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Enhancement of the second-order NLO responses of boron–nitrogen oligomers by copolymerization with polyyne

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ABSTRACT

The enhancement of the static electronic second-order NLO properties of the linear boron–nitrogen chains by copolymerization with polyyne that is related mainly to the changes in the bond length alternation (BLA) parameter has been investigated at the HF and MP2 levels using the 6-311G(d,p) and 6-311+G(d,p) basis sets. The non-zero BLA parameter combined with ununiform electron distribution along the chain yields a unit cell asymmetry necessary for large second-order NLO responses. Alternance of the single and triple bonds brings an efficient electron delocalization resulting in large polymeric electronic dipole polarizability (186 ± 1 a.u. per unit cell). The unit cell asymmetry and large delocalization lead to sizeable longitudinal first hyperpolarizability (5850 ± 100 a.u. per unit cell).

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1. Introduction

Efficient nonlinear interactions between light waves and electric fields require specifically designed materials. Conjugated organic molecular materials are in this context increasingly being recognized as promising substances possessing several advantages compared to traditional inorganic nonlinear optical (NLO) materials (LiNbO₃, KTP, etc.) [1,2]. First of all, the presence of multiple bonds combined with the versatility of synthetic organic chemistry can be used to easily alter the molecular structure to maximize NLO responses and other properties. Organic structures can be often prepared in a form of thin layers, while many of them exhibit high thermal and optical stabilities. Another important point is that they usually present maximum NLO responses out of the resonance region. On the contrary, it is typical for inorganic materials that their NLO responses are large only in the resonance region leading to increased thermal dissipation and finally to shorter operating time. Moreover, their effective NLO responses decrease due to the absorption. Consequently, conjugated organic oligo- and polymeric materials represent the most interesting class of NLO materials.

From a microscopic point of view, the first hyperpolarizability (β) is related to the macroscopic second order NLO phenomena (second harmonic generation, dc-Pockels effect and optical rectifi-

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cation). In order to maximize β of the system, it is necessary to combine efficiently electron delocalizability and asymmetry. While the former is related to mobility of π electrons, the latter is necessary, since β is strictly zero for centro-symmetric molecules. However, the increase in asymmetry often leads to decrease of the degree of electron delocalization, so it is not easy to maximize both effects simultaneously. One way to overcome this problem is to use so-called push–pull systems [3–7], which consist of a symmetric delocalizable chain capped at its end by electron donor and acceptor groups. Alternatively, one can design conjugated (to keep delocalization large) systems with an asymmetric unit cell. In such AB systems, a purely electric response may indeed be obtained for any chain length and the β value of the polymer may be different from zero. On top of that, these molecules may combine small dipole moment amplitudes with large beta values. In AB systems, the evolution of β/N (N being the number of unit cells) with increasing chain length can be more complex than in push–pull systems. Indeed, it may or need not present a maximum, a sign reversal or a non-zero polymeric limit ($N \rightarrow \infty$). In order to rationalize this complex behavior, it was found useful to split asymmetry of the system into chain-end and unit-cell contributions, both being affected by the increase of delocalizability occurring when the chain lengthens [8–10]. It follows from a theoretical analysis that in the infinite-chain limit, where the chain-end term is zero, both nuclear and bond length alternation (BLA) are necessary (if either one is zero, $[\beta]_{N \rightarrow \infty}$ is also zero). Simple Hückel results show that the largest $[\beta/N]_{N \rightarrow \infty}$ value would be obtained with a large delocalization (i.e. small BLA) and a small (but non-zero) asymmetry rather than

the reverse [11]. Such conclusions are confirmed at *ab initio* level [12]. Optimum combination of these characteristics in case of the model phosphorus-boron (PB) chain leads to extremely large β/N values [13] what shows a direction for obtaining high-grade NLO materials. Boron–nitrogen (BN) chains are natural analogs of the PB systems. However, we showed that prolongation of the BN chain leads to the decrease of the BLA parameter and consequently also to low NLO responses [14]. Contrary to the model PB chains, in which the bonding corresponds to conjugation of triple bonds, i.e. $-\text{[P}\equiv\text{B]}_N-$, in the BN oligomers one could possibly speak of the sequence of double bonds, i.e. $=\text{[B=N]}_N=$, that are equally long (in the infinite-chain limit), and thus BLA is zero.

Our main idea was therefore to increase the asymmetry of these chains by incorporating carbon atoms into the chain skeleton. One way is to follow the idea by Černušák et al. [15–18] proposing various types of cyclic as well as acyclic B/C/N structures. We will report the NLO properties of such systems in a related paper [19]. The second option is to improve the BLA characteristics of the BN chains by copolymerization with their isovalent polyyynes (PY) (see Fig. 1). Due to the strength of the triple $\text{C}\equiv\text{C}$ bond, it can be expected that the sequence of double bonds in BN will be changed to alternation of single and triple bonds. Our idea to modify the second-order NLO responses by copolymerization has been successfully applied to several conjugated systems [20–23]. In this work, we present the analysis of the bond-orders in the BNCC co-oligomers and we show that the increase of the BLA parameter in these systems leads to a significant enhancement in their polymeric longitudinal second-order NLO properties.

2. Computational details

All the calculations have been performed with the Gaussian 03 program [24], using the following procedure:

1. The ground-state geometry of each linear co-oligomer $\text{H-B}\equiv\text{N}[\text{C}\equiv\text{B}\equiv\text{N}]_N\text{-H}$ ($N=0\text{--}15$) has been determined by full optimization of its structural parameters at the Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory (MP2) using the 6-311G(d,p) basis set. Optimized geometries have been checked for positiveness of the force constants.

2. In order to understand the nature of bonding in the co-oligomers, the natural bond order (NBO) analysis [25,26] has been performed at the HF level. As shown below, the alternation of single and triple bonds in BNCC systems have been confirmed. Nevertheless, since triple BN bonds naturally differ from CC bonds, BLA parameter was calculated by the formula:

$$\text{BLA} = \frac{1}{2}(r(\text{N}_1\text{C}) + r(\text{CB}_2)) - \frac{1}{3}(r(\text{B}_1\text{N}_1) + r(\text{CC}) + r(\text{B}_2\text{N}_2)) \quad (1)$$

where $r(\text{N}_1\text{C})$, $r(\text{CB}_2)$, $r(\text{B}_1\text{N}_1)$, $r(\text{CC})$, and $r(\text{B}_2\text{N}_2)$ are the bond distances for the central fragment of a molecule, i.e. $-\text{B}_1\text{N}_1\text{--CC--B}_2\text{N}_2-$, which was considered to minimize the chain end effects. The first term therefore corresponds to an averaged single bond distance and the second term gives an estimation of the averaged triple bond distance.

3. In the next step, static longitudinal properties have been calculated. It is well-known that longitudinal components dominate over all the other components of the (hyper)polarizability tensors. As the chains considered are perfectly linear, the definition of the longitudinal axis is obvious. In this work we focus on the electronic

contribution to the properties, though the vibrational contributions to β and γ can be important counterparts in case of the static limit. Nevertheless, the increase of BLA parameter by the proposed co-polymerization should affect primarily the electronic contribution.

At the HF level, μ , α_L^e , and β_L^e have been evaluated analytically by the coupled-perturbed Hartree–Fock (CPHF) method implemented in Gaussian 03. HF longitudinal second hyperpolarizabilities as well as MP2 (hyper)polarizabilities have been determined by adopting the numerical finite field (FF) procedure described in more details in our previous works [27]. The problem of higher-order terms was taken care of by using the iterative Romberg procedure [28] whose robustness was increased by its generalization for arbitrary quotient [29]. In our FF calculations, the minimum external electric field F_L was set equal to 1×10^{-4} a.u. ($1 \text{ a.u.} = 5.1422 \times 10^{11} \text{ V m}^{-1}$) and the other field amplitudes were given by $\pm 2^k F_L$ with $k = 1, 2, \dots, 6$.

In order to compare evolution of β_L^e with increasing chain length for BNCC and BN oligomers we introduce for the former the effective number of unit cells, N' , defined as $N' = 2N + 1$, where N gives the number of unit cells in the molecular formula $\text{H-B}\equiv\text{N}[\text{C}\equiv\text{B}\equiv\text{N}]_N\text{-H}$ with $N = 0, 1, 2, \dots$. In this way, N' is equal to the number of triple bonds and is directly related to the number of unit cells in the BN oligomer.

4. Estimations of the polymeric values of BLA and molecular properties have been obtained by extrapolation techniques. In particular, the BLA limit was obtained by using the extrapolation formula

$$\text{BLA}(N') = \text{BLA}(\infty) + Ae^{-cN'} \quad (2)$$

We note that only $\text{BLA}(N')$ for oligomers with odd N' were considered in the extrapolation, since these exhibit more symmetric environment for the central fragment of a molecule than the even N' oligomers.

Extrapolation of molecular properties is generally required because $P_L^e(N')/N'$ (P being μ , α , β , and γ) usually converge slowly with respect to N' . In order to carry out the extrapolations, we employed an alternative definition of P_L^e per unit cell:

$$\Delta P_L^e(N') = (P_L^e(N') - P_L^e(N' - 2))/2 \quad N' = 3, 5, \dots \quad (3)$$

This definition removes most of the chain-end effects and thus it leads to a faster convergence than $P_L^e(N')/N'$ though to the same asymptotic limit ($[P_L^e(N')/N']_{N' \rightarrow \infty} = [\Delta P_L^e(N')]_{N' \rightarrow \infty}$). The polymeric value, $[P_L^e(N')/N']_{N' \rightarrow \infty}$, was obtained from least-square fits of the same function as Eq. (2). The number of points included in the fits (typically 7–9 points) was checked with respect to the square of the correlation coefficient (threshold for R^2 was 0.999) as well as with respect to the stability of the predicted asymptotic limit.

3. Results and discussion

3.1. Bond characteristics in BN and BNCC oligomers

We start our discussion with comments on bond characteristics in BN and BNCC oligomers. Let us take the BNCC pentamer ($N = 5$) corresponding (in sense of the number of bonds) to the BN undecamer ($N = 11$) as an example for the NBO analysis. This analysis shows that *both* molecules can be represented by Lewis structures containing alternating triple and single bonds describing about 98% of the total electron density with high occupancies of the valence bonding orbitals. Therefore, in spite of the diminishing BLA value for $N \rightarrow \infty$ in case of BN systems, the structure $-\text{[B}\equiv\text{N]}_N-$ is preferable to the formula $=\text{[B=N]}_N=$ (which is moreover not applicable for description of the chain end electron densities). The decrease of the BLA parameter with increasing chain length can be under-

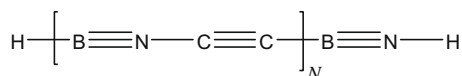


Fig. 1. Structure of the BNCC co-polymer ($N = 0, 1, 2, \dots$).

stood in terms of the simple model of the asymmetric potential due to different effective nuclear charges on boron and nitrogen atoms. This potential shifts the maximum of the HOMO (π bonding orbitals) electron density towards the nitrogen atom, which leads to weakening (i.e. prolongation) of triple bonds and strengthening (i.e. shortening) of single bonds.

When focusing on the central fragment of the BNCC pentamer, one can find (see Table 1) that the BN bond length is about 1.25 Å. A comparison with the BN bond lengths observed in the central part of the BN undecamer (1.28 and 1.31 Å) reveals that the BN bond in the copolymer is slightly stronger than in the pure system. The CN single bond length (1.28 Å) is significantly reduced compared to the bonding e.g. in $\text{CH}_3\text{-NH}_2$ ($r(\text{CN}) = 1.45$ Å at the same level of theory) indicating strong delocalization. Similarly, other geometry parameters are in agreement with the proposed delocalized Lewis structure (e.g. HF/6-311G(d,p): $r(\text{CC}) = 1.20$ Å vs. 1.18 Å in acetylene and extrapolated HF/6-311G value 1.20 Å for polyne [30]; $r(\text{BC}) = 1.46$ vs. 1.58 Å in methylborane). As can be observed in Table 1, similar bond length values are found for longer oligomers leading to extrapolated HF and MP2 polymeric BLA values of 0.114 and 0.092 Å, respectively. Interestingly, it is the BC bond that has the most profound effect on the BLA parameter. It has been theoretically predicted that having BLA in the range of 0.08–0.24 Å, BN chains would exhibit promising NLO responses (the largest NLO responses were predicted for BLA equal to ~ 0.20 Å) [14]. Our calculated BLA values for optimized structures of BNCC oligomers are clearly in this range and thus the evaluation of their NLO properties appears to be worth investigating.

In BNCC, asymmetric environment of the central CC triple bond leads to an asymmetric electron distribution. Mulliken population analysis predicts a partial positive charge of 0.11e on carbon atom bounded to nitrogen atom and approximately equal negative charge on the second carbon atom. This ununiform charge distribution in CC bonds alternates with pairs of opposing partial charges on B (+0.65e) and N (−0.65e) atoms giving rise to a unit cell asymmetry necessary for the second-order NLO responses.

3.2. Dipole moment and polarizability

The presence of pairs of opposing partial charges along the BNCC chains brings about a non-zero dipole moment value in polymeric limit. Its magnitude can thus be related to the unit cell asym-

metry. Evolution of the dipole moment reduced per unit cell, $\mu^e(N')/N'$, with increasing chain length evaluated at the HF and MP2 levels using the 6-311G(d,p) and 6-311+G(d,p) is presented in Table 2 and Fig. 2. Importance of inclusion of diffuse functions decreases with increasing system size: for longer chains ($N' > 15$) the differences between the values obtained with the two basis sets fall below 2% (4%) at the HF (MP2) level. Consideration of electron correlation (EC) effects appears to be much more important. In particular, it tunes down the dipole moment by 10–15%. Extrapolation of the oligomeric values to the infinite chain length at the HF and MP2 levels (using the larger basis set) leads to the values 1.635 ± 0.001 and 1.586 ± 0.002 a.u., respectively. These values can be compared to other AB systems, e.g. the MP2/6-311G(d) value for polymethineimine (PMI) is 0.7 a.u. [31], the MP2/6-31G(d) values are 1.7 a.u. for polyphosphazene (PP) [32], and 2.5–3.2 a.u. for polysilaacetylene (PSA) [33]. The BNCC copolymer can thus be classified as highly polar system [34].

Longitudinal electronic dipole polarizability reduced per unit cell, $\alpha_L^e(N')/N'$, is a property related to electron delocalization that usually needs to be maximized in order to get efficient NLO materials. HF and MP2 values of $\alpha_L^e(N')/N'$ are reported in Table 3 and their evolution with the chain length is shown in Fig. 3. It can be seen that the property saturates with respect to the inclusion of diffuse functions even faster than the dipole moment. On the other hand, the EC effects are huge, what can be explained by the presence of conjugated triple bonds. In fact, they bring about 50–60% increase of the polarizability for medium sized oligomers. The extrapolated MP2/6-311+G(d,p) value of $[\alpha_L^e(N')/N']_{N' \rightarrow \infty}$ for BNCC polymer is about 186 a.u., which is significantly more than $[\alpha_L^e(N')/N']_{N' \rightarrow \infty}$ of PMI (126 a.u.) [31] suggesting that electron delocalization in the BNCC chains is sufficiently large to give rise high NLO responses.

3.3. First hyperpolarizability

Table 4 lists the HF and MP2 $\beta_L^e(N')/N'$ values obtained with our two selected basis sets. Fig. 4 shows the corresponding evolution of $\beta_L^e(N')/N'$ with the chain length of BNCC oligomers and provides a comparison with $\beta_L^e(N')/N'$ curves obtained at the same level of theory for BN oligomers [14]. While the HF hyperpolarizabilities were evaluated for geometries optimized at the HF/6-311G(d,p) level, the correlated results were obtained for MP2/6-311G(d,p)

Table 1
Evolution of the central bond lengths^a and bond length alternation (BLA) parameter for a co-oligomer $\text{H-[BN-CC]}_N\text{-BN-H}$ calculated at the RHF and MP2/6-311G(d,p) levels of theory.

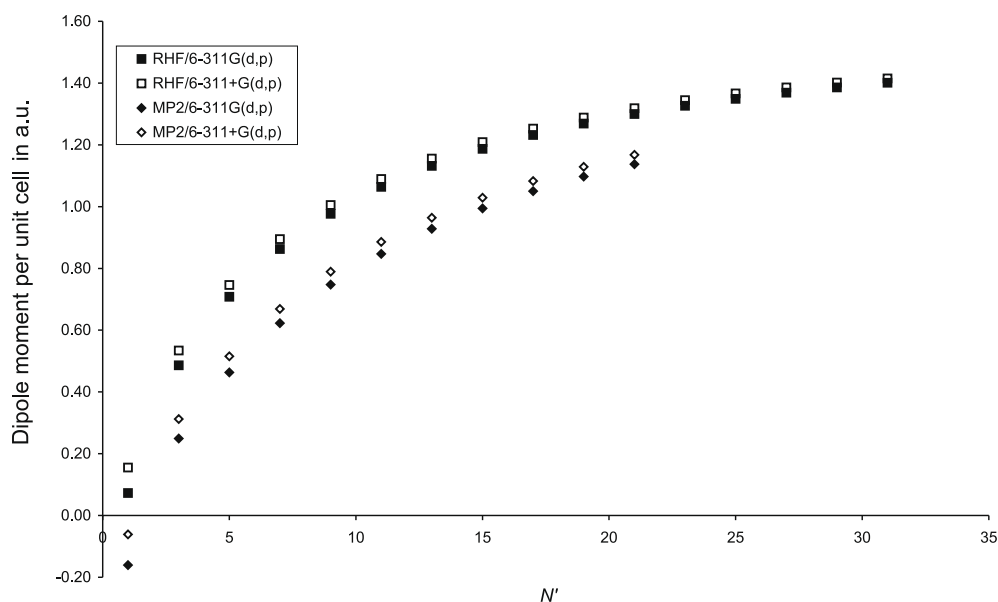
Number of unit cells, N	Effective number of unit cells, N'	RHF						MP2
		B_1N_1	N_1C	CC	CB_2	B_2N_2	BLA	BLA
0	1	–	–	–	–	–	–	–
1	3	1.2577	1.2995	1.1924	1.4874	1.2241	0.1772	0.1465
2	5	1.2396	1.2938	1.1945	1.4844	1.2256	0.1692	0.1385
3	7	1.2442	1.2852	1.1975	1.4652	1.2424	0.1471	0.1188
4	9	1.2478	1.2824	1.1989	1.4626	1.2438	0.1424	0.1154
5	11	1.2504	1.2783	1.2005	1.4557	1.2496	0.1335	0.1086
6	13	1.2525	1.2766	1.2014	1.4540	1.2506	0.1305	0.1060
7	15	1.2540	1.2743	1.2024	1.4504	1.2536	0.1257	0.1017
8	17	1.2552	1.2732	1.2029	1.4493	1.2543	0.1238	0.0998
9	19	1.2562	1.2719	1.2035	1.4473	1.2560	0.1210	0.0970
10	21	1.2569	1.2713	1.2039	1.4466	1.2564	0.1199	0.0957
11	23	1.2575	1.2705	1.2042	1.4454	1.2574	0.1182	
12	25	1.2580	1.2700	1.2045	1.4450	1.2577	0.1175	
13	27	1.2584	1.2695	1.2047	1.4442	1.2583	0.1164	
14	29	1.2587	1.2693	1.2048	1.4440	1.2585	0.1159	
15	31	1.2589	1.2689	1.2050	1.4435	1.2589	0.1153	
∞^b							0.1139	0.0918

^a Central bonds correspond to the central fragment of a molecule, i.e. $-\text{B}_1\text{N}_1\text{-CC-B}_2\text{N}_2-$.

^b Extrapolated BLA values (see Eq. (1)) were obtained by using Eq. (2). We note that only $\text{BLA}(N')$ with odd N' were considered in the extrapolation.

Table 2Evolution of the dipole moment^a reduced per unit cell (in a.u.), $\mu^e(N')/N'$, with the chain length for a co-oligomer H-[BN-CC]_N-BN-H.

Number of unit cells, <i>N</i>	Effective number of unit cells, <i>N'</i>	RHF		MP2	
		6-311G(d,p)	6-311+G(d,p)	6-311G(d,p)	6-311+G(d,p)
0	1	0.0729	0.1555	−0.1609	−0.0610
1	3	0.4862	0.5344	0.2493	0.3124
2	5	0.7083	0.7462	0.4630	0.5155
3	7	0.8627	0.8949	0.6226	0.6690
4	9	0.9766	1.0050	0.7475	0.7895
5	11	1.0638	1.0894	0.8471	0.8859
6	13	1.1322	1.1557	0.9280	0.9643
7	15	1.1870	1.2090	0.9946	1.0290
8	17	1.2318	1.2525	1.0503	1.0831
9	19	1.2688	1.2886	1.0974	1.1288
10	21	1.3000	1.3189	1.1373	1.1677
11	23	1.3264	1.3446		
12	25	1.3491	1.3667		
13	27	1.3688	1.3858		
14	29	1.3860			
15	31	1.4011			
∞ ^b		1.627 ± 0.001	1.635 ± 0.001	1.566 ± 0.002	1.586 ± 0.002

^a Positive value of μ means that the dipole moment is oriented towards the H-B chain end.^b Polymeric values were obtained from least-square fits of the function (2) using the alternative definition for P_L^e reduced per unit cell (see Eq. (3)). For more details see text.**Fig. 2.** Evolution of the dipole moment reduced per unit cell (in a.u.) with the chain length of the BNCC co-oligomers evaluated at the HF and MP2 levels using the 6-311G(d,p) and 6-311+G(d,p) basis sets (N' is the effective number of unit cells).

geometries. Consequently, the EC contribution includes both indirect and direct EC corrections: the former coming from the change in optimal ground-state geometry and the latter originating from the modifications of the electronic structure.

It can be seen that both HF and MP2 $\beta_L^e(N')/N'$ curves of BNCC chains (with the exception of HBNH at the MP2 level) are first anti-parallel to the dipole moment for small chains, reach a minimum (for $N' = 5$), pass through zero between $N' = 9$ and $N' = 13$, change the sign and finally saturate for long chains. This means that the unit cell and the chain end contributions to β present opposite sign. For short chains, the chain-end contribution which is increasing with chain length due to delocalization enhancement dominates the total response. For intermediate chain lengths the two contributions almost cancel each other resulting in small $\beta_L^e(N')/N'$ values. For long chains, the unit cell component dominates the total response and saturates towards the polymeric limit. This situation is analogous to *trans-transoid* PMI chains [31,35,36]. Interestingly, the theoretical MP2/6-311G curve obtained by us [14] for BN

chains with BLA forced to be equal to 0.08 (the closest value to our calculated BLA for BNCC chains) nicely reproduce all features of $\beta_L^e(N')/N'$ curves described above, although a smaller basis set was used in Ref. [14]. Anyway, the arguments about the necessity of non-zero BLA to obtain non-zero $[\beta_L^e(N')/N']_{N' \rightarrow \infty}$ have been confirmed.

Comparison of results obtained with the two basis sets at both uncorrelated and correlated levels reveals that inclusion of diffuse functions especially for long chains affect $\beta_L^e(N')/N'$ negligibly. On the other hand, the electron correlation has dramatic influence on $\beta_L^e(N')/N'$. While the indirect EC correction related to the optimum geometry changes brings about only 20% increase of $\beta_L^e(N')/N'$ for decamer, in total, the EC effects increase the first hyperpolarizability by factor of 4 for long chains. As in the case of α_L , this observation can be expected in chains containing a sequence of conjugated triple bonds. As mentioned in Computational details (point 4), direct extrapolation of $\beta_L^e(N')/N'$ to the polymeric limit can sometimes hardly be performed (see Fig. 4). However,

Table 3

Evolution of the longitudinal dipole polarizability reduced per unit cell (in a.u.), $\alpha_L^e(N')/N'$, with the chain length for a co-oligomer H–[BN–CC]_N–BN–H.

Number of unit cells, <i>N</i>	Effective number of unit cells, <i>N'</i>	RHF		MP2	
		6-311G(d,p)	6-311+G(d,p)	6-311G(d,p)	6-311+G(d,p)
0	1	25.60	27.34	27.97	30.49
1	3	41.12	42.56	48.98	51.50
2	5	53.50	54.60	69.49	71.73
3	7	62.42	63.27	85.80	87.70
4	9	69.06	69.71	98.59	100.19
5	11	74.17	74.66	108.86	110.20
6	13	78.20	78.57	117.28	118.40
7	15	81.45	81.71	124.30	125.22
8	17	84.11	84.29	130.21	130.95
9	19	86.33	86.44	135.23	135.83
10	21	88.19	88.24	139.53	139.99
11	23	89.77	89.78		
12	25	91.14	91.10		
13	27	92.32	92.24		
14	29	93.35			
15	31	94.26			
∞^a		108 ± 0.5	107 ± 0.5	187 ± 1	186 ± 1

^a Polymeric values were obtained from least-square fits of the function (2) using the alternative definition for P_L^e reduced per unit cell (see Eq. (3)). For more details see text.

using Eq. (3) we are able to get closer to the saturation region and make at least rough estimates of $[\beta_L^e(N')/N']_{N' \rightarrow \infty}$ (see Fig. 5). E.g., extrapolation of MP2/6-311+G(d,p) values leads to the polymeric limit equal to 5850 ± 100 a.u. This value is only slightly less than half of that obtained at the MP2/6-311G(d) level for *trans-transoid* PMI (14011 a.u.) [31], which is considered to be one of the most efficient NLO systems of the AB type.

3.4. Second hyperpolarizability

In the context of the third-order NLO properties, the BNCC co-oligomers with alternating triple and single bonds are analogues

of PY. The electronic (and vibrational) second hyperpolarizabilities of PY have been subject of several theoretical [37–39] and more recently also experimental [40] studies. Due to problems with basis set quasi-linear dependences (QLD) [30] the determination of $\text{BLA}(\infty)$ of PY either by the oligomeric or crystal orbital (CO) approaches is not a trivial task. Based on the oligomeric approach at the MP2/6-311G level Toto et al. came to the value of 0.104 Å, which is somewhat larger than the CO/MP2/6-31G(d) value of 0.057 Å found by Poulsen et al. [41] but still consistent with a very recent CCSD(T)/cc-pVTZ value of 0.1276 Å reported by Zeinalipour-Yazdi and Pullman [42] as well as with Yang and Kertesz's BHandHLYP/6-31G(d) estimate of 0.13 Å [43]. As shown below, though the BLA values are comparable for PY and BNCC, the larger delocalization in PY related to smoother nuclear potential leads to significantly larger third-order NLO responses of PY. In the context of QLD issue, contrary to PY we have not encountered problems in the geometry optimizations, though some SCF convergence difficulties have been met when strong electric fields ($F > 0.0064$ a.u.) were applied on long chains (typically for $N' > 17$).

Static longitudinal electronic second hyperpolarizabilities reduced per unit cell, $\gamma_L^e(N')/N'$, of the BNCC chains are reported in Table 5. The corresponding evolution of $\gamma_L^e(N')/N'$ with the chain length and its comparison with the MP2/6-311G curve obtained by Toto et al. for PY [38] are shown in Fig. 6. As in case of lower order properties, inclusion of diffuse function does not affect γ_L^e significantly. On the other hand, electron correlation effects lead to the increase of γ_L^e by about factor of 4. Since MP2 BLA values are smaller than the HF ones, it can be anticipated that the indirect EC contribution plays a non-negligible role in the increase of γ_L^e . As comes from the comparison of the BNCC and PY curves in Fig. 4, asymmetric nuclear potential within the BNCC unit cell resulting in smaller delocalization has a huge influence on γ_L^e . While the PY curve is far from the saturation region (its curvature is positive for investigated chain lengths), for BNCC oligomers we can make a crude estimation of the polymeric $\gamma_L^e(N')/N'$ values: $4\text{--}5 \times 10^5$ a.u. at the HF and about 2×10^6 a.u. at the MP2 levels,

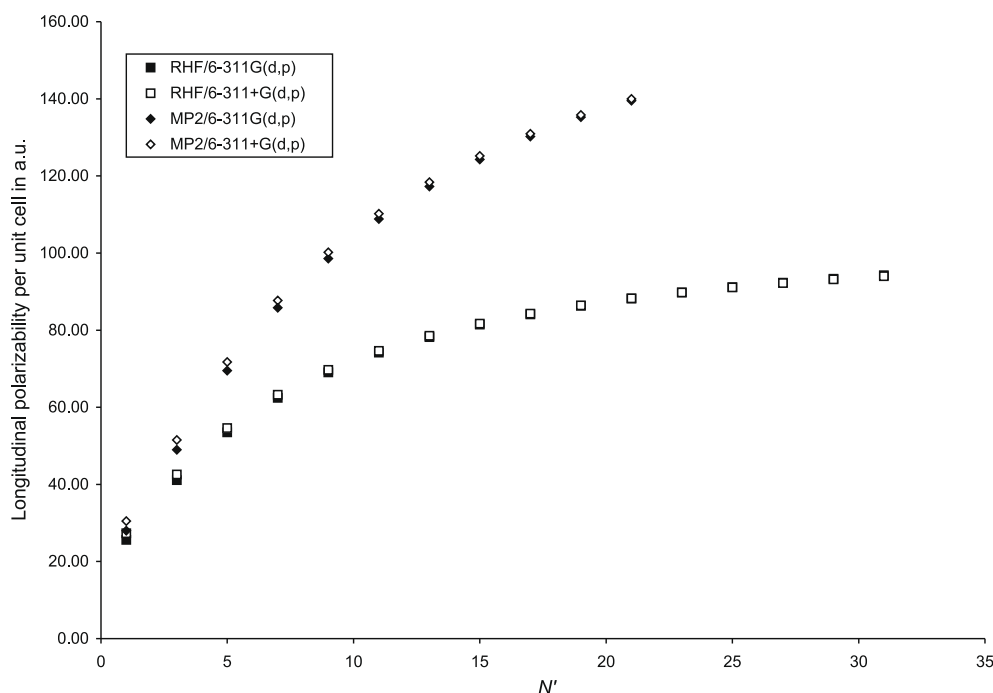
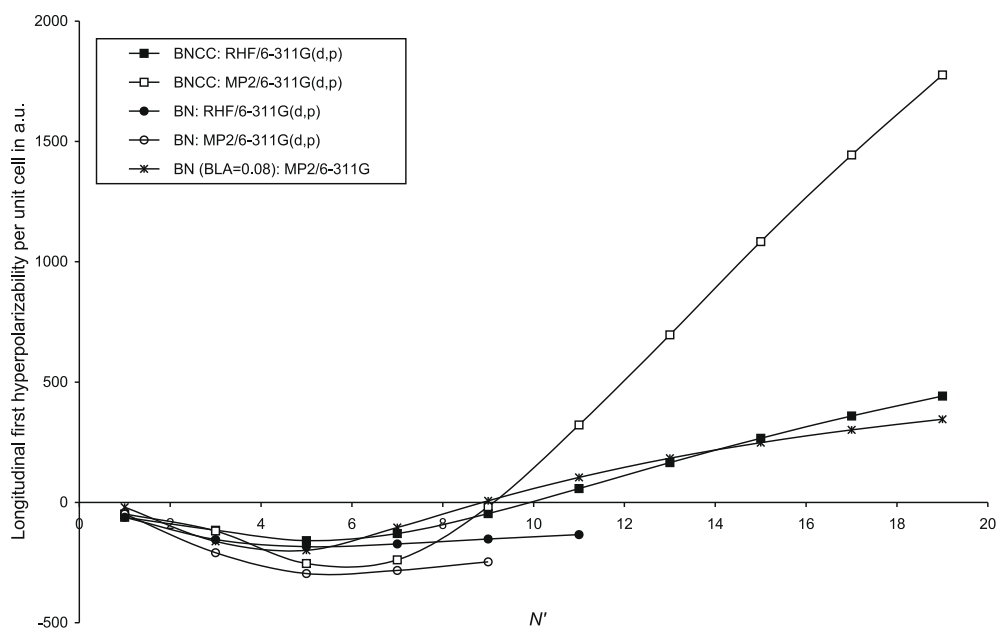


Fig. 3. Evolution of the longitudinal dipole polarizability reduced per unit cell, $\alpha_L^e(N')/N'$, (in a.u.) with the chain length of the BNCC co-oligomers evaluated at the HF and MP2 levels using the 6-311G(d,p) and 6-311+G(d,p) basis sets.

Table 4Evolution of the longitudinal first hyperpolarizability reduced per unit cell (in a.u.), $\beta_L^e(N')/N'$, with the chain length for a co-oligomer H-[BN-CC]_N-BN-H.

Number of unit cells, <i>N</i>	Effective number of unit cells, <i>N'</i>	RHF		MP2		<i>r</i> (MP2/RHF)	
		6-311G(d,p)	6-311+G(d,p)	6-311G(d,p)	6-311+G(d,p)	6-311G(d,p)	6-311+G(d,p)
0	1	−61	−69 (−73) ^b	−48	−55	0.786	0.797
1	3	−116	−100 (−127)	−119	−101	1.029	1.008
2	5	−159	−135 (−200)	−254	−220	1.598	1.637
3	7	−129	−101 (−177)	−238	−189	1.844	1.880
4	9	−46	−18 (−78)	−18	35	0.380	−2.006
5	11	58	85 (53)	322	368	5.556	4.338
6	13	165	189 (189)	697	741	4.216	3.915
7	15	267	288 (318)	1084	1111	4.061	3.861
8	17	359	377 (436)	1444	1458	4.017	3.863
9	19	442	457 (543)	1777	1780	4.018	3.891
10	21	516	528 (638)	2079	2067	4.031	3.912
11	23	581					
12	25	638	646				
13	27	689	695				
14	29	734					
15	31	775					
∞ ^a		1400 ± 50	1380 ± 50	6050 ± 100	5850 ± 100		

^a Polymeric values were obtained from least-square fits of the function (2) using the alternative definition for P_L^e reduced per unit cell (see Eq. (3)). For more details see text.^b Values presented in parentheses were obtained by the RHF/6-311+G(d,p) method using the MP2/6-311G(d,p) geometries.**Fig. 4.** Evolution of the longitudinal first hyperpolarizability reduced per unit cell, $\beta_L^e(N')/N'$, (in a.u.) with the chain length of the BNCC co-oligomers evaluated at the HF and MP2 levels using the 6-311G(d,p) basis set and its comparison with the curves obtained at the same level of theory for the linear BN chains in their optimum geometries as well as with the theoretical curve obtained for the BN chains with BLA forced to 0.08 Å.

which are still well below PY tridecamer (the longest investigated PY oligomer) γ_L^e value (3.8×10^6 a.u.). Consequently, the BNCC chains do not have a large potential for third-order NLO applications.

4. Conclusions

We have shown that the zero polymeric BLA limit for linear BN chains leading to low second-order NLO responses can be increased by copolymerization with PY. NBO and Mulliken population analyses have revealed that BNCC chains can be represented by Lewis structures containing alternating triple and single bonds with a sequence of pairs of opposing partial charges on B and N as well as on neighboring carbon atoms giving rise to a unit cell asymmetry necessary for the second-order NLO responses. Extrapolated

HF and MP2 BLA(∞) values of BNCC are 0.114 and 0.092 Å, which are comparable to BLA(∞) of PY. The extrapolated MP2/6-311+G(d,p) value of $[\alpha_L^e(N')/N']_{N' \rightarrow \infty}$ is about 186 a.u. indicating that electron delocalization in the BNCC chains is quite large – as can be expected for a system with conjugated triple bonds. The non-zero BLA, unit cell asymmetry resulting from ununiform charge distribution and large delocalization give rise to large longitudinal second-order NLO properties. Evolution of $\beta_L^e(N')/N'$ with increasing chain length can be rationalized in terms of the chain end and unit cell contributions. Our findings confirm previous arguments about the relation of the BLA parameter and first hyperpolarizability. Extrapolation of MP2/6-311+G(d,p) values leads to $[\beta_L^e(N')/N']_{N' \rightarrow \infty}$ equal to 5850 ± 100 a.u. that is only slightly less than half of that found for *trans-tranoid* PMI, which is considered to be one of the most efficient NLO systems of the AB type. Due to smaller electron

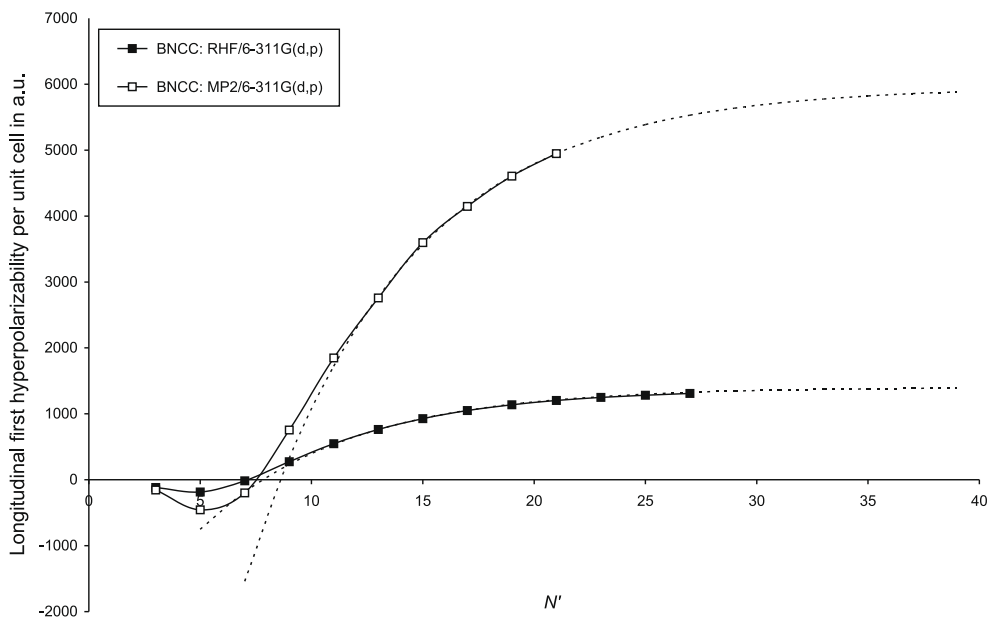


Fig. 5. Evolution of the longitudinal first hyperpolarizability reduced per unit cell, $\Delta\beta_L^e(N')$, (in a.u.) defined by Eq. (3) with the chain length of the BNCC co-oligomers evaluated at the HF and MP2 levels using the 6-311G(d,p) basis set. Dashed lines correspond to the fits obtained by using Eq. (2) for the presented data.

Table 5
Evolution of the longitudinal second hyperpolarizability reduced per unit cell (in 10^3 a.u.), $\gamma_L^e(N')/N'$, with the chain length for a co-oligomer $H-[BN-CC]_N-BN-H$.

Number of unit cells, N	Effective number of unit cells, N'	RHF		MP2		$r(MP2/RHF)$	
		6-311G(d,p)	6-311+G(d,p)	6-311G(d,p)	6-311+G(d,p)	6-311G(d,p)	6-311+G(d,p)
0	1	1	1	1	1	0.75	0.99
1	3	12	15	22	30	1.92	2.01
2	5	44	49	115	128	2.61	2.63
3	7	85	90	263	282	3.08	3.12
4	9	128	130	419	438	3.28	3.38
5	11	162	165	567	578	3.49	3.51
6	13	194	197	699	708	3.61	3.58
7	15	223	217	821	826	3.67	3.80
8	17	248	247	931	938	3.75	3.80
9	19	270	271	1032	1034	3.82	3.81
10	21	290	294	1121	1121	3.87	3.81

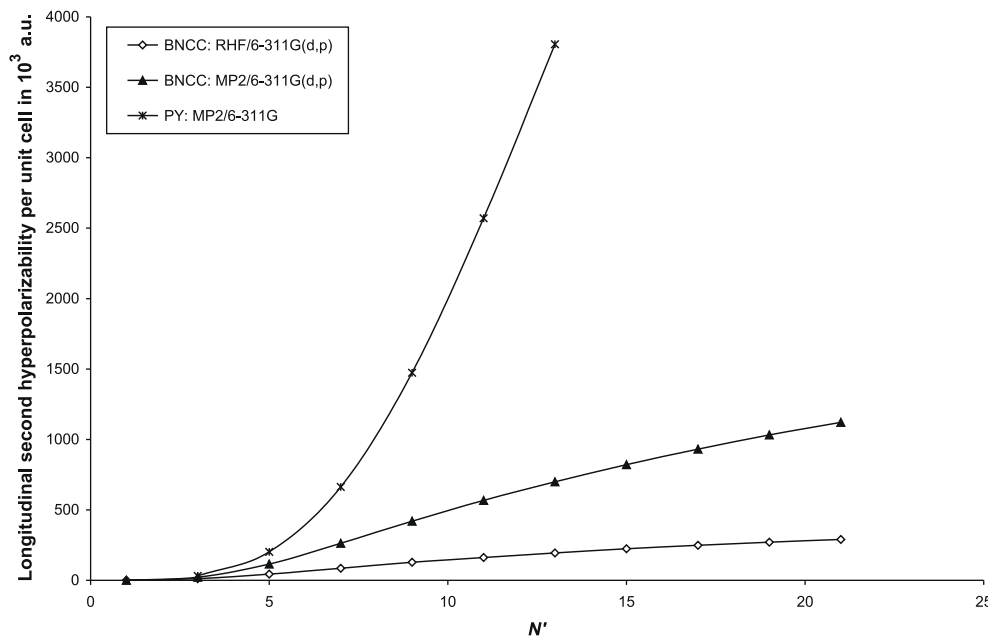


Fig. 6. Evolution of the longitudinal second hyperpolarizability reduced per unit cell, $\gamma_L^e(N')/N'$, (in 10^3 a.u.) with the chain length of the BNCC co-oligomers evaluated at the HF and MP2 levels using the 6-311G(d,p) basis set and its comparison with the MP2/6-311G curve computed for oligomers of polyyne.

delocalization the second hyperpolarizabilities of BNCC chains are significantly smaller than those exhibited by PY oligomers.

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