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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).

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 ($LiNbO_3$, 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 rectification). 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 ($N \to \infty$). 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, $[\beta]_{N \to \infty}$ is also zero). Simple Hückel results show that the largest $[\beta/N]_{N \to \infty}$ value would be obtained with a large delocalization (i.e. small BLA) and a small (but non-zero) asymmetry rather than

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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. $=[\text{B}{=}\text{N}]_N=$, 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 polyynes (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 $\text{H}{-}\text{B}{\equiv}\text{N}{-}[\text{C}{\equiv}\text{C}{-}\text{B}{\equiv}\text{N}]_N{-}\text{H}$ (N = 0–15) 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:

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

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. $-\text{B}_1\text{N}_1{-}\text{CC}{-}\text{B}_2\text{N}_2-$, 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.

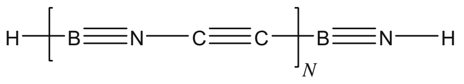

Fig. 1. Structure of the BNCC co-polymer (N = 0, 1, 2, ...).

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 a.u. = 5.1422×10^{11} V m^{-1}) and the other field amplitudes were given by $\pm 2^k F_L$ with k = 1, 2, ..., 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 $\text{H}{-}\text{B}{\equiv}\text{N}{-}[\text{C}{\equiv}\text{C}{-}\text{B}{\equiv}\text{N}]_N{-}\text{H}$ with N = 0, 1, 2, ... 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

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

We note that only 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:

$$\Delta P_L^e(N') = (P_L^e(N') - P_L^e(N'-2))/2 \quad N' = 3, 5, \ldots \tag{3}$$

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 ($[P_L^e(N')/N']_{N'\to\infty} = [\Delta P_L^e(N')]_{N'\to\infty}$). The polymeric value, $[P_L^e(N')/N']_{N'\to\infty}$, 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 $N \to \infty$ in case of BN systems, the structure $-[\text{B}{\equiv}\text{N}]_N-$ is preferable to the formula $=[\text{B}{=}\text{N}]_N=$ (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-