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High second-order NLO responses of dehydrogenated hydrogen cyanide borane(1) oligomers

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ABSTRACT

Second-order non-linear optical (NLO) properties of dehydrogenated hydrogen cyanide borane(1) oligomers (up to dodecamers) are investigated by the Hartree–Fock, hybrid DFT (including long-range corrected functionals) and MP2 approaches. Due to one-dimensional extension of the systems the longitudinal component of the properties is addressed with focus on the electronic contributions. Direct and indirect electron correlation effects are evaluated at the MP2 level paying particular attention to the basis set effects. Unit-cell asymmetry and delocalization effects in the NLO responses are discussed in terms of the evolution of the bond-length alternation parameter, dipole moment and polarizability (reduced per unit cell) with the increasing chain length. It was found that suitable combination of the unit-cell asymmetry and electron delocalization leads to extremely large NLO response (MP2/6-311++G(d,p) value for the dodecamer is 43.7×10^3 a.u. per unit cell) what makes the conjugated BCN oligomers (if one takes into account their thermodynamic stability) a promising material for NLO applications.

1. Introduction

There is increasing interest in materials with high non-linear optical (NLO) properties due to their potential application in technologies such as lasers, telecommunications, information processing and holography. Organic π-conjugated oligomers and polymers represent an excellent alternative to traditional inorganic NLO crystals because they can be easily synthesized and chemically modified. Extremely fast switching times, resistance to high intensity radiation, possibility of thin-layer fabrication, and low electric permittivity (related to low-frequency dependence in non-resonant regime) are important properties in favor of organic NLO materials [1].

At the macroscopic level the relevant NLO properties are the second- and third-order non-linear susceptibilities, whereas their microscopic analogues correspond to the first and second hyperpolarizabilities, $\beta(-\omega;\omega_1,\omega_2)$ and $\gamma(-\omega;\omega_1,\omega_2,\omega_3)$. In the search for the large β, various strategies have been adopted. The most obvious is the so-called push–pull strategy, in which a conjugated chain (e.g. oligomethylene, phenylene groups) is capped at its ends by an electron-donor group on one side and an electron-acceptor group on the other [2]. The large second-order NLO response of these systems comes out from a strong coupling between the first excited state (corresponding to a charge transfer between the end moieties) and the ground state. Due to the separation of donor and acceptor groups the push–pull systems exhibit large dipole moment values. A similar approach to achieve large β is to choose structures with large charge transfer in the ground state, i.e. zwitterions [3], or to obtain a large charge separation by distortion of the molecule [4,5]. Another appealing way is based on taking advantage of the presence of chiral atoms [6,7]. In our recent studies we have been interested in the so-called AB systems following an alternative idea to push–pull systems: a suitable combination of delocalizability and asymmetry can be achieved by designing π-conjugated chains from asymmetric unit cells (containing two or more different nuclei). Contrary to push–pull systems, the AB chains can exhibit non-zero NLO response in polymeric limit. Various AB compounds have been investigated [8–14]. According to the evolution of β/N (N being the number of unit cells) with the chain length, the compounds can be classified in three main categories:

(i) β/N first increases and then saturates to the infinite polymeric limit [13];
(ii) β/N first increases, reaches a maximum, and then decreases toward zero – similarly to push–pull systems [9,14]; and
(iii) β/N is first negative, reaches a minimum, then increases changing the sign, and then saturates to the infinite chain limit [12,15].

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Obviously, from a practical point of view, the first and third groups of compounds are more interesting for design of new candidates for non-linear optics. Nevertheless, very different macromolecular responses ($[\beta/N]_{N\to\infty}$) have been predicted for conjugated AB systems in these categories. Detailed analysis of structure-response relationships shows that large $[\beta/N]_{N\to\infty}$ can be obtained with a large delocalization related to small (but non-zero) bond-length alternation (BLA) parameter and a small asymmetry rather than the reverse. Keeping this rule in mind new high-grade NLO materials can be designed by suitable selection of back-bone nuclei. Inspired by extremely large responses of the linear boron-phosphorus (BP) chains [16] we recently resumed the idea of investigating BN analogues of unsaturated hydrocarbon chains. Though it was earlier found that lengthening of the BN chain (being a valence isoelectronic analogue of BP) leads to a too fast decrease of the bond-length alternation (BLA) parameter and consequently also to low NLO responses [9], we have shown that copolymerization of BN with polyyne stabilizes the non-zero BLA parameter and results in $[\beta/N]_{N\to\infty}$ values half as large as those of PMI [17].

Alternative way to design oligomers containing B, N and C skeleton atoms is to follow an idea by Černušák et al. proposing various types of cyclic as well as acyclic B/C/N structures [18–22]. In this study we focus on short and medium-size open chain structures, which are expected to undergo further polymerization [23]. As follows from the study by Pappová et al. [20], two types of acyclic oligomers can be considered (see Fig. 1): hydrogen cyanide borane(1) oligomers, $(HCNBH)_N$, (type 1) and their dehydrogenated analogues, $\{H\}(HCNB)_NH$ or simply HCNB, (type 2). The former show up a staggered structure with two neighboring HCNBH units perpendicular to each other and they present a small degree of delocalization (isolated islands of delocalization spread over the two units) leading to a relatively large band gap for the polymer (~7 eV). On the other hand, the dehydrogenated analogues are planar, fully conjugated and the band gap for polymer is estimated to about 3 eV at the MP2 level [24], which can be compared to the band gaps of PA and PMI being 4.03 and 4.78 eV, respectively, evaluated at the same level of theory [25]. Moreover, the stability of dehydrogenated oligomers in terms of initial "cracking" of the weakest bond is higher than that of the former, ranging from 329 to 589 kJ/mol. Considering the stability, back-bone asymmetry, electron delocalization and band gap aspects, the oligomers of type 2 appear to be suitable candidates for NLO materials, and thus they are a subject of the present study.

A particular attention in our analysis is given to the assessment of the accuracy of selected hybrid and long-range corrected (LC) DFT methods. It is well-known that standard DFT methods tend to perform poorly in evaluation of NLO properties. This failure, particularly dramatic for π-conjugated molecules [26], has been thoroughly analyzed and it was attributed to the incorrect asymptotic behavior of the exchange–correlation part of the functional [27]. A promising way to improve DFT description of NLO properties has been be to keep DFT-like short-range exchange while switch to the HF exchange smoothly at longer distances. There are several implementations of this basic idea. One can either employ gradient or local functionals to obtain long-range corrected functionals like LC-BLYP [28], or use the well-known hybrid B3LYP functional in the CAM-B3LYP hybrid [29]. Both schemes have been tested for electric or NLO properties evaluation, though the overall performance of the LC functionals is still not without a dispute. On one hand, there are several studies supporting preference of LC functionals over the standard DFT: e.g. Limacher et al. [30] based on the evaluation of α and γ of polyacetylene recommend to use CAM-B3LYP rather than B3LYP for π-conjugated systems; Zaleśny et al. [31] in their study of *meta*-dinitrobenzene found that LC–DFT tend to provide more accurate electronic as well as vibrational hyperpolarizability values than traditional functionals; Czyżnikowska et al. [32] showed that LC–DFT methods significantly improve first hyperpolarizability values obtained for betaine by uncorrected DFT counterparts (though they have still difficulties to get closer to CCSD(T) values); and Krawczyk et al. [33] also claim to obtain much better agreement with experimental data for two-photon absorption cross-sections of azobenzene derivates with the CAM-B3LYP functional than with traditional hybrids: B3LYP and PBE0. On the other hand, Kirtman et al. [34] found a strong dependence of second hyperpolarizability on systems studied (polydi-

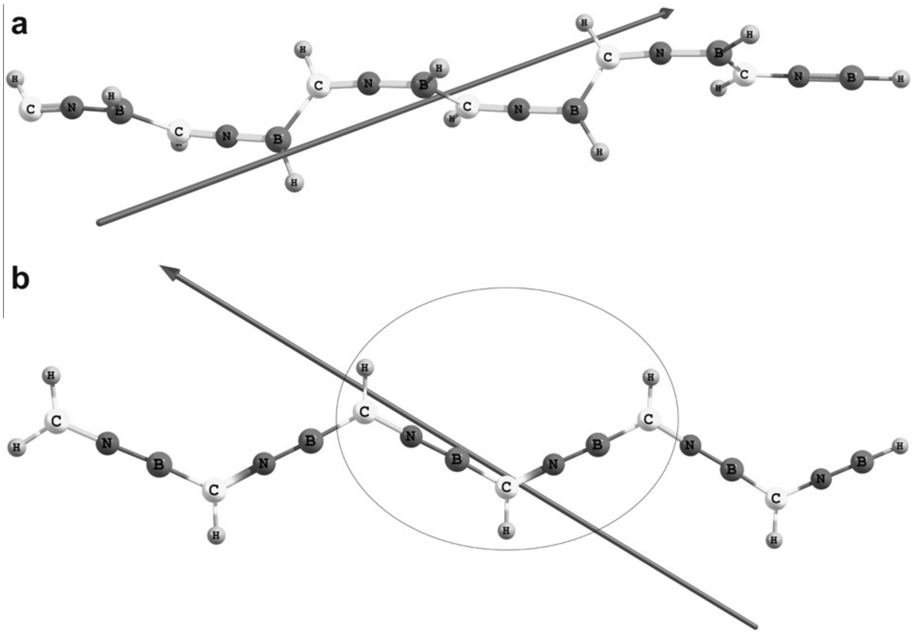

Fig. 1. Two types of acyclic BCN oligomers: (a) hydrogen cyanide borane(1) hexamer, $(HCNBH)_6$, and (b) its dehydrogenated analogue, $\{H\}(HCNB)_6H$ or simply HCNB. The arrows indicate a direction of the dipole moment. The central fragment is encircled.