Chapter 3

Hyperpolarizabilities of Push–Pull Polyenes
Molecular Orbital and Valence-Bond Charge-Transfer Models

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In this paper we review two theoretical approaches that illustrate the
relationships between molecular (hyper)polarizabilities and bond-
length alternation (BLA). In one approach, we employ sum-over-
states calculations at the INDO-SCF level on (CH3)2N-(CH=CH)2-
CHO, including an external, static, homogeneous electric field that
uniforms the degree of ground-state polarization and BLA. In the second
approach, we use a simple semiclassical model, wherein the mixing
of valence bond (VB) and charge-transfer (CT) states along a BLA
coordinate is treated. Qualitatively, the two approaches give very
similar structure-property trends, that are consistent with experimental
hyperpolarizability data on donor-acceptor polyenes. The agreement
of the calculated trends reflects the importance of VB-CT energetics in
determining them.

Recent experimental work has demonstrated a correlation between the bond length
alternation and the first and second hyperpolarizabilities (β and γ) of donor-acceptor
(DA) substituted (push-pull) polyenes (1, 2). The bond length alternation, BLA, in
DA polyenes is defined as the average of the difference in the length between adjacent
carbon-carbon bonds in the polymethylene, (CH)n, chain. The structure of such
molecules can be understood qualitatively as resulting from a superposition of
valence-bond (VB) and charge-transfer (CT) limiting resonance structures (Figure 1).
Experimentally, molecules have been examined where BLA was varied from the
polyene limit of ~0.1 Å to values approaching the opposite BLA limit of ~0.1 Å, by
use of acceptors of varying strength and groups that gain aromaticity on polarization
for coarse tuning. Additionally, the structures have been fine tuned by the use of
solvents of varying polarity. It was shown that μβ (2) and γ (1, 3) exhibit positive

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and negative peaks and sign changes as the ground-state polarization is increased, with BLA varying concomitantly from -0.12 towards 0.12Å. These experimental trends are consistent with those calculated with a finite-field AM-1 molecular orbital method, described previously (4). In this paper, we provide an overview of recent work, presented in part at the 1994 fall American Chemical Society meeting in Washington, DC, on detailed sum-over-states molecular orbital calculations (5, 6) at the intermediate neglect of differential overlap level (including configuration interaction with single and double excitations, INDO-SDCl) and a semiclassical valence-bond/charge-transfer (VB-CT) model (7, 8) that elucidate the relationships between BLA, the related π-bond order alternation, BOA, (vide infra) and α, β and γ.

Relationships between BOA and α, β, and γ at the INDO-SDCl level

In order to correlate α, β, and γ with geometric and electronic structure, we examined, at the semi-empirical INDO level, the molecule (CH₃)₂N-(CH=CH)₄CHO (Figure 1) in the presence of a static, homogeneous electric field. Fields of high strength were used to tune the degree of ground-state polarization, BLA and the related parameter, BOA (Figure 2). The molecular polarizabilities were evaluated using a sum-over-states approach in combination with INDO-SDCl calculations (5, 6). These calculations allowed us to identify the electronically excited states that play an important role in the nonlinear optical response (5, 6). The correlation of the polarizabilities with BOA is shown in Figures 3-5 (note that ground-state polarization increases concomitantly with BOA). In addition, this analysis allowed us to compare the values of the polarizabilities obtained from the full sum-over-states expressions for α₀₀₀₀, β₀₀₀₀ and γ₀₀₀₀ and simplified two or multilevel level models in which:

\[ \alpha_{\text{model}} \propto \frac{\mu_{g}^{2}}{E_{g}} \]  
\[ \beta_{\text{model}} \propto \frac{\mu_{e}^{2}(\mu_{e}^{2}+\mu_{g}^{2})}{E_{g}} \]  
\[ \gamma_{\text{model}} \propto -\left(\frac{\mu_{e}^{4}}{E_{g}^{2}}\right) + \sum_{e'} \left(\frac{\mu_{e}^{2}(\mu_{e}^{2}+\mu_{e'}^{2})}{E_{g}^{2}}\right) + \left(\frac{\mu_{e}^{2}(\mu_{e}^{2}+\mu_{e}^{2})}{E_{g}^{2}}\right) \]  

where \( \mu \) and \( E \) are the dipole matrix element and transition energy, respectively, between the subscripts states. The subscripts g, e, and e' label the ground, first excited and upper excited states, respectively.

The first-order polarizability, \( \alpha \), exhibits a peak at zero BOA (referred to here as the cyanine limit) (Figure 3). In the two-level model expression (eq. 1) \( \alpha \) is dependent on two factors, \( 1/E_{g} \) and \( \mu_{g}^{2} \). As can be seen in Figure 3 there is a very good correlation between the converged sum-over-states calculation (30 states) and that of the two level model. Examination of the dependence of \( 1/E_{g} \) and \( \mu_{g}^{2} \) on BOA reveal that they both peak near the cyanine-limit (Figure 3), thus providing insight into the dependence of \( \alpha \) on BOA.

Figure 1. Valence-bond and charge-separated resonance structures for (CH₃)₂N-(CH=CH)₄CHO.

Figure 2. Evolution of BLA and BOA vs. applied field (F) for (CH₃)₂N-(CH=CH)₄CHO.
Figure 3. Evolution of: $\alpha_{\text{obs}}$ (crosses) and $\alpha_{\text{model}}$ (full circles, dashed line) in $10^{-24}$ esu; $1/E_0$ (short dashed line) and $\mu_{\text{eq}}$ (long dashed line) in arbitrary units, plotted vs. BOA.

Figure 4. Evolution of: $\beta_{\text{obs}}$ (crosses) and $\beta_{\text{model}}$ (full circles, dashed line) in $10^{-30}$ esu; $\mu_{\text{es}}$, $\mu_{\text{eq}}$ (short dashed line) in Debye, plotted vs. BOA.

Figure 5. Evolution of: $\gamma_{\text{obs}}$ (crosses) and $\gamma_{\text{model}}$ (full circles, dashed line) [top], and the D- (triangles), N- (squares), and T-terms (diamonds) [bottom] in $10^{-36}$ esu, plotted vs. BOA.
The first hyperpolarizability, $\beta$, as a function of increasing ground-state polarization, exhibits a positive peak, a sign change at zero BOA, and a negative peak (Figure 4). Again, the two level calculation for $\beta$ describes well the basic correlation of $\beta$ and BOA, in terms of both peak position and magnitude. Accordingly, the relation between $\beta$ and BOA can be understood in terms of the model expression (eq. 2) in which $\beta_{\text{model}}$ is proportional to $\alpha_{\text{model}}$ scaled by a factor of $(\mu_{\text{ee}} - \mu_{\text{gg}})/E_g$. Thus, the two peaks in the $\beta$ curve are a result of the form of $\alpha$ and the sign change and peaks in $(\mu_{\text{ee}} - \mu_{\text{gg}})$ (Figure 3). The position of the $\beta$ peaks is closer to zero BOA than the $(\mu_{\text{ee}} - \mu_{\text{gg}})$ peaks since both $(1/E_g^2)$ and $\mu_{\text{gg}}$ peak at zero BOA.

The correlation of $\gamma$ with BOA obtained from the converged sum-over-states calculation and the three-term model (0-12) also agree quite well. The expression in eq. 3 consists of a negative term, $N$, proportional to $\alpha_{\text{model}}^2$, a two-photon term, T, and a term, D, proportional to $\beta_{\text{model}}^2/\alpha_{\text{model}}$. For chromophores with large negative BOA, such as unsubstituted polyenes, the D term is negligible due to a small $(\mu_{\text{ee}} - \mu_{\text{gg}})$ and the T term dominates the N term resulting in positive $\gamma$ (Figure 5). By increasing the ground-state polarization and thus increasing BOA, the D term, like $\beta$, starts to increase and hence $\gamma$ increases. However, increasing the ground-state polarization toward the cyanine-limit also increases $\alpha$, ultimately leading to a decrease in $\gamma$. As a result of $\alpha$ increasing in this region, the peak in the $\gamma$ curve occurs at a larger magnitude of BOA than the peak in the D term. Upon further polarization, D peaks in a positive sense and starts to decrease and $\gamma$ continues to increase and thus $\gamma$ decreases and goes through zero when $|\alpha| = |T| + |D|$. As the bond-equivalent cyanine-limit the D term is zero since $(\mu_{\text{ee}} - \mu_{\text{gg}})$ is zero and the $\gamma$ curve exhibits a negative peak, since both $|\alpha|$ and T peak but $|\alpha| > |T|$ (Figure 5). To a first approximation, the behavior of $\gamma$ in the region of positive BOA mirrors that in the negative BOA region.

Relationships between BLA and $\alpha$, $\beta$, and $\gamma$ in the VB-CT model

The structural evolution of the DA polyenes as calculated by AM-1 or INDO-SCFD methods as a function of a strong static field can qualitatively described in terms of a superposition of valence-bond and charge-transfer resonance structures. We recently developed a simple semiclassical VB-CT model based on such a picture for DA polyenes, to illustrate the dependence of the structural evolution on VB-CT energetics and thereby provide further insights into the structure-hyperpolarizability relationships. In the VB-CT model, (7) the mixing of the two resonance forms along a continuous BLA coordinate, $q$, is treated. This mixing results in a ground-state potential surface whose equilibrium value of BLA depends on, among other factors, the zero-order adiabatic energy difference, $V_0 = E_{\text{CT}} - E_{\text{VB}}$, and the charge transfer matrix element, $t$. When $V_0$ is large, the ground state resembles the neutral resonance form, whereas when $V_0$ is negative and large in magnitude, the ground state resembles the charge-transfer resonance form. For intermediate values of $V_0$, the structure evolves rapidly, with the greatest rate of change at $V_0 = 0$, where the structure is cyanine-like. The value of $V_0$ depends on the donor and acceptor strength and the difference in energy of the bridge in the two states. Additionally, since the two states have a large difference in dipole moment, $\mu_{\text{VB}} - \mu_{\text{CT}} - e \cdot R_{\text{DA}}$, the application of an electric field or the screening of the charges due to the solvent dielectric response also affects the energy difference.

In order to calculate the structure-property relationships as $V_0$ is varied, we computed the eigenstate potential surfaces (see Figure 6), obtained the equilibrium structure on the ground state potential surface, and then calculated the dipole moment, polarizability and hyperpolarizabilities, for a given value of $V_0$. The zero-order potential surfaces were taken to be harmonic in this simple model. The calculation was repeated over a range of $V_0$, from which we obtained the dependence of the polarization, polarizabilities, and BLA on $V_0$. The ground state wavefunction is written in terms of VB and CT wavefunctions as:

$$\Psi_{\text{VB}} = \sqrt{1-f}\Psi_{\text{VB}} + \sqrt{f}\Psi_{\text{CT}}$$

(4)

where $f$ is the charge-transfer fraction, $f = 1/2 \cdot V/(V^2 + 4t^2)^{1/2}$. Here $V$ represents the vertical energy difference between VB and CT harmonic surfaces at a particular $q$. The ground-state energy (taking $E_{\text{VB}} (q = 0.12\lambda) = 0$) for the two-state system is:

$$E_{\text{VB}} = \frac{1}{2} \left( V - \sqrt{V^2 + 4t^2} \right)$$

(5)

To find the equilibrium structure we solved $dE_{\text{VB}}/dq = 0$, from which one can show (7) that $q_{\text{eq}} = -0.12 + 0.24f$. Thus, BLA and the charge transfer fraction are linearly related in this model. The value of $q_{\text{eq}}$ for a given value of $V_0$ was found either by a numerical search for the minimum or by solving the equation for $q_{\text{eq}}$ iteratively. Recognizing that $\mu = f \cdot \mu_{\text{CT}}$ and that the polarizabilities are the derivatives of $\mu$ with respect to field strength, we obtained analytic expressions for $\alpha$, $\beta$, $\gamma$, and $\delta$:

$$\alpha = \frac{2t^2 \mu_{\text{CT}}^2}{E_g^3}$$

(6)

$$\beta = \frac{3t^3 \mu_{\text{CT}} V}{E_g^3}$$

(7)

$$\gamma = \frac{4t^4 \mu_{\text{CT}} (V^2 - t^2)}{E_g^3}$$

(8)

$$\delta = \frac{5t^5 \mu_{\text{CT}}^2 (V^2 - 3t^2)}{E_g^3}$$

(9)

where $E_g = (V^2 + 4t^2)^{1/2} = \hbar c/\lambda_{\text{max}}$ is the energy gap. It should be emphasized that $V$ and $E_g$ are the values at $q_{\text{eq}}$ for a particular $V_0$. The relationships between the polarizabilities, as function of static field strength, and the structural evolution have been discussed in earlier papers (3, 7).

To a first approximation, molecules of a given length and bridge type can be taken to have the same $t$ and $\mu_{\text{CT}}$, thus the polarizabilities and the structure vary primarily due to variations in $V_0$. Figure 7 shows the calculated dependencies for $\alpha$, $\beta$, and $\gamma$ as a function of $V_0$. The calculated dependencies exhibit very similar trends to those discussed above in the context of the molecular orbital calculations. Since $E_g$ is at a minimum (i.e., $E_g = 2t$) when $V_0 = 0$, which is where $\text{BLA} = 0$, $\alpha$ is peaked, $\beta$ is zero, and $\gamma$ is at a negative extreme. With further stabilization of the CT state, whereupon it becomes the lower energy zero-order state, $V$ becomes negative.
Figure 6. Potential energy surfaces for zero-order VB and CT states, and the ground and excited eigenstates, corresponding to a zero-order adiabatic energy difference of 1 eV. A harmonic force constant of 33.5 eV/Å² was used for the zero-order surfaces and the charge transfer matrix element, $\alpha$, was taken as 1.18 eV. The equilibrium coordinates for VB and CT are -0.12 Å and 0.12 Å, respectively. The $x$ marks the equilibrium coordinate ($q_{eq}$) on the ground state potential surface.

Figure 7. $\alpha$, $\beta$, and $\gamma$ as a function of $V_o$ calculated using the VB-CT model for a DA polyene with nine conjugated atoms. The left extreme corresponds to zwitterionic structures and the right side to neutral polyene like structures.


and from eq. 7 so does $\beta$. Of course, this sign change is also associated with a change in sign of $(\mu_\alpha \mu_\beta H_{\alpha\beta})$, which was discussed above. The value of $\beta$ reaches extremes when $V = \pm \sqrt{3}t$, thus $E_\beta = \sqrt{3}t$, which is also where $\gamma = 0$. The value of $\gamma$ reaches maxima when $V = \pm \sqrt{3}t$, whereupon $E_\gamma = \sqrt{3}t$.

While the trends calculated using the VB-CT model agree qualitatively well with the AM1 and INDO sum-over-states calculations, there are some small differences, particularly in the detailed shape of the $\gamma$ curve (7). In the sum-over-states calculations, the positive peak value of $\gamma$ (relative to that of the negative peak) is larger than is found in the valence bond model. In the VB-CT model used here only two states contribute to $\gamma$, however, as we have discussed above, there are significant positive contributions from higher lying two-photon states (the $T$ term in eq. 3). We believe that the omission of such terms in the valence bond treatment may lead to these differences. It is possible to develop a more complete valence bond model in which various bridge localized excited states are taken into account. The treatment of such states has been described recently (6) and its inclusion with the present VB-CT model is being investigated.

Figures 8 and 9 show plots of the $\mu\beta$ product, which is the microscopic quantity relevant to EFISH and poled-polymer electro-optic responses, and $\gamma$ versus $\lambda_{max}$ for a DA octatetraene calculated using the VB-CT model as $V_o$ was varied from -2 to 2 eV. These plots illustrate the nonlinearity-transparency trade-off (as measured by $\lambda_{max}$) for DA molecules of a fixed length that vary over the domain of BLA. The value of $\mu\beta$, Figure 8, reaches a maximum when $\lambda_{max}$ is about 490 nm (for DA polyenes with nine conjugated atoms) but decreases and goes to zero as $\lambda_{max}$ reaches its maximum at ~520 nm (the so-called cyanine-limit). Thus, structural changes that lead to an increase in $\lambda_{max}$ at fixed length do not always lead to an increase in $\mu\beta$. The lower arm of the $\mu\beta$ plot corresponds to highly polarized molecules that are dominantly zwitterionic. Since the dipole moment increases as the CT form is stabilized, the negative peak of $\mu\beta$ is substantially larger in magnitude than positive peak. The negative $\mu\beta$ peak occurs near 540 nm, substantially blue shifted relative to the positive peak. This increased nonlinearity and transparency of zwitterionic molecules near the negative extreme of $\mu\beta$ makes such molecules attractive candidates for poled polymer applications.

Because the dependence of $\gamma$ on $V_o$ is symmetric about $V_o = 0$ (Figure 7) the $\gamma$ versus $\lambda_{max}$ plot folds back on top of itself as the polarization is increased, giving the simple curve in Figure 9. Accordingly, in contrast to what was calculated for the $\mu\beta$ values, there is no intrinsic advantage to highly zwitterionic DA polyenes for $\gamma$. The positive peak of $\gamma$ occurs near 400 nm but the negative peak, which is several times larger in magnitude, occurs when $\lambda_{max}$ is at its maximum of 520 nm (the cyanine limit). With their large negative $\gamma$ values, cyanines or DA molecules at the cyanine limit could be of interest for self-defocusing applications (like optical power limiting), or for the engineering of materials with vanishing third-order nonlinearity, through the destructive interference of the negative contribution of the cyanine and the positive nonlinearity of a host medium.

It is not uncommon to find in the literature fits of $\mu\beta$ and $\gamma$ to power laws in $\lambda_{max}$. In view of the dependencies in Figures 8 and 9, it can be seen that for DA polyenes at a fixed length, a simple power law relation is not obeyed over the domain of structural variation. For DA polyenes varying in length considerable caution is needed in interpreting power law fits in length or in $\lambda_{max}$. This is because the degree of polarization and the BLA of the molecules could be length dependent.
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Conclusions

For simple DA polyene dyes, $\alpha$, $\beta$, and $\gamma$ can be correlated with either BLA or BOA as demonstrated using semi-empirical INDO/SDCI calculations. The trends obtained through these calculations are in qualitative agreement with a simple model based on VB and CT mixing that involves harmonic potentials for the zero-order states. This model provides a simple physical picture for the evolution of the structure of DA polyenes as the CT state is stabilized. In this model, analytical dependencies of the polarization and polarizabilities on the energetics and interaction of VB and CT states are obtained, although the equilibrium structure must be found numerically. The agreement obtained between the different levels of theory (AM-1, INDO/SDCI, and VB-CT model) suggests that the trends obtained are robust and, therefore, provide useful guidelines for the design of optimized molecules for nonlinear optics.

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