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# THE RELATIONSHIP BETWEEN SECOND-ORDER NONLINEAR OPTICAL PROPERTIES AND GROUND-STATE POLARIZATION


Grant Bourhill,[a] Lap-Tak Cheng,[b] Ging Lee,[c] Seth R. Marder,[a,c] Joseph W. Perry,[a] Matthew J. Perry[c] and Bruce G. Tiemann[a,c]

a: Jet Propulsion laboratory, 67-201, California Institute of Technology, Pasadena, CA 91109.

b: *Central* Research and Development, Science and Engineering 1 laboratories, E. I. Du Pent de Nemours & Co. (Inc.), Experimental Station, P. O. Box 80356, Wilmington, DE 19880.

c: The Beckman institute, 139-74, California Institute of Technology, Pasadena, CA 91125.



## ABSTRACT

A review is presented describing our recent work to correlate the first hyperpolarizability, β, of organic materials with the molecular parameter bond length alternation (BLA). Donor-acceptor polyenes displaying a wide BLA range were synthesized. For a particular chromophore, BLA was fine-tuned *by* varying solvent polarity. The degree of BLA was analyzed by X-ray diffraction, $^1$H-NMR and electronic absorption spectroscopy. Non-resonant, solvent-dependent, electric field induced second harmonic generation (EFISH) measurements were performed to probe the variation in the second-order nonlinearity as a function of ground-state polarization. The resulting trend, which is fully consistent With theoretical predictions, identified chromophores possessing optimized positive *and* negative hyperpolarizabilities. An optimized chromophore was incorporated in a polymer matrix and poled. The resulting electro-optic coefficient was found to be significantly enhanced relative to the longer chromophore Disperse Reel 1.


## Introduction

Optimizing the first hyperpolarizability, β, of donor-acceptor compounds requires a specific donor/acceptor strength for a given conjugated bridge [1,2]. For donor-acceptor polyenes, β can be maximized when an optimal degree of mixing between neutral and charge-separated canonical resonance forms exists. This degree of mixing is related to the donor/acceptor strength and a molecular parameter, bond length alternation (BLA), defined as the difference between the average carbon-carbon single ant] double bond lengths in the polymethine backbone. The degree of BLA arises from the linear combination, or mixing, of the two-limiting charge-transfer resonance forms of the molecule, Figure 1, [3,4].

For unsubstituted polyenes, or chromophores with weak donors/acceptors, the neutral canonical form is the dominant contributor to the ground state (A, Figure 1), resulting in large positive BLA [3]. As the acceptor strength increases (B), the charge-separated resonance structure contributes more to the ground state resulting in smaller BLA [3] until both resonance forms contribute equally (C) and the ground-state structure possesses essentially zero BLA analogous to a symmetrical cyanine [5]. increasing the ground-state polarization further (D) results in the charge-separated canonical form dominating the ground state, leading to negative BLA [6].

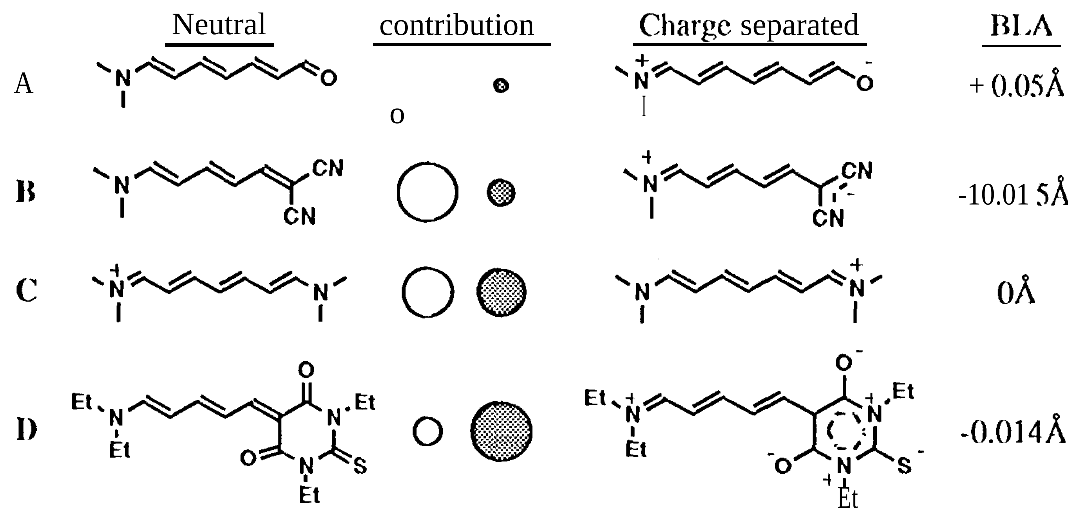


Figure 1. contribution of neutral and charge-separated resonance forms to the ground state. BLA values, tuned by varying donor/acceptor strengths, were determined by X-my diffraction [3, 5, 6].

The relationship between β and BLA can be understood within the context of a two-state model [7] in which the dominant component of the β tensor is given as:

$$\beta \propto (\mu_{ee} - \mu_{gg}) \frac{\mu_{ge}^2}{E_{ge}^2} \qquad (1)$$

where $g\,(e)$ is the index of the ground (charge-transfer excited) state, $\mu$ and $E$ are the dipole matrix element and transition energy between two subscripted states, respectively. It has been predicted [1,8] that as a function of increasing polarization (decreasing BLA), starting from the polyene limit (maximum positive BLA): (i) $\mu_{ee} - \mu_{gg}$, starts positive, increases and reaches a positive peak (region A, Figure 2); (ii) decreases, (region B); (iii) continues to decrease, passing through zero at the cyanine-limit, becomes negative (region C); (iv) becomes increasingly negative (region D) and (v) exhibits a negative peak and decreases in magnitude (region E). It is also predicted that $\mu_{ge}^2$ and $1/E_{ge}^2$ peak at the cyanine-limit (Figure 2) and thus β, which is a product of these three terms, exhibits positive and negative peaks closer to the cyanine-limit than where $(\mu_{ee} - \mu_{gg})$ peaks. The molecular second-order nonlinear optical properties of a series of donor-acceptor polyenes have been evaluated by EFISH to test the structure-property relationships proposed in Figure 2.

Molecules **1-6** (Figure 3) were examined since strong evidence exists that they cover approximately the BLA range **A-E** (Figure 2.) [9]. For example, BLA values for **1** and 2, determined by X-ray crystallography, are 0.05 Å and 0,015 Å respectively, suggesting that **1** lies in region A and 2 in region **B**. X-ray crystallographic studies on 4, possessing a stronger acceptor than 1 or 2, reveal a BLA of -0.014 Å, suggesting that 4 lies in region **C**. Additionally, **3** and 4 exhibit positive solvatochromism in nonpolar solvents and negative solvatochromism in polar solvents (Table 1), indicative of BLA changing sign as a function of solvent polarity [11]. These data suggest that **3** and 4 fall in region **C**. Compounds **5** and 6 arc negatively solvatochromic in all solvents used. Furthermore, the large $^1$H-$^1$H coupling constant across the central carbon-carbon bond is consistent with a trans double bond as depicted in the zwitterionic form of **5** and 6 (Figure 3, right). These data imply that **5** falls in region 1) and that 6 falls in 1) in moderate polarity solvents possibly region E in highly polar solvents. For a given molecule, BLA can be fine-tuned by varying solvent polarit y since mixing of the neutral and charge-separated canonical forms is sensitive to this perturbation [3,4,11]. For example, the progression of 5 and 6 towards a more charge-separated structure with increasing solvent polarity is evidenced by the increase in the. 1,1-] H coupling constant across the central carbon-carbon bond (Figure 4).

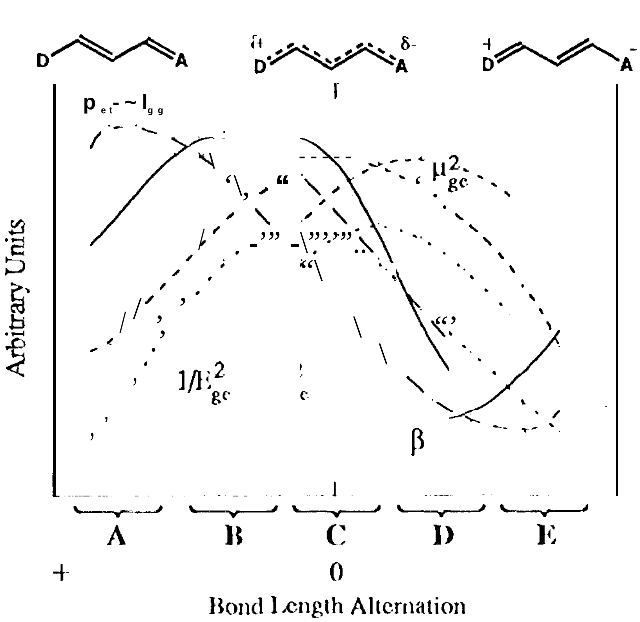


Figure 2. Dependence of the ground-state structure on $\mu_{ge}^2$ (- - -), $1/E_{ge}^2$ (····), $\mu_{ee}$ - $\mu_{gg}$ (- -) and β (—) [1,8]. Ground-state polarization increases from A-E. The point where ($\mu_{ee}$ - $\mu_{gg}$) and β are zero corresponds to the "cyanine-limit" of zero BLA (center of **C**).

Non-resonant EFISH measurements of μ·β were performed, at 1907 nm, on **1**-**6** in solvents of varying polarity using apparatus and methodology described elsewhere [12]. The μ·β product and absorption maxima as a function of the normalized solvent polarity parameter $E_T(30)$ are presented in Table 1 [9]. The μ·β product of 1 increases with solvent polarity, consistent with the trend expected given the large BLA from previous structure determinations [3]. The stronger dicyano moiety (2) increases the contribution of the charge-separated canonical form to the ground state, BLA decreases and μ·β exhibits a positive peak (region **B**, Figure 2). A positive peak in μ·β has been reported previously [1]. increasing the acceptor strength further by utilizing the diethylbarbituric (3) and diethylthiobarbituric acid (4) moieties, results in decreasing hyperpolarizabilities with increasing solvent polarity. in fact, for **3** in the most polar solvent and 4 in nonpolar solvents μ·β *changes sign*, consistent with the structural assignment of **3** and 4 being in region **C**, as a result of solvent stabilization of the charge-separated canonical form tuning BLA through the cyanine-limit [11]. The values of $\lambda_{max}$ for 4 arc. maximized when μ·β is close to zero, consistent with the relationship depicted in Figure 2.. As the donor/acceptor strength is further increased (5 and 6), a negative peak in μ·β, with increasing solvent polarity, is observed consistent with the predicted behavior for region 1).

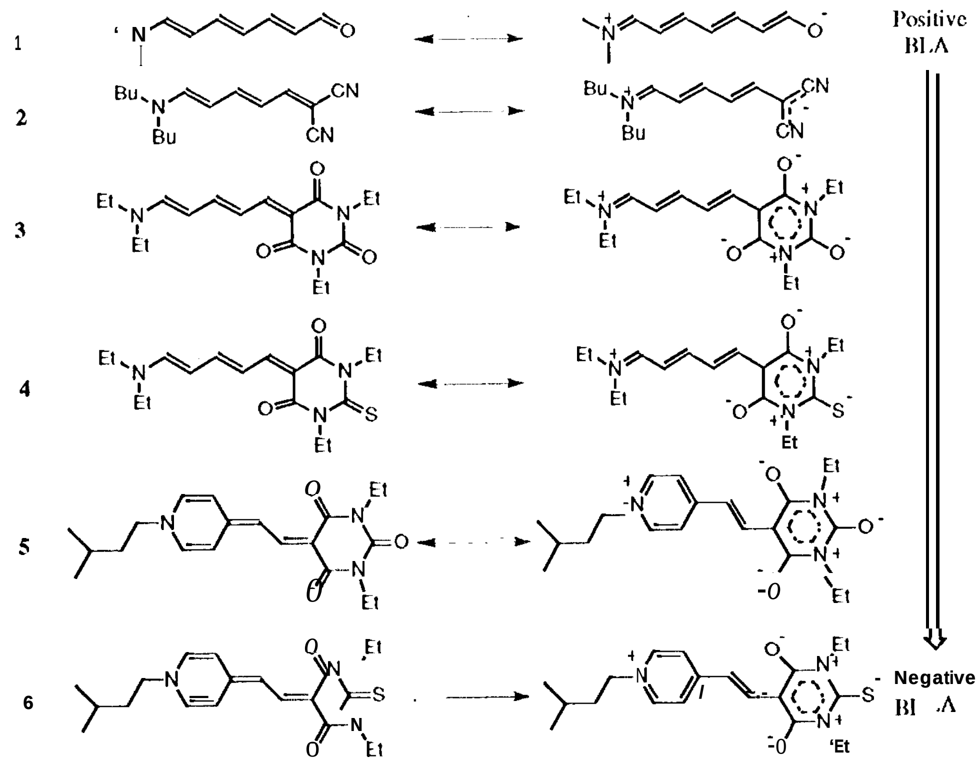

Figure 3. Canonical charge-transfer resonance structures for the donor-acceptor polyenes investigated. Electron donor/acceptor strength in the neutral form increases from 1-6. Et ≡ C2115 and Bu ≡ n-C4119.

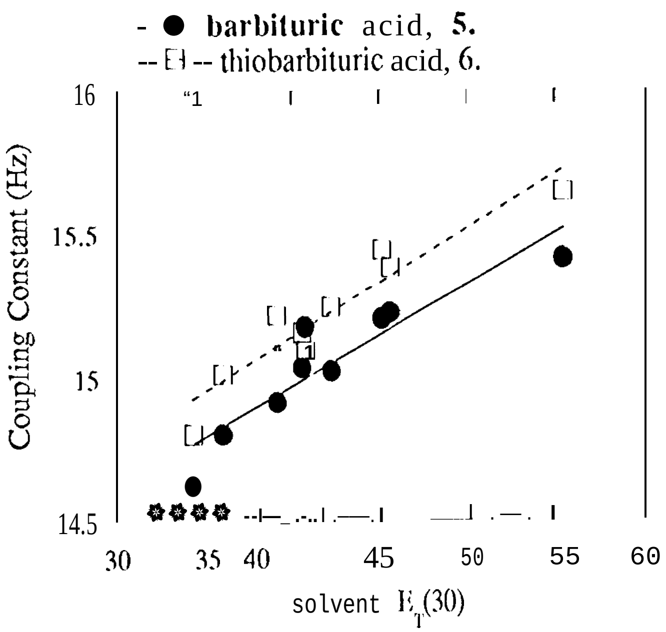


Figure 4. 1 }]-]}] coupling constants for 5 and 6 as a function of solvent polarity [ 1 ()]. The trend of increasing coupling constant with increasing solvent polarity is indicative of an evolution rewards a more charge-separated ground state (Figure 3, right).

“J’able 1. Solvent-dependent $\mu\cdot\beta$ (units of 1(1-48 esu) for 1-6. The estimated precision in $\mu\cdot\beta$ is ±10%. ‘] ’he polarity of the solvents increase (the contribution of the charge-separated resonance structure to the ground-state geomet ry increases) from left to right. Normali zed $E_T(30)$ values of the solvents [10] are presented within parentheses. “l’he maximum absorption wavelength ($\lambda$max, units of nm) of the chromophores are given below the $\mu\cdot\beta$ values. insolubility precluded the determination of $\mu\cdot\beta$ for **5** and 6 in certain solvents.

| | | Solvent | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Molecule | | $CCl_4$ (**0.0525**) | $C_6H_6$ (0.1111) | $CHCl_3$ (0.2593) | c112C12 (().3086) | $CH_3CN$ (().456()) | $CH_3NO_2$ (0.481s) | Region |
| **1** | $\mu\cdot\beta$ | **299** | 272 | 322 | **343** | **348** | 430 | A |
| | $\lambda$max | 396 | 404 | 420 | 420 | 418 | 426 | |
| **2** | $\mu\cdot\beta$ | **332** | 360 | ’400 | 340 | 231 | **195** | **B** |
| | $\lambda$max | 446 | 472 | 478 | 480 | 476 | 480 | |
| **3** | $\mu\cdot\beta$ | **401** | 205 | 200 | **141** | 109 | .6S | **C** |
| | $\lambda$max | 498 | 504 | 510 | 508 | 502 | 506 | |
| **4** | $\mu\cdot\beta$ | **276** | 264 | -22 | -60 | -240 | **-316** | **C** |
| | $\lambda$max | 526 | 532 | 536 | 534 | 524 | 526 | |
| **5** | $\mu\cdot\beta$ | - | **-180** | -374 | -414 | - | -350 | 1) |
| | $\lambda$max | 528 | 520 | 510 | 506 | 488 | 490 | |
| **6** | $\mu\cdot\beta$ | - | - | **-600** | **-770** | **-550** | **-363** | **D/E** |
| | $\lambda$max | 548 | 538 | 526 | 520 | 496 | 496 | |

Electro-optic measurements

The electro-optic coefficient, $r_{33}$, of the optimized $\mu\cdot\beta$ chromophore, 2, was measured at 820 nm using the thin-film ellipsometric technique [13]. The electro-optic coefficient is presented in Table II along with the value for the conventional chromophore Disperse Red 1 (DR1) for comparison. Despite DR1 being 4 atoms longer, its electro-optic coefficient is significantly less than that of the optimized chromophore. This comparison underscores the benefit of the proposed structure-property relationship in realizing chromophores possessing enhanced nonlinearities.

Table 11. Electro-optic coefficients, conjugation lengths and maximum absorption wavelengths for DR1 and 2 in PMMA, both samples having identical chromophore loading (2 mole %) and poling condit ions (108 V/m at 120°C). Sample preparat ion details arc reported elsewhere [14].

| Molecule | Length | $\lambda_{max}$ | $r_{33}$ |
|---|---|---|---|
| DR1 | 13 atoms | 487 nm | 1.0 pmV$^{-1}$ |
| **2** | 9 atoms | 480 nm | 2.5 pmV$^{-1}$ |

In summary, donor-acceptor polyenes of comparable conjugation length have been synthesized and their solvent-dependent, non-resonant hyperpolarizabi lities measured. Optimization in a positive *and* negative sense, as well as a sign change in $\mu\cdot\beta$, was observed. These observations were explained by molecular structure changes resulting from the variation of mixing of neutral and charge-separated resonance forms upon changing donor/acceptor strengths and solvent polarity. The trend of these geometry-dependent hyperpolarizabilities was fully consistent with theoretical predictions. An optimized $\mu \cdot \beta$ chromophore was incorporated in a polymer host, poled and the resulting electro-optic coefficient measured. The optimized molecule exhibited an enhanced response compared to the longer, conventional chromophore DR 1.


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