

Origin of High Second- and Third-Order Nonlinear Optical Response in Ammonio/Borato Diphenylpolyene Zwitterions: the Remarkable Role of Polarized Aromatic Groups

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Abstract: We present a quantum-chemical analysis of the molecular structure and second- and third-order polarizabilities in a series of promising nonlinear optical (NLO) chromophores, the zwitterionic ammonio/borato diphenylpolyenes, $R_3N^+Ph(C=C)_nPhB^-R_3$, whose synthesis has been reported recently. The molecular geometries are obtained via MP2/6-31G optimization, while the NLO properties are calculated with the INDO Hamiltonian using the sum-over-states and finite-field real-space methods. The real-space approach allows the direct evaluation of the NLO-active segments of the molecules, while the sum-over-states results illustrate the virtual excitations and charge-transfer pathways that are essential in the NLO response. Both methods highlight the remarkable and unexpected result that it is the strongly polarized phenylene groups that play the key role in generating a high NLO response.

1. Introduction

The search for efficient organic nonlinear optical (NLO) materials has been attracting major interest both in academia and in industry. A class of much studied organic NLO chromophores consists of push-pull molecules containing a donor and an acceptor connected via a conjugated bridge.¹ To reach high values of hyperpolarizabilities with a given donor/acceptor pair, trans-polyene segments are among the most efficient bridges. However, push-pull polyenes suffer from chemical and thermal instability and often present strong linear absorption in the visible; other bridges are therefore desirable. For instance, introduction of aromatic units leads to more stable and practical chromophores, and push-pull compounds with a trans-stilbene bridge, such as DANS, are reference organic second-order NLO chromophores (see Scheme 1). When an increase in conjugation length to reach higher (hyper)polarizabilities is considered, the trans-stilbene moiety can be viewed as the starting point for both diphenylpolyenes and oligophenylene vinylenes (OPV).

The presence of phenylene groups is usually seen as detrimental to intramolecular charge transfer; according to a number of theoretical and experimental studies, aromatic stabilization favors electron localization, which shields the donor and acceptor and decreases the molecular NLO response.^{2–5} In this context, replacing phenylenes with less aromatic heterocycles

in push-pull stilbene analogues is a logical step.⁶ However, more creative exploitations of groups have also been recognized. Heteroaromatic electron rich/poor substituents can function as D/A substituents themselves, leading to *weakly polar* second-order NLO chromophores.⁷ *Highly polar* aromatic derivatives have also received much attention. Stilbazolium, a stilbene analogue where one of the phenylenes is replaced by a *charged heteroaromatic ring* (pyridinium) yields highly efficient second-order NLO chromophores such as DAST.^{8–11} Diphenylpolyene analogues of stilbazolium containing up to five double bonds between the benzene and pyridinium rings have been recently synthesized and tested for their second-order NLO properties.¹² The family of cationic chromophores has been extended from quasi-one-dimensional to two- and three-dimensional compounds and also includes other acceptors and

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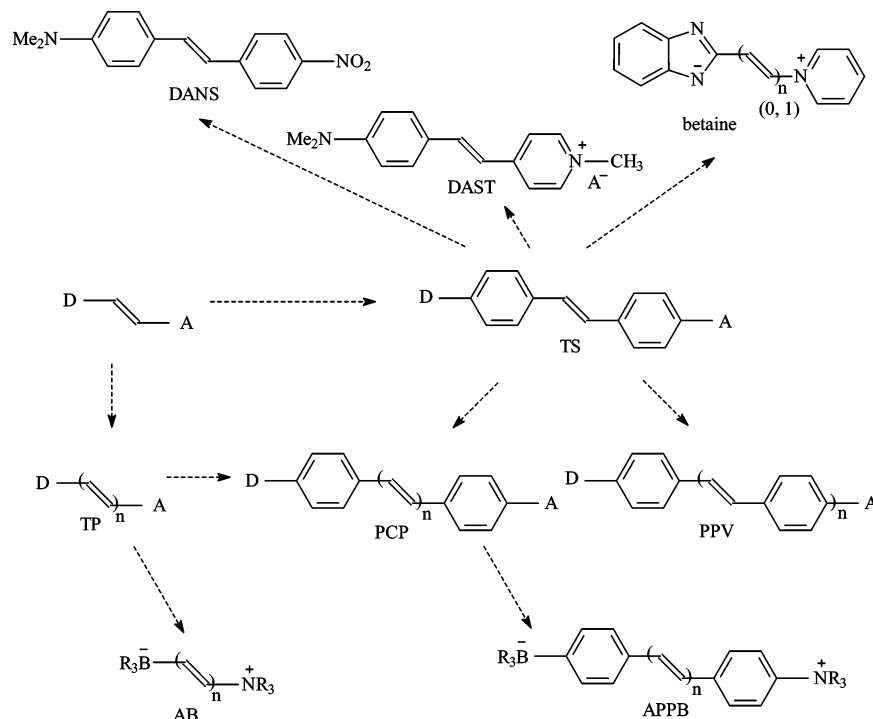
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Scheme 1



conjugated bridges.¹³ To further increase charge separation in the ground state, betaine analogues, that is, *zwitterions* containing *two oppositely charged heteroaromatic rings* linked directly or via a vinylene unit, have been considered as second-order NLO chromophores theoretically^{14,15} and experimentally.¹⁶

Recently, Lambert et al. have studied a new family of *zwitterionic* NLO chromophores in which a polyene bridge is capped by *phenylene rings* substituted at one end by an NR_3^+ group and at the other end by BR_3^- groups; these chromophores are referred to as ammonio/borato (A/B) diphenylpolyenes.¹⁷ This molecular design leads to (i) a very high degree of ground-state polarization (high dipole moment) and (ii) higher transparency in the visible with respect to push-pull diphenylpolyenes, presumably due to a shorter conjugation length, from which the A/B saturated groups can be considered to be at least partially excluded (see also ref 13 for discussion).

In this work, we present a detailed quantum-chemical analysis of the origin of the second-order and third-order NLO response in the ammonio/borato diphenylpolyene (APPB) family; see Figure 1. We show that the APPB molecules are remarkable in the sense that their high (hyper)polarizabilities primarily originate in the presence of the polarized phenylene groups. Instead of playing the role of aromatic buffers, under the strong chemical polarization due to NR_3^+ and BR_3^- groups, the nonlinearity of the phenylene rings increases to such an extent that it dominates the (hyper)polarizabilities of the molecules.

We have used two complementary approaches, the perturbational sum-over-states (SOS) method (see, e.g., ref 18) and the variational finite-field (FF) method in its real-space local-

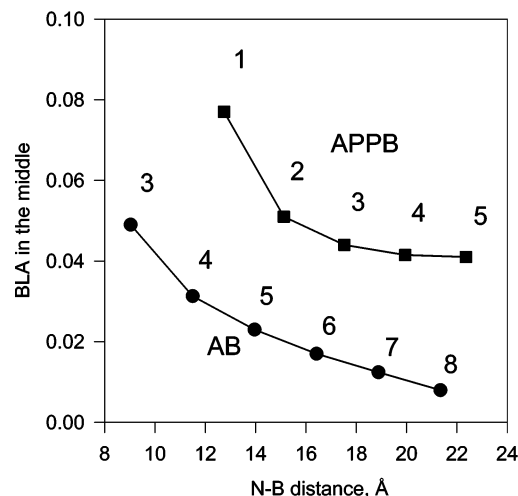


Figure 1. Bond length alternation (BLA) in the middle of the polyene chain as a function of molecular length (B–N distance) in the APPB and AB series (MP2/6-31G optimized geometries). The labels over each data point indicate the number of carbon pairs in the polyene bridge.

contribution formulation.^{19,20} The real-space approach directly highlights the NLO-active segments in a molecule; this is less straightforward to do in the framework of SOS that operates with global molecular properties. In the case of the APPB family, the comparison of both approaches is facilitated by the applicability of the two-state model. This constitutes another peculiarity of this family since in traditional push-pull stilbenoids it usually turns out that multiple highly correlated excited states contribute to the NLO response.²¹ The conclusions

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of our work are confirmed by comparison of the APPB compounds with hypothetical ammonio/borato polyenes (see Figure 1) that do not contain aromatic groups (denoted AB).

2. Theoretical Methodology

The geometries of the APPB and AB molecules, with trimethyl-substituted boron and nitrogen atoms, were optimized in the all-trans conformation at the MP2/6-31G level; note that the structures obtained at lower theoretical levels (semiempirical, ab initio Hartree–Fock, and DFT) can turn out to be qualitatively different.²² Here we do not take solvent effects into account, although we recognize that in solution the structure and NLO response of such polar and polarizable molecules can be affected by the nature of the medium.²³

The second- and third-order static electric-dipole polarizabilities, β and γ , were calculated for these optimized geometries with the INDO semiempirical Hamiltonian (spectroscopic parameters, Ohno–Klopman electron repulsion scheme) as implemented in the ZINDO code.²⁴ For sum-over-states (SOS) hyperpolarizabilities (see, e.g., ref 18 for the standard expressions), the electronic properties in the ground and excited states (energies, state and transition dipole moments) were evaluated from correlated SD-CI (single and double configuration interaction) wave functions including all single and double excitations among typically the 10 highest occupied and 10 lowest unoccupied π -MOs. The perturbational series summations to obtain the static β and γ values was performed over the full set of excited states.

The real-space approach to molecular (hyper)polarizability has been developed by Chopra et al.²⁵ and Nakano et al.²⁶ It is based on the analysis of the field-induced electron-density shifts that lead to the changes in dipole moment. The dipole moment is the moment of both the positive nuclear charges Q_i and the electron density; the latter, to a good approximation, can be partitioned into “atomic” charges q_i , so that $\mu_x \approx \sum_i x_i(Q_i + q_i)$. Here, we do not include any vibrational effects; thus, the nuclear coordinates x_i are independent of external electric field F . In addition, the nuclear charges Q_i are constant. The longitudinal (x -axis) components of the static second-order and third-order polarizabilities β and γ then write

$$\beta_{xxx} = (\partial^2 \mu_x / \partial F^2)|_{F=0} \approx \sum_i x_i (\partial^2 q_i / \partial F^2)|_{F=0} \equiv \sum_r x_r q_i^{(2)}; \gamma_{xxx} \approx \sum_r x_r q_i^{(3)} \quad (1)$$

In this real-space approach, n th order polarizabilities are partitioned into local contributions, (hyper)polarizability moments $x_i q_i^{(n)}$, based on the (hyper)polarizability charges of atoms/orbitals $q_i^{(n)} = \partial^n q_i / \partial F^n|_{F=0}$. Note that only ground-state properties are required. In this work, β - and γ -charges, $q^{(2)}$ and $q^{(3)}$ (leading to the second- and third-order longitudinal polarizabilities, β_{xxx} and γ_{xxx} , respectively) were obtained from INDO/HF Mulliken π -charges via finite-difference formulas to approximate derivatives.^{19,26} The maximum electric field applied was ca. 1×10^7 V/cm.

The energies of the strongly allowed transition to the lowest charge-transfer excited state were also calculated for the APPB molecules with time-dependent density functional theory (TD-DFT), using the hybrid BHandHLYP functional and the 6/31G* basis set as implemented in Gaussian 98.²⁷ Failures of TD-DFT with a number of functionals leading to underestimations of long-range intramolecular^{28–30} and intermolecular³¹ charge-transfer excitation energies have recently been documented; however, TD-DFT appears to be reliable for π -conjugated molecules

of moderate size, especially when considering hybrid functionals. Since π -conjugated systems usually require a greater extent of Hartree–Fock exchange, Becke’s half-and-half potential, free of excessive parameterization, appears as a reasonable choice. The basis set convergence of TD-DFT calculations is fast,³² hence the adequacy of the 6-31G* basis set.

3. Results and Discussion

3.1. Ground-State Structure. We first discuss the geometries and charge distributions of the APPB and AB molecules, obtained at the MP2 level.²² In an NLO context, it is convenient to represent conjugated-chain structures by their bond length alternation (BLA) pattern. A so-called local BLA value is defined as the difference between the adjacent CC bond lengths. The BLA values in the middle of the APPB and AB molecules are plotted in Figure 1. The main observations are as follows: (i) In both series, the BLA values are significantly lower than in unsubstituted polyenes, for which values of 0.08–0.10 Å are typical.^{33,34} (ii) In both series, BLA decreases as the molecules become longer; while saturation of the central BLA value is reached in the longest APPB molecules, it is not the case yet for the longest AB studied. (iii) BLA in the middle of AB molecules is considerably lower than in APPB molecules for similar chain lengths (D/A separation).

For comparable chain lengths, the BLA values in the middle of the chain can serve as a measure of the degree of ground-state polarization, an important parameter defining the NLO response.¹⁸ Therefore, higher BLA values in the APPB molecules with respect to AB molecules of comparable length confirm the usual buffer effect of the phenylene buffers: in AB molecules, where D/A substituents are attached to the polyene segment directly, the polyene backbone is more strongly polarized. It is remarkable that our calculations indicate that the AB geometry approaches the cyanine limit (zero BLA) in the middle of longer chains; we stress that this occurs in the absence of any external electric field or point charges, which confirms the very strong polarization ability of the charged A/B groups.

Figure 2 displays the evolutions of the dipole moments in the APPB and AB series, as a function of the distance separating the nitrogen and boron atoms. The evolutions are nearly linear in both cases with the magnitudes of the dipole moments higher in the APPB series. A detailed analysis of these evolutions has been presented in ref 22; there, it was confirmed

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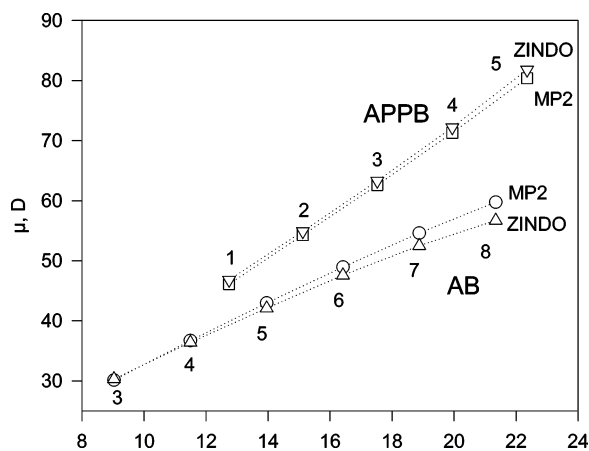


Figure 2. Evolution of the ground-state dipole moments in the APPB and AB series as a function of molecular length (B–N distance); MP2/6-31G and ZINDO/SCF values at MP2/6-31G optimized geometries. The labels over each data point indicate the number of carbon pairs in the polyene bridge.

that the phenylene rings effectively act as buffers preventing as high a degree of polarization of the polyene backbone in the APPB series as that in the AB series. This is consistent with the lower degree of BLA calculated in the middle of the AB molecules. We note that Mulliken population analysis indicates that, in all molecules, the end groups (NR_3^+ and BR_3^-) each carry a charge on the order of 0.4 $|e|$ (in absolute value) while the phenylene rings each carry a charge of ca. 0.35 $|e|$ (in absolute value), of the same sign as the end group they are attached to.

3.2. Second-Order and Third-Order Polarizabilities. The static longitudinal second- and third-order polarizabilities for the APPB molecules calculated via SOS/SDCI and real-space FF/SCF procedures with the INDO Hamiltonian are shown in Figure 3. The agreement among the values obtained with different approaches is remarkably good. A most interesting aspect to be stressed is that the second-order polarizabilities are negative, while the third-order polarizabilities are positive. In the framework of the unified description of polarization, relating the geometric structure as described by BLA to the linear and nonlinear optical properties of polymethines,^{18,23} this combination of signs would correspond to a BLA pattern beyond the cyanine limit toward the charge-separated zwitterionic structure (in other words, a situation where the BLA pattern of the bridge is inverted with respect to that in a nonpolarized or only weakly polarized neutral polyene; see Figure 7 of ref 18). However, in the APPB series, the BLA pattern remains similar to that of a weakly polarized polyene. This apparent discrepancy actually is a first indication that the NLO properties of the APPB series are not simply due to a polarized polyene backbone but come from a different mechanism; as will be shown below, the main NLO-active segments are the pair of strongly polarized phenylene groups.

The β and γ values grow superlinearly with chain length. When their evolutions as a function of the number of double bonds n in the bridge are approximated by a power law dependence, as is usually done for organic oligomer series,

$$\log(-\beta_{xxx}) = b_0 + b \log(n)$$

$$\log(\gamma_{xxx}) = g_0 + g \log(n)$$

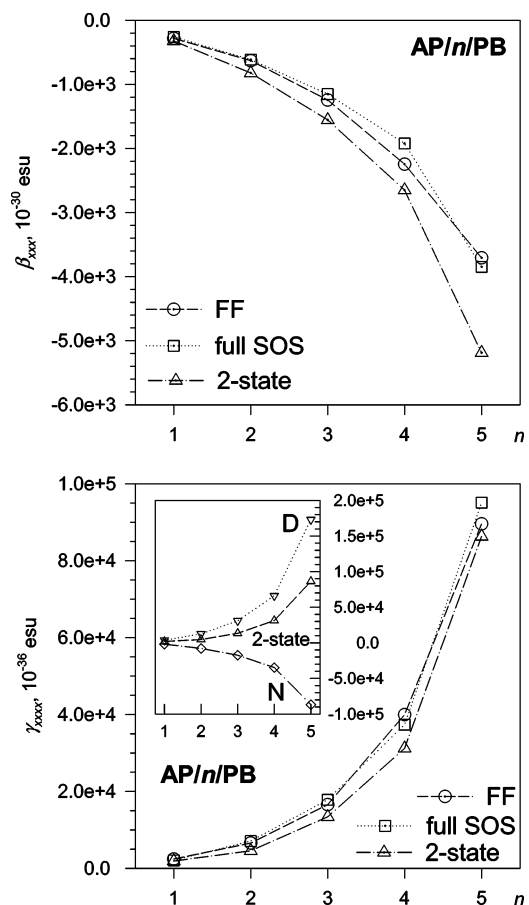


Figure 3. NLO response of APPB molecules. Longitudinal static second-order polarizability β_{xxx} (a) and third-order polarizability γ_{xxx} (b) calculated with INDO Hamiltonian: real-space finite-field (FF), full sum-over-states (SOS), and two-state approximation to the latter. The inset shows the evolution of the dipolar (D) and negative (N) terms (eq 2) that enter the two-state model for γ .

we find the exponents $b = 1.6$ and $g = 2.3$ for the second- and third-order polarizabilities, respectively (b_0 and g_0 are equal to 1.9 and 2.6). Such exponents are typical for short chains; see for instance ref 35 for a discussion.

It should also be stressed that the calculated β and γ values are very high. The static second-order and third-order polarizabilities, on the order of 10^{-27} and 10^{-32} esu, respectively, for the APPB compounds with four and five double bonds, are characteristic of polarized carotenoids with conjugated backbones that are 2 and 3 times longer (note that the second-order polarizabilities of these carotenoids are positive).^{23,35,36} Thus, the APPB series holds much promise in terms of its NLO characteristics.

We now turn to an analysis of the origin of the NLO response in APPB molecules. To do so, we make use of the complementary aspects provided by the FF and SOS methods.

3.2.1. Real Space FF Formulation. The real-space analysis can be restricted to π -electron contributions. In fact, no significant field-induced population transfer is found between the π - and σ -subsystems; therefore, these subsystems can be treated independently, and their contributions to the overall

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molecular polarizabilities are practically additive. Moreover, even though individual σ -contributions can be significant, the sum of all the hyperpolarizability moments due to the σ -subsystem is small with respect to the π -contributions; that is, nonlinearity is primarily due to the π -electrons.

When analyzing the molecular polarizabilities using real-space contributions, it should be borne in mind that while polarizability charges are origin-independent quantities that characterize the response of each atom, individual molecular polarizability moments in eq 1 have no absolute meaning because of their dependence on the arbitrary choice of the coordinate origin. However, at all orders, the sum of all the moments in a molecule that yields the static molecular polarizabilities is origin-invariant.¹⁹ Therefore, to obtain a real-space image of the molecular polarizability moments, it makes sense to choose a convenient coordinate system able to shed the most light on the origin of the NLO response of the molecule. Here, the coordinate origin is chosen to be the center of the molecular center of mass.

Figure 4 shows the second- and third-order π -orbital polarizability charges and moments for AP/4/PB (i.e., the APPB molecule containing 4 double bonds in the polyene bridge) plotted as a function of the longitudinal coordinate x . The moments are obtained by multiplying these atomic π -polarizability charges by the atomic x -coordinate values.

There are many similarities between the real-space images of the second- and third-order responses of an APPB molecule: (i) The ammonio and borato groups provide negligible π -contributions to the molecular polarizabilities. (ii) The polyene chain presents highly alternating $q^{(2)}$ and $q^{(3)}$ charges from carbon to carbon; their values peak around the middle of the segment. (iii) The $q^{(2)}$ and $q^{(3)}$ charges have the same sign within each phenylene group. (iv) The two phenylene groups have opposite signs of the $q^{(2)}$ and $q^{(3)}$ charges.

As a result, there occurs a marked cancellation of the $q^{(2)}$ and $q^{(3)}$ moments within the polyene backbone. On the contrary, the polarizability moments coming from the phenylene groups all have the same sign (negative for the second-order polarizability and positive for the third-order polarizability) and are amplified by their long moment arms. This analysis highlights the role of the polarized phenylene groups in the NLO response of APPB molecules.

For the sake of comparison, we also present in Figure 4 the real-space images of the polarizabilities for an AB molecule of comparable length, that is, A/7/B (with seven double bonds in the polyene bridge). At the second order, the cancellation of the moments is so significant that the overall β value is about the same as that of just a single one of the higher atomic moments. The individual $q^{(2)}$ values are generally higher than those in AP/4/PB, but their pattern is inefficient; as a result, the magnitude of the second-order polarizability of A/7/B is lower than that in AP/4/PB. The same trend is obtained for the entire series. Thus, the introduction of terminal phenylene groups that replace part of the polyene segment actually contributes to increase the second-order NLO response in these ammonio–borato push–pull molecules.

At the third order, the real-space polarizability image of A/7/B is qualitatively different from that of AP/4/PB discussed above and also from its second-order pattern. Unlike AP/4/PB, the

third-order polarizability of A/7/B is negative. The real-space approach indicates that this is primarily due to the high contributions from the ends of the polyene segments. Note that negative γ values are predicted^{18,23} to be a characteristic feature of strongly polarized polyenes near the cyanine limit (vanishing BLA, see Figure 1).

3.2.2. SOS Formulation. In addition to the fully converged SOS hyperpolarizability values for the APPB series, Figure 3 also shows those obtained when considering only the terms corresponding to excitations from the ground state to the first charge-transfer excited state, that is, when taking into account the two-state model. The two-state approximation turns out to be most satisfactory for all chain lengths studied, especially for the third-order polarizability. It should be noted at this stage that the two-state model is often applicable to the description of the second-order response in organic compounds of moderate length; it usually becomes increasingly insufficient to describe β in longer chains. It is also generally severely inadequate for the description of the third-order NLO processes, where two-photon virtual excitations (i.e., involving two excited states) are of considerable importance.^{18,21,36} However, in APPB molecules, the origin of the NLO response is remarkably simple and can be interpreted within the two-state approximation.

In the two-state model, the static second- and third-order polarizabilities are expressed as follows:

$$\beta^{[\text{two-state}]} = \mu_{10}^2 \Delta\mu_{10} / E_{10}^2 \quad (2)$$

$$\gamma^{[\text{two-state}]} = \mu_{10}^2 \Delta\mu_{10}^2 / E_{10}^3 - \mu_{10}^4 / E_{10}^3 \equiv D + N = (\Delta\mu_{10}^2 - \mu_{10}^2) \mu_{10}^2 / E_{10}^3 \quad (3)$$

(D and N in eq 3 denote the so-called dipolar and negative terms.) The β and γ values depend on three parameters only: the transition dipole moment μ_{10} between the ground state $|0\rangle$ and the charge-transfer excited state $|1\rangle$; the difference in state dipole moments $\Delta\mu_{10} = \mu_1 - \mu_0$; and the transition energy $E_{10} = E_1 - E_0$. The evolution of these parameters with chain length in the APPB series is shown in Figure 5.

Figure 5a compares the evolutions with chain length of the transition energy for the APPB molecules, as obtained at the INDO SD-CI and TD-DFT levels; the results are presented in terms of the absorption wavelength $\lambda = hc/E_{10}$, with λ [in nm] = 1240/ E_{10} [in eV]. The results of both methods are in good mutual agreement; the somewhat less regular evolution of the INDO values is likely related to the limited size consistency of the SD-CI approach, making it more difficult to describe the entire homologous series with the same precision. The overall linear evolution of λ with chain length is characteristic of conjugated systems. (We note that plugging the TD-DFT transition energies instead of the INDO SD-CI transition energies in eqs 2 and 3 leads to variations of less than 5% in the two-state β and γ values.)

Turning to Figure 5b, we recall that the sign of the second-order polarizability β (eq 2) is determined by the sign of $\Delta\mu$. The ground state having here a high degree of polarization, the excited state turns out to be actually less polar, which implies that $\Delta\mu < 0$; this results in negative solvatochromism, a feature which has been experimentally observed for these compounds.¹⁷

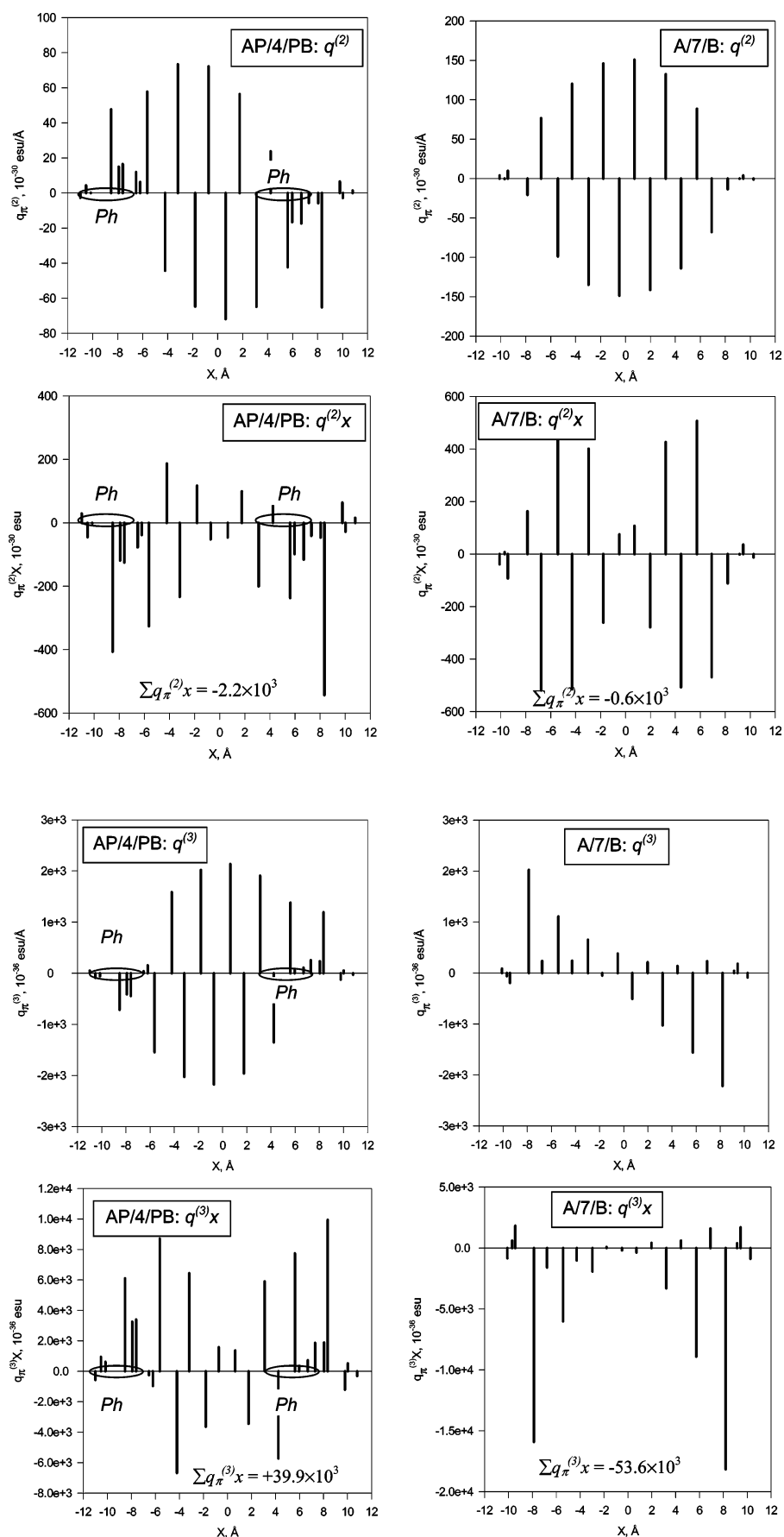


Figure 4. Real-space finite-field decomposition of the NLO response in the AP/4/PB and A/7/B molecules (these have similar length). The longitudinal hyperpolarizability π -charges $q_{\pi}^{(2)}$ and $q_{\pi}^{(3)}$ and their moments $q_{\pi}^{(2)}x$ and $q_{\pi}^{(3)}x$ are plotted vs x -coordinates. The circles labeled Ph indicate the positions of the phenylene rings.

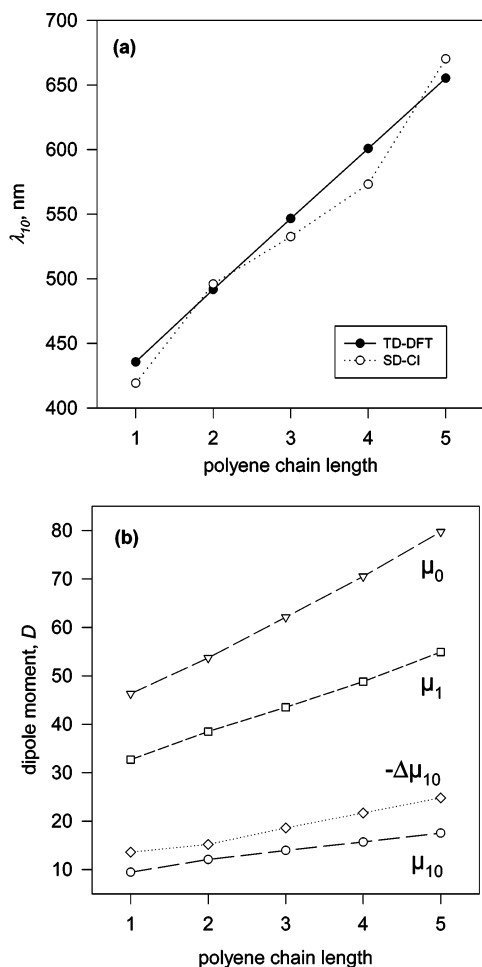


Figure 5. Quantities relevant to the NLO response in the APPB series (the polyene length is expressed in number of carbon pairs along the polyene segment): (a) evolution of the INDO SD-CI and TD-DFT transition wavelengths; (b) evolution of the INDO SD-CI ground-state (μ_0) and excited-state (μ_1) dipole moments, of their differences ($-\Delta\mu_{10} = \mu_0 - \mu_1$), and of the transition dipole moments (μ_{10}).

The sign of the third-order polarizability γ (eq 3) is determined by the sign of $(\Delta\mu - \mu_{10})$, thus by the relative magnitude of the transition and difference in dipole moments, irrespective of their signs: $\gamma > 0$ when $|\Delta\mu| > |\mu_{10}|$, $\gamma < 0$ when $|\Delta\mu| < |\mu_{10}|$. Figure 5b shows that the magnitude of $\Delta\mu$ exceeds that of the transition dipole moment at all chain lengths studied, resulting in the positive sign of γ . However, eq 3 underlines that there occurs much cancellation between the positive dipolar term D and the negative term N in the two-state expression for the third-order polarizability (Figure 3).

To gain an idea how the magnitudes of β and γ evolve with chain length, it is instructive to observe in Figure 5b that the transition and the difference in dipole moments increase, as well as the difference between $\Delta\mu$ and μ_{10} , while the transition energy decreases for the moderate chain lengths studied. Therefore, all the terms in eqs 1 and 2 favor an increase of the molecular polarizabilities, which accounts for the highly superlinear growth of β and γ with chain length.

In the two-state model for APPB, the NLO response is due to the strongly allowed virtual excitation from the ground state to the first excited state. Gaining more insight into the NLO response is possible by considering the nature of these states. The ground state is well described with the HF determinant (its

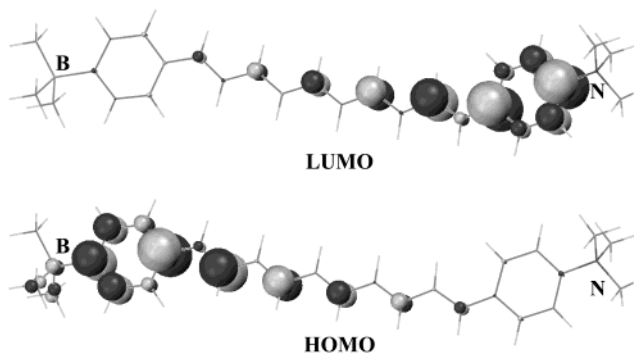


Figure 6. Sketch of the HOMO and LUMO orbitals in the AP/5/PB molecule (INDO calculations).

coefficient in the SD-CI expansion is 0.96 at any chain length). The first excited state, though more correlated, predominantly contains the HOMO→LUMO singly excited determinant (whose coefficient smoothly decreases from 0.90 to 0.78 with the chain length in the range studied) with the HOMO→LUMO doubly excited determinant as a major admixture. Thus, the characteristics of the HOMO→LUMO excitation determine the NLO properties of the APPB molecules. The HOMO and LUMO are found to have the same nature throughout the APPB series; they are depicted in Figure 6 for the longest molecule, AP/5/PB. As expected, both the HOMO and LUMO are π -orbitals. The electron densities are located toward the phenylene donor and phenylene acceptor sides of the molecule, respectively. The excitation mostly consists of charge transfer between the two phenylene rings, with the participation of adjacent polyene carbon atoms. In this respect, the polarized phenylene rings do play the role of π -donor and π -acceptor (D_π/A_π); they are the reservoirs releasing charge under excitation,¹³ which explains the lower polarization found in the excited state. Thus, the charge transfer between the polarized aromatic rings is the primary source for the NLO response in the APPB series. Note that the electron density on the ammonio and borato groups in the HOMO and LUMO is low (especially on the ammonio group) despite their high charge; this is in agreement with their inductive, σ -donor–acceptor character (D_σ/A_σ).

The similarity of conclusions reached by the FF and SOS analyses, both highlighting the role of polarized phenylene groups, can be considered as an illustration of basic similitude between these theoretical approaches. This analogy can be demonstrated analytically for the two-state case.

4. Synopsis

We have analyzed the electronic structure and the origin of the second- and third-order NLO response in zwitterionic ammonio/borato diphenylpolyenes (APPB). The polyene bridge, when capped with the phenylene rings, is somewhat screened from the donor and acceptor, as indicated by the higher BLA values (lower ground-state polarization) in the APPB molecules, compared to the AB molecule in which the A/B substituents are attached directly to the polyene. In the AB series, the ground-state polarization is so high that the cyanine limit (zero BLA) is practically reached.

The NLO response in the phenylene-capped APPB molecules is calculated to be significantly higher than that in the AB

analogues of comparable length. This is an unexpected result, given that aromatic substitution within the bridge generally worsens the NLO properties of push–pull molecules with conventional π -donor/acceptor pairs.

The origin of the remarkable NLO response of the APPB molecules was elucidated with the help of two complementary theoretical frameworks. Real-space finite-field results directly point to the most NLO-active segments in the molecules: in the APPB molecules, these are primarily phenylene groups. The sum-over-states analysis highlights the essential role of a single excitation channel in the APPB series. It consists of the ground-state to lowest excited-state channel, corresponding to the HOMO→LUMO excitation. This transition involves an inter-phenylene electron density transfer, again underlining the critical role of the phenylene rings in generating the NLO response.

The exceptional contribution of the rings to the molecular polarizabilities, while preserving their aromaticity under strong polarization, is an important finding of this work.

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