

HYPERPOLARIZABILITIES OF PUSH-PULL POLYENES:
EXPERIMENTAL RESULTS AND A NEW TWO-STATE MODEL

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Recent work has demonstrated a correlation between the geometry (i.e., the bond length alternation, *BLA*) and the first and second hyperpolarizabilities (β and γ) of donor-acceptor substituted (push-pull) polyenes.^{1,2} The structure of such molecules can be understood as resulting from a superposition of limiting resonance structures, VB and CT, Figure 1. By use of acceptors of increased strength and groups that gain aromaticity on polarization for coarse tuning, along with increased solvent polarity for fine tuning, molecules were examined where *BLA* was varied from the polyene limit of -0.12Å to values approaching the opposite *BLA* limit of 0.12Å. It was shown that $\mu\beta^2$ and $\gamma^{1,3}$ exhibit positive and negative peaks and sign changes as the ground state polarization is increased, concomitant with *BLA* varying from -0.12 towards 0.12Å. The experimental trends are consistent with those calculated with a finite-field AM-1 molecular orbital method by Gorman and Marder.⁴ Recent sum-over-states calculations at the INDO-SDCI level by Meyers et al.⁵ have illustrated how the different terms in a three term-expression for γ vary as a function of *BLA*, to produce the observed trends. Given the simplicity with which we can qualitatively describe the structural evolution of the donor-acceptor polyenes using resonance theory, we were motivated to develop a simple quantitative valence bond model for such molecules, in order to provide further insight into the structure-hyperpolarizability relationships.

In the VB-CT model,⁶ the mixing of the two resonance forms along a *BLA* coordinate, q , is treated. This results in a ground state potential surface whose equilibrium value of *BLA* depends on the zero-order adiabatic energy difference, $V_0 = E_{CT} - E_{VB}$, 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 large and negative, the ground state resembles the charge transfer resonance form. For intermediate V_0 , the structure evolves continuously from one limit to the other, with the greatest rate of change around $V_0 = 0$. 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, $\mu_{VB} \sim 0$, $\mu_{CT} \sim e R_{DA}$, the application of an electric field or the screening of the charges due to solvent molecules affects the energy difference. In order to calculate the structure-property relationships, we compute the ground state potential surface (see Figure 2), find the equilibrium structure and calculate the dipole moment and its derivatives, for a given value of V_0 . This calculation is repeated over a range of V_0 , from which we can obtain the dependence of the properties on V_0 or on *BLA*. The ground state wavefunction is written in terms of VB and CT wavefunctions as:

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

where f is the charge transfer fraction, $f = ((V^2 + 4t^2)^{1/2} - V)/2(V^2 + 4t^2)^{1/2}$. Here V represents the vertical energy difference between VB and CT at a given value of q . The ground state energy for the two state system is:

$$E_g = \frac{1}{2}(V - \sqrt{V^2 + 4t^2})$$

To find the equilibrium structure we solve $dE_{gr}/dq = 0$ numerically. One can show that $q_{eq} = -0.12 + 0.24f$, demonstrating that BLA and the charge transfer fraction are linearly related. Recognizing that $\mu = f\mu_{CT}$ and that the polarizabilities are the derivatives of μ with respect to field strength, we obtain analytic expressions for α , β , γ , and δ :

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

$$\beta = \frac{3t^2\mu_{CT}^3V}{E_g^5}$$

$$\gamma = \frac{4t^2\mu_{CT}^4(V^2 - t^2)}{E_g^7}$$

$$\delta = \frac{5t^2\mu_{CT}^5V(V^2 - 3t^2)}{E_g^9}$$

where $E_g = (V^2 + 4t^2)^{1/2} = hc/\lambda_{max}$ is the energy gap. To a first approximation, molecules of a given length and bridge type can be taken to have the same t and μ_{CT} , thus the polarizabilities vary with structure due to the variation in E_g and V . In Figure 3 are shown plots of the calculated dependencies for α , β and γ as a function of V . These dependencies are in agreement with those calculated with the AM-1 and INDO methods. Since E_g is at a minimum (i.e. $E_g = 2t$) when $V_0 = 0$, which is where $BLA = 0$, we can see readily that α is peaked, β is zero and γ is at a negative extreme. The value of β reaches extremes when $V = \pm t$, and thus $E_g = \sqrt{5}t$, which is also where $\gamma = 0$. The value of γ reaches maxima when $V = \pm \sqrt{3}t$, whereupon $E_g = \sqrt{7}t$.

In Figure 4 we compare the $\mu\beta$ values recently measured² for a series of polyenes that span nearly the full range of BLA . Since we lack experimental solution phase values of BLA , we plot the results as a function of λ_{max} to allow a global comparison. The theoretically calculated curves used a value of $t = 1.18$ eV, as estimated from the energy gap of a seven carbon cyanine. Because of possible differences in the effective conjugation lengths of these molecules, a global comparison may not be valid however, the calculated $\mu\beta$ curve gives a reasonable description of the observed dependence for the whole series. The differences between members of the series are more evident in the plot of γ vs. λ_{max} , as shown in Figure 5. Whereas the results for the aldehyde and dicyanovinyl substituted polyenes are relatively well described, the results for the barbituric acid and thiobarbituric acid acceptors appear to lie on different members of a family of curves, consistent with a slightly longer effective conjugation length. The contribution of excited states other than CT, such as those involving excitations of the bridge, to the functional behavior of γ may also be a factor leading to the different behaviors observed. The treatment of such states has been described recently,⁷ and its inclusion with the present VB-CT model is being investigated.

We have described a simple model for the hyperpolarizabilities of conjugated donor-acceptor molecules, that provides a clear physical picture for the relationship between the bond length alternation and the polarizabilities in terms of the energetics and interaction of neutral and charge transfer valence bond states. The

model is able to provide a reasonable global description of the hyperpolarizabilities of a range of molecules in different solvent environments by using a small set of parameters, that can be obtained from experiments.

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References

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Figures

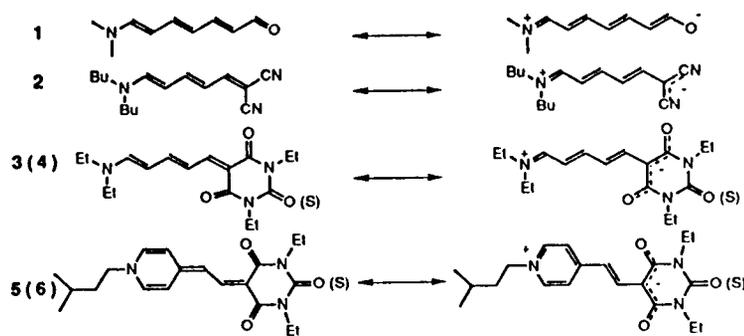


Figure 1. Resonance structures of molecules examined by solvent dependent EFISH and THG studies.

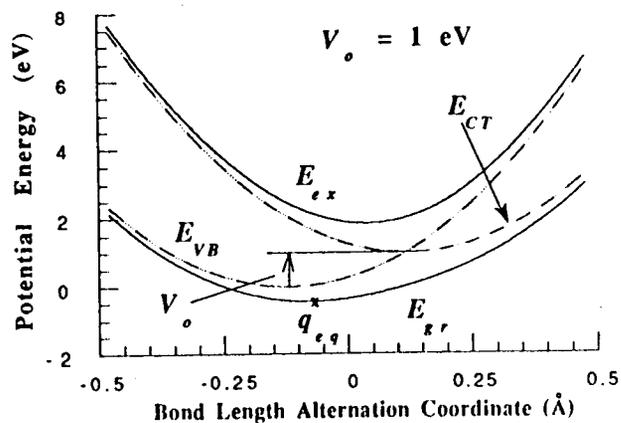


Figure 2. Potential energy surfaces for zero-order neutral and charge transfer states and ground and excited eigenstates.

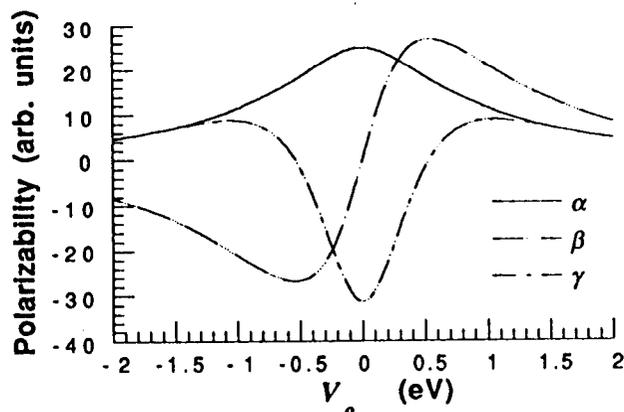


Figure 3. Plots of the linear polarizability, α , and the hyperpolarizabilities β and γ , as a function of the adiabatic energy difference of the zero-order neutral and charge transfer states, for a donor-acceptor polyene with nine conjugated atoms.

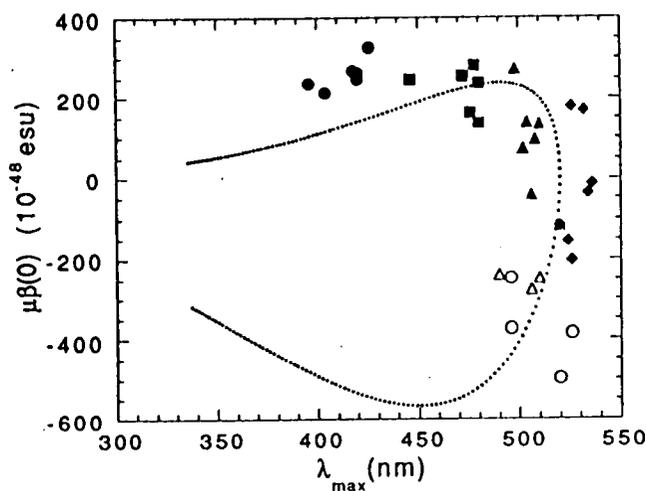


Figure 4. Comparison of the experimental dependence of $\mu\beta$ vs. λ_{max} measured for 1 (filled circles), 2 (filled squares), 3 (filled triangles), 4 (open triangles), 5 (filled diamonds), and 6 (open circles) with that calculated using the VB-CT model.

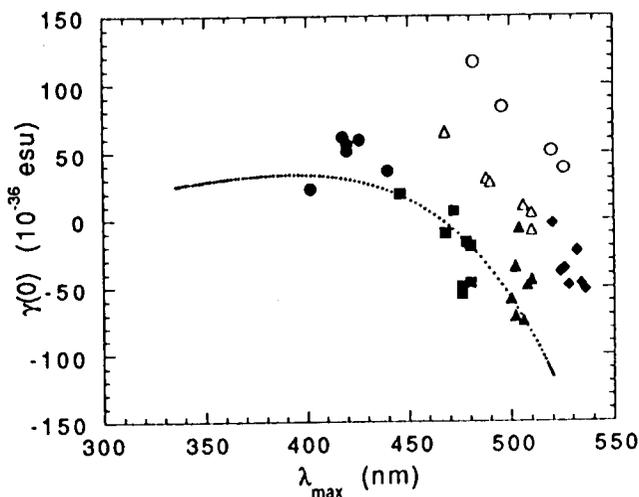


Figure 5. Comparison of the experimental dependence of γ vs. λ_{max} with that calculated using the VB-CT model, symbols as in Figure 4. The experimental χ (THG) values were extrapolated to $\chi(0)$ values using a two-state dispersion correction.