus on longitudinal components in this paper. The vibrational contributions to α and β (α^v and β^v) have been neglected. α^v and β^v could make an important contribution to the total static values in conjugated systems,[32,33] but practical determinations at EC levels remain difficult for extended oligomers. Moreover, the relative importance of β^v is strongly decreased when dynamic β values (i.e., β corresponding to second-harmonic generation, optical rectification, and electrooptic dc-Pockels effects) are considered. At the HF level, static α_L and β_L have been computed by using the coupled-perturbed Hartree−Fock (CPHF) method implemented in Gaussian 98[24] whereas dynamic values have been obtained with the time-dependent Hartree−Fock scheme (TDHF) method included in Gaussian 03.[34] At the Møller−Plesset level of approximation, static α_L and β_L have been evaluated by using the numerical finite-field procedure. We refer the reader to ref 16 for a complete description of this procedure. For the long compounds investigated in this paper, it is not possible, in practice, to obtain dynamic NLO responses at the MP2 level.

However, using the multiplicative correction,[35,36] one can obtain reasonable estimates of these responses. For push−pull oligomers, although the HF and electron-correlated β_L differ by a factor of 2, the multiplicative correction reproduces the electron-correlated frequency dispersion effect with only 1 to 4% error.[37] In this paper, we adopt the usual sign convention for β_L (i.e., positive when orientated in the same direction as the dipole moment, negative otherwise).

4. The polymeric responses have been obtained by extrapolating the oligomeric values. To carry out extrapolations, an alternative definition of the β_L (and μ_L and α_L) per unit cell,

$$\Delta\beta_L(N) = \frac{1}{2}[\beta_L(N) - \beta_L(N-2)]$$

is employed. This definition removes most of the chain-end effects, leads to a faster convergence than β_L/N, and converges to the same asymptotic limit ($N \rightarrow \infty$). Our fitting procedure allows us to obtain the average $\Delta\beta_L(\infty)$ and its standard deviation. We refer the reader to ref 38 for more details.

III. Results

A. Geometries. One important geometric descriptor for NLO applications is the bond length alternation (Δr).[5] Tables 1 and 2 give the Δr obtained at the center[39] of PPB and DHPPB. For PPB, an experimental X-ray structure of the substituted dimer (PHPh$_2$−BH$_2$−PPh$_2$−BH$_3$) is available.[21] It turns out that the central bond is longer (1.944 Å) than the terminal bonds (1.923 and 1.932 Å). Being positive, our MP2/6-31G(d) Δr reproduces this feature. Using our convention,[39] the experimental Δr is 0.02 Å whereas the MP2/6-31G(d) Δr is 0.01 Å. This difference is probably related to the presence of phenyl groups in the experimental compound. The Δr values obtained for PPB and DHPPB are smaller than in polyphosphazene or polyacetylene: for $N = 8$, the Δr values for PPB, DHPPB, PP, and PA are 0.014, 0.005, 0.024 [25] and 0.070 Å,[40] respectively. In PPB, the Δr converges quickly with chain length, and the polymeric Δr is predicted to be small but nonzero [HF/6-31G(d): 0.018 ± 0.002 Å]. This contrasts with the saturated carbon system (i.e., polyethylene, in which all bond lengths are equal). The DHPPB Δr changes sign when the chain lengthens. In the polymer, the shortest bonds are parallel to the longitudinal axis (i.e., this system favors a cis−transoïd conformation over a trans−cisoïd conformation). The HF/6-31G(d) Δr extrapolated for DHPPB

TABLE 1: Bond Length Alternation (Å), Charge Alternation (*e*), Longitudinal Dipole Moment (a.u.), Longitudinal Static Polarizability (a.u.), and Longitudinal Static First Hyperpolarizability (a.u.) of trans–cisoïd PPB Chains[a]

N	Δr	Δq^b	Δq^c	μ_L[HF]	μ_L[MP2]	α_L[HF]	α_L[MP2]	β_L[HF]	β_L[MP2]
				MP2/6-31G(d) Geometry					
2	0.009	0.48	0.49	−1.93	−1.90	77	79	−49	−70
4	0.010	0.51	0.90	−5.36	−5.28	177	188	−185	−295
6	0.013	0.48	0.83	−9.18	−9.07	285	306	−229	−367
8	0.014	0.48	0.92	−13.16	−13.03	396	427	−214	−332
10	0.014	0.47	0.95	−17.19	−17.05	508	550	−168	−239
				HF/6-31G(d) Geometry					
2	−0.020	0.44	0.42	−2.01	−1.98	77	80	−48	−68
4	0.000	0.48	0.79	−5.63	−5.55	181	191	−185	−288
6	0.007	0.45	0.75	−9.66	−9.55	292	312	−232	−350
8	0.010	0.45	0.84	−13.84	−13.72	406	437	−224	−310
10	0.013	0.45	0.85	−18.09	−17.94	522	563	−187	−215
12	0.014	0.45	0.87	−22.37	−22.21	638	690	−134	−89
14	0.015	0.45	0.88	−26.66	−26.49	755	817	−73	51
16	0.015			−30.97	−30.78	872	945	−6	203
18	0.016			−35.27		989		64	
20	0.016			−39.59		1106		136	
∞^d	0.018	0.45	0.91	−2.19	−2.20	60	67	39	109
$\Delta\infty^d$	0.02	0.01	0.03	0.02	0.05	2	3	2	28

[a] All results have been obtained with the 6-31G(d) basis set. Δq values have been obtained with the MP2 approach. At the bottom of the Table, the extrapolated polymeric values are given. (See the text for more details on the procedure used to obtain these values.) 1 a.u. of μ = 2.5418 D. 1 a.u. of α = 1.6488 10^{-41} C^{2}m^{2}J^{-1} = 0.14818 Å^3. 1 a.u. of β = 3.2063 10^{-53} C^{3}m^{3}J^{-2} = 8.641 10^{-33} esu. [b] Calculated on the basis of Mulliken charges. [c] Calculated on the basis of ESP charges. [d] ∞ gives the extrapolated value whereas $\Delta\infty$ is the estimated extrapolation error (i.e., polymeric values are given by $\infty \pm \Delta\infty$).

TABLE 2: Bond Length Alternation (Å), Charge Alternation (*e*), Longitudinal Dipole Moment (a.u.), Longitudinal Static Polarizability (a.u.), and Longitudinal Static First Hyperpolarizability (a.u.) of trans–cisoïd DHPPB Chains[a]

N	Δr	Δq^b	Δq^c	μ_L[HF]	μ_L[MP2]	α_L[HF]	α_L[MP2]	β_L[HF]	β_L[MP2]
				MP2/6-31G(d) Geometry					
2	0.070	−0.07	0.55	−0.43	−0.66	98	110	$(-)^d$58	$(-)^d$160
4	0.026	−0.06	0.78	−0.41	−0.66	272	341	$(-)^d$1266	$(-)^d$1852
6	0.011	−0.06	0.79	−0.20	−0.37	478	636	$(-)^d$3864	$(-)^d$5798
8	0.005	−0.06	0.83	0.09	0.06	698	960	7450	11 835
10	0.000	−0.06	0.79	0.43	0.56	924	1299	11 634	19 312
12	−0.002	−0.06	0.83	0.79	1.11	1154	1646	16 171	27 699
				HF/6-31G(d) Geometry					
2	0.059	−0.09	0.56	−0.40	−0.61	100	112	$(-)^d$40	$(-)^d$130
4	0.015	−0.06	0.79	−0.35	−0.58	275	346	$(-)^d$1187	$(-)^d$1651
6	0.005	−0.07	0.79	−0.13	−0.29	481	642	$(-)^d$3667	$(-)^d$5392
8	0.001	−0.07	0.84	0.13	0.11	700	965	7060	11 168
10	−0.001	−0.07	0.80	0.43	0.57	926	1303	10 983	18 297
12	−0.002	−0.07	0.85	0.73	1.04	1154	1647	15 207	26 248
14	−0.003	−0.07	0.80	1.04	1.53	1383	1995	19 604	34 693
16	−0.004	−0.07	0.85	1.36	2.03	1614	2345	24 105	43 440
18	−0.004			1.68	2.53	1846	2697	28 670	52 375
20	−0.004			2.00		2077		33 276	
∞^e	−0.007	−0.07	0.83	0.17	0.27	117	178	2329	4795
$\Delta\infty^e$	0.003	0.01	0.03	0.01	0.02	2	2	8	314

[a] See Table 1 for more details. [b] Calculated on the basis of Mulliken charges. [c] Calculated on the basis of ESP charges. [d] β_L is negative up to the hexamer because it points toward the direction opposite to the dipole moment. However, it is the dipole, rather than β_L, that changes sign between N = 6 and 8. Indeed, the direction of β_L is constant for all oligomers, and β_L could be considered to be positive for all chain lengths: it is parallel to the dipole moment of the polymer. [e] ∞ gives the extrapolated value whereas $\Delta\infty$ is the estimated extrapolation error (i.e., polymeric values are given by $\infty \pm \Delta\infty$).

is −0.007 ± 0.003 Å. Contrary to PA, DHPPB presents almost equal bonds. Therefore, the consequence of the dehydrogenation of PPB is a change of sign and a decrease in the magnitude of Δr.

From a more methodological point of view, we see that the MP2/6-31G(d) and HF/6-31G(d) Δr values follow the same trends with regard to chain length. Actually, provided the oligomer considered is long enough, the two techniques agree very well, although HF/6-31G(d) is unable to reproduce the experimental Δr sign for the dimer. For these phosphorus-containing systems, one could expect that the inclusion of a d orbital in the atomic basis set is necessary. This has been

checked by optimizing (at the HF level) the octamer with 6-31G and 6-31G(2d). For PPB, the obtained Δr are 0.00, 0.01, and 0.01 Å for 6-31G, 6-31G(d), and 6-31G(2d), respectively. This highlights the importance of including one set of polarization functions in the basis set. Finally, contrary to most conjugated compounds such as polyenes[40] or polymethineimine,[17] we note that HF Δr are smaller than MP2 Δr.

B. Charges and Dipole Moments. Whereas Δr describes the bond alternation, other parameters are important for assessing the delocalization and the asymmetry along the oligomeric backbone. Among these parameters is the nuclear alternation (i.e., the difference between A and B in AB systems). As a
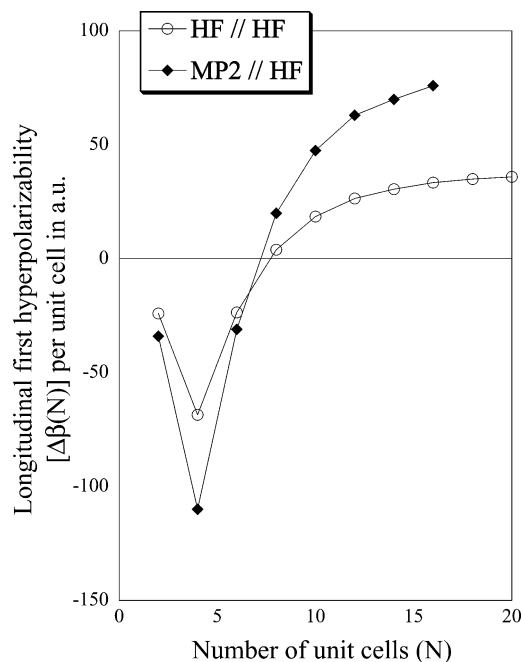
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Figure 2. Evolution with chain length of the longitudinal first hyperpolarizability per unit cell, $\Delta\beta_{L(N)}$, of PPB. These 6-31G(d) $\Delta\beta_{L(N)}$ have been obtained with the HF/6-31G(d) geometry.
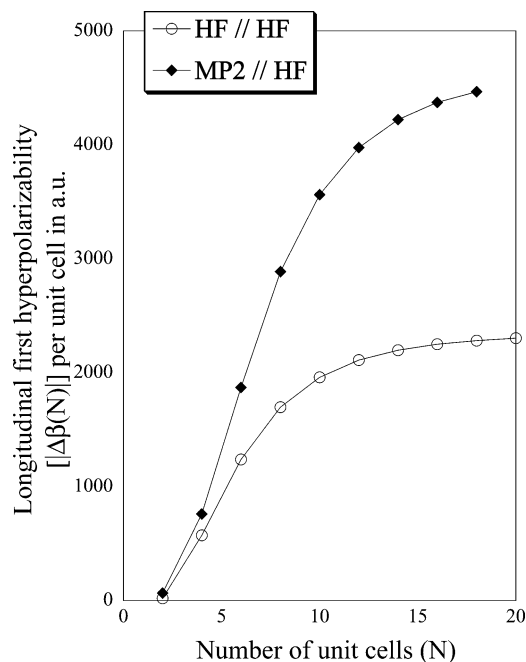

Figure 3. Evolution with chain length of the longitudinal first hyperpolarizability per unit cell, $|\Delta\beta_{L(N)}| = {}^{1}/_{2}[|\beta_{L(N)}| - |\beta_{L(N-2)}|]$, of DHPPB. These 6-31G(d) $|\Delta\beta_{L(N)}|$ have been obtained with the HF/6-31G(d) geometry.

crude approximation to this parameter, we use the difference between the charges on adjacent atoms. It is the charge alternation $\Delta q = q^{P} - q^{B}$ measured at the center of the chain. Within the Mulliken approximation, Δq converges extremely quickly with respect to N and becomes constant when $N \geq 6$. The saturation speed is slower with ESP charges and ESP predicts the charge separation of PPB to be twice as large as $\Delta q^{Mulliken}$. Nevertheless, for both schemes, Δq of PPB is relatively small. Indeed, in polyphosphazene the backbone atoms (P and N) exchange almost one electron (i.e., $\Delta q \approx 2$)[25] whereas for polymethineimine we obtained $\Delta q^{Mulliken} = 0.65$ for the octamer.[41] The effect of reduction is described very differently by Mulliken and ESP schemes. Within the former, the charge transfer becomes extremely limited in DHPPB, and in addition, the sign of Δq is modified [P bears a negative charge in DHPPB (positive in PPB)]. Within the latter, removing hydrogens from PPB has mainly no impact on Δq.

Tables 1 and 2 give the μ_L of PPB and DHPPB, respectively. The evolution with chain length of $\Delta\mu_L$ of both systems presents a standard shape: it increases with chain length for small oligomers and then enters the saturation regime where it converges toward the polymeric value. Consistent with the sign change noted for $\Delta q^{Mulliken}$, the sign of μ_L reverses between the hexamer and octamer of DHPPB. Reduction strongly decreases $\Delta\mu_L(\infty)$ from -5.59 to 0.69 D. These values may be compared to the $\Delta\mu_L(\infty)$ of PP: 4.35 D.[42] As a first approximation, μ_L depends primarily on the asymmetry,[43] so this falloff of $\Delta\mu_L(\infty)$ upon reduction could be related to a smaller asymmetry in DHPPB with regard to that in PPB. This is consistent with decreases of Δr and $\Delta q^{Mulliken}$ obtained when removing hydrogens.

C. (Hyper)polarizabilities. *1. Static Values.* Tables 1 and 2 give the static α_L and β_L of PPB and DHPPB whereas Figures 2 and 3 depict the evolution with chain length of the static $\Delta\beta_L$. For both systems, the HF and MP2 geometries lead to very similar responses, so we can already trust the lower-level geometries. Performing an MP2/6-31G//HF/6-31G calculation on the octamer of PPB leads to a β_L of -597 a.u., almost twice

the value obtained with the 6-31G(d) basis set. As for the Δr, this example highlights the importance of polarization functions.

As expected for increasingly long compounds,[43-47] the $\Delta\alpha_L$ of PPB (and DHPPB) increases rapidly with chain length for small oligomers and then enters the saturation regime where it tends toward the asymptotic value characteristic of the infinite polymer. This polymeric value per unit cell is 67 a.u. (178 a.u.) for PPB (DHPPB). For comparison, PA[48] and polysilane[49] present $\Delta\alpha_L(\infty)$ close to 131 a.u. Because α does not depend on the asymmetry but only on the delocalizability, this stresses that DHPPB chains are highly delocalizable. The strong polarizability enhancement due to reduction is related to an increase in electron mobility, which in turn can be associated with the small Δr of DHPPB. To rationalize these findings further, natural bond order[50] (NBO) analysis has been performed on the two systems. For long oligomers, chain-end perturbations are reduced, and NBO analysis predicts a localized structure constituted only of single bonds (occupancy > 1.98e) in PPB. These bonds mostly present sp[2.3] (sp[3.2]) character on phosphorus (boron) atoms. In contrast, for DHPPB, NBO analysis finds a delocalized structure with an alternation of single (occupancy > 1.98e) and double bonds (occupancy > 1.98e and 1.80e). The single bonds are mostly constituted of an sp[1.7] (sp[2.0]) hybrid on phosphorus (boron) atoms. The extra links in the double bonds present almost 100% p character on both atoms. In other words, the NBO leads to results that are quite consistent with an sp[3]/sp[2] evolution between PPB and DHPPB (at least for boron), which in turn is consistent with the increase in delocalizability observed. However, the NBO approach does not predict the importance of including d functions in the basis set, and the single/double alternation in DHPPB is questionable in regard to the small Δr observed. This multiplicity of results is not surprising if one compares to PP[25] where the nature of the bonds is also predicted differently in regard to the analysis chosen.

In PPB, $\Delta\beta_L$ is first negative, reaches a minimum, changes sign, and then saturates toward the polymeric limit. This shape stays the same for the different level of theory used and is similar

TABLE 3: Dynamic Longitudinal Polarizability and First Hyperpolarizability (a.u.) of trans−cisoïd PPB and DHPPB Chains[a]

	static		$\lambda = 1907$ nm			$\lambda = 1064$ nm		
N	$\alpha_L(0; 0)$	$\beta_L(0; 0, 0)$	$\alpha_L(-\omega; \omega)$	$\beta_L(-\omega; \omega, 0)$	$\beta_L(-2\omega; \omega, \omega)$	$\alpha_L(-\omega; \omega)$	$\beta_L(-\omega; \omega, 0)$	$\beta_L(-2\omega; \omega, \omega)$
				PPB				
2	77	−48	78	−48	−49	78	−49	−52
4	181	−185	181	−187	−190	183	−191	−204
6	292	−232	293	−235	−240	296	−240	−257
8	406	−224	408	−227	−231	411	−232	−247
10	522	−187	524	−189	−193	529	−192	−204
12	638	−134	641	−135	−137	647	−137	−143
14	755	−73	758	−73	−72	765	−73	−73
16	872	−6	876	−5	−3	884	−3	5
18	989	64	993	66	70	1003	70	85
20	1106	136	1111	139	145	1122	146	168
				DHPPB				
2	100	40	100	39	36	102	36	21
4	275	1187	279	1204	1236	287	1239	1320
6	481	3667	489	3755	3939	509	3959	4634
8	700	7060	714	7270	7722	746	7771	9641
10	926	10 983	944	11 349	12 150	989	12 239	15 753
12	1154	15 207	1179	15 751	16 950	1237	17 083	22 541
14	1383	19 604	1413	20 338	21 966	1487	22 148	29 737
16	1614	24 105	1650	25 038	27 113	1737	27 346	37 184
18	1846	28 670	1887	29 806	32 340	1989	32 625	44 790
20	2077	33 276	2125	34 618	37 620	2241	37 958	52 499

[a] All results have been obtained with the TDHF/6-31G(d)//HF/6-31G(d) method. See Table 1 for mode details.

to the one found in PMI.[17,38,43] To rationalize this shape, one can divide β into different components. Indeed, the total β value can be divided into chain-end (PH$_3$ versus BH$_3$ terminal groups) and unit cell contributions, both being affected by the increase in delocalization obtained when the chain is growing. Additionally, the unit cell contribution can be divided into a nuclear alternation (P versus B) and a bond alternation (longer versus shorter bonds). In the case of PPB, the evolution of $\Delta\beta_L$ can be interpreted as follows: (1) for short oligomers, the chain-end contribution (which is negative) dominates the total response; (2) this chain-end contribution increases when the chain lengthens due to the increase in electron delocalization; (3) for long chains, the unit cell contribution (which is positive) dominates the β response; and (4) for very long oligomers, $\Delta\beta_L$ is constant, each unit cell bringing the same contribution to β_L. Similar to PMI, the combination of (1), (2), (3), and (4) explains the presence of the minimum, the sign change, and the saturation.[16,17,38,43] In PPB, contrary to PMI, the $|\Delta\beta_L|$ at the minimum (110 a.u.) is of the same order of magnitude as $\Delta\beta_L(\infty)$. Because delocalization is limited in PPB, the saturation of β_L toward the polymeric limit is fast, and the polymeric value, $\Delta\beta_L(\infty)$, is small (109 a.u. at the MP2/6-31G(d)//HF/6-31G(d) level).

As could be expected from the important variations of Δr, $\Delta q^{Mulliken}$, $\Delta\mu_L$, and $\Delta\alpha_L$, the amplitude and shape of the $\Delta\beta_L$ versus N curve is deeply modified when shifting from PPB to DHPPB. Indeed, in DHPPB, the shape of the curve (Figure 3) does not present a sign change or minimum and is similar to a "polarizability curve" with first an increase due to delocalization and then the saturation toward the polymeric limit. The fact that neither a minimum nor a sign change is present indicates that the chain-end contribution to β_L is probably small and parallel to the unit cell contribution. Also, the polymeric $\Delta\beta_L$ (4795 a.u. at the MP2/6-31G(d)//HF/6-31G(d) level) is much larger than in PPB. This can be related to the large delocalizability in DHPPB ($\Delta\alpha_L$ is large, Δr is small). $\Delta\alpha_L(\infty)$ is 2.7 times larger in DHPPB than in PPB whereas for $\Delta\beta_L(\infty)$ the ratio is 44, showing that differences are much stronger for nonlinear effects than for linear responses. Note that DHPPB is also less asymmetric (see $\Delta\mu_L$) than PPB, which could, in

theory, lead to a falloff of β_L. The present result is consistent with model calculations performed on AB polymers,[51] which showed that bond and charge alternations have to be quite small to obtain large macromolecular β_L (i.e., it seems preferable to have small asymmetry ($\Delta\mu_L$) and large delocalization ($\Delta\alpha_L$) rather than the opposite).

2. Dynamic Values. In the sum-over-state framework,[52] the (hyper)polarizabilities are proportional to the inverse of the energetic differences measured between the ground and excited states. In a crude approximation, this means that large β values would be obtained for small-gap systems. Because frequency dispersion effects tend to be larger for small-gap compounds, this means that the larger the static β, the larger the frequency dispersion effects. This simple qualitative approach is verified for PPB and DHPPB, for which dynamic β values are given in Table 3 (two standard laser frequencies have been used). For the largest chain treated ($N = 20$), $\beta(-2\omega; \omega, \omega)$ is increased by 7% (24%) in the case of PPB for $\lambda = 1907$ nm (1064 nm). The increase is twice as much in DHPPB: 13% (58%) for $\lambda = 1907$ nm (1064 nm). This confirms that DHPPB presents the best potential for NLO applications. For this compound, the dynamic/static ratio is converging quite rapidly with respect to N, and we can estimate the polymeric dynamic value to be ~15 and ~70% larger than the static value for $\beta(-\omega; \omega, 0)$ and $\beta(-2\omega; \omega, \omega)$ evaluated with a laser frequency of 1064 nm.

Figures 4 and 5 represent the dispersion plots obtained for the dodecamer of PPB and DHPPB. The dynamic β can be related to static values using a power series expansion:[53,54]

$$\beta(-\omega_\sigma; \omega_1, \omega_2) = \beta(0; 0, 0)[1 + A\omega_L^2 + B\omega_L^4 + C\omega_L^6 + ...] \quad (1)$$

with

$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 \quad (2)$$

In this expansion, A and B depend only on the molecule but not on the optical process considered:[55] for a given system, only

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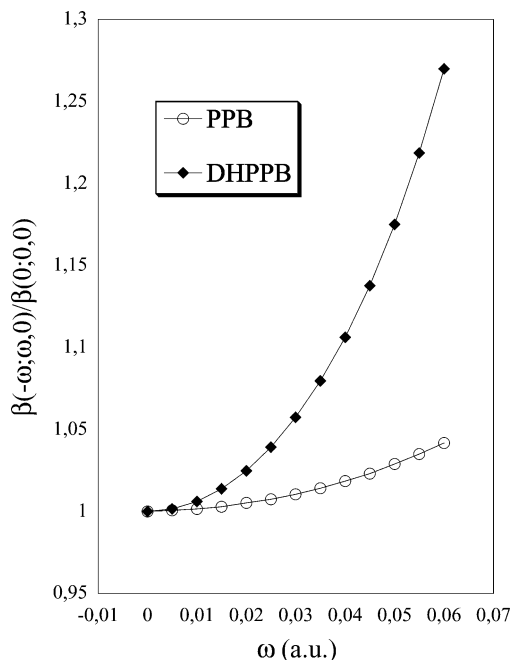
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Figure 4. TDHF/6-31G(d)//HF/6-31G(d) dispersion curve (optical rectification) obtained for the dodecamer of PPB and DHPPB. The values reported are the ratio with respect to the static response.
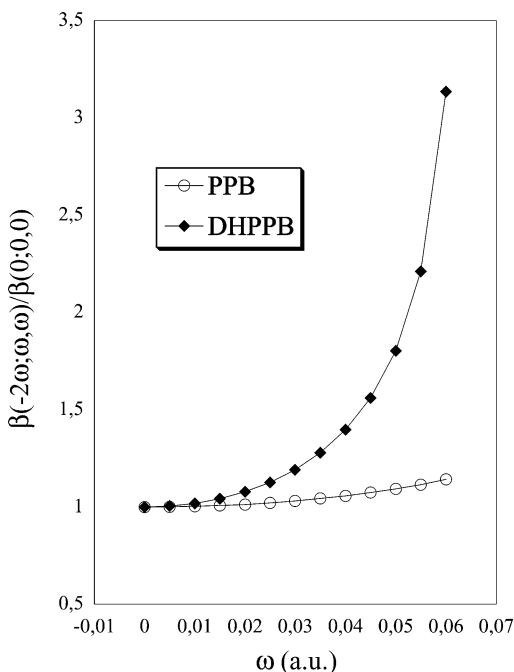

Figure 5. TDHF/6-31G(d)//HF/6-31G(d) dispersion curve (second-harmonic generation) obtained for the dodecamer of PPB and DHPPB. The values reported are the ratio with respect to the static response.

ω_L^2 determines the dynamic first hyperpolarizability. Because ω_L^2 is similar for $\beta(-2\omega; \omega, \omega)$ when $\lambda = 1907$ nm and for $\beta(-\omega; \omega, 0)$ when $\lambda = 1064$ nm, these two processes lead to almost identical β as confirmed by Table 3. We have obtained the A value for the dodecamer of PPB and DHPPB by a least-squares fitting with the function $[1 + A\omega_L^2 + B\omega_L^4 + C\omega_L^6]$ realized on a set of $\beta(-\omega; \omega, 0)$ points corresponding to frequencies of 0.000, 0.005, ... 0.060 a.u. It turns out that $A = 6$ for PPB and 30 for DHPPB, confirming that frequency dispersion effects are much larger in the latter system. For comparison, the A value for α,ω-nitro,amino-transhexatriene is 45.[37]

IV. Conclusions

We have investigated the dehydrogenation effects upon geometries, charges, dipole moments, polarizabilities, and second-order NLO coefficients of polyphosphinoboranes. It appears that PPB presents a limited delocalizability (small polarizability) but substantial asymmetry (large dipole moment). In addition, the bond and charge alternations of PPB are relatively small compared to those of other phosphorus-containing compounds (polyphosphazene). Both alternations become even smaller when hydrogens are removed from the chain, leading to smaller dipole moments and larger polarizabilties. This can be interpreted as an increase in electron mobility and a decrease in asymmetry. As a consequence, the static $\Delta\beta_L(\infty)$ of PPB is multiplied by 44 when hydrogens are removed. This factor is even larger when frequency dispersion effects are taken care of.

The static β_L/W of the systems investigated here can be easily obtained from the corresponding $\Delta\beta_L(\infty)$: 0.02×10^{-30} cm^5 esu^{-1} g^{-1} mol for PPB and 0.95×10^{-30} cm^5 esu^{-1} g^{-1} mol for DHPPB. One may compare them with the values of 0.10×10^{-30} reported for the 3-methyl-4-nitroaniline (MNA) monomer,[18] 0.06×10^{-30} for *N*-(4-nitrophenyl)-(L)-prolinol (NPP),[19] 0.66 for α,ω-nitro,amino-transhexatriene,[37] and 4.2×10^{-30} for PMI.[17] This means that PPB presents a negligible response whereas DHPPB turns out to have a better potential for NLO applications.

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