

## OPTIMIZATION OF THE FIRST AND SECOND HYPERPOLARIZABILITIES OF ORGANIC DYES

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We have been attempting, to correlate hyperpolarizabilities with bond-length alternation (BLA), which is defined as the difference in the average length between adjacent carbon-carbon bonds in a polymethine  $(\text{CH})_n$  chain. (1, 2) Polyenes have alternating double and single bonds (bond length equal to 1.34 Å and 1.45 Å, respectively), and thus show a high degree of bond-length alternation (BLA = -0.11 Å). In donor-acceptor polyenes, this parameter is related to the degree of ground-state polarization in the molecule. To better understand this correlation, it is illustrative to discuss the wave function of the ground state in terms of a linear combination of the two limiting charge-transfer resonance structures. For substituted polyenes with weak donors and acceptors, the neutral resonance form dominates the ground-state wavefunction, and the molecule has a high degree of (conventionally negative) bond-length alternation. With stronger donors and acceptors, the contribution to the ground state, of the charge-separated resonance form increases and simultaneously, BLA decreases in absolute value. When the two resonance structures contribute equally, as in a symmetrical cyanine, the molecule exhibits essentially no bond-length alternation. Finally, if the charge-separated form dominates the ground-state wave function, the molecule acquires a positive bond-length alternation. Neutral molecules with aromatic rings have a diminished contribution of the charge-separated form to the ground-state wave function, due to the energetic price associated with the loss of aromaticity in that form. (3) As a result, push-pull molecules with aromatic ground states tend to be more bond-length alternated for a given donor and acceptor pair than for a polyene of comparable length.

Bond-length alternation is thus a measurable parameter that is related to the *mixing* of the two charge-transfer resonance forms in the actual ground state of the molecule. Note that for molecules with aromatic rings, the neutral form exhibits minimal bond-length alternation, whereas at the charge-separated form corresponds significant bond-length alternation. Thus, to