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Experimental Demonstration of the Dependence of the First **Hyperpolarizability** of
Donor-Acceptor Substituted **Polyenes** on the Ground-State Polarization and
Bond Length Alternation

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ABSTRACT.

The dependence of the product of the first hyperpolarizability, β , and the ground-state dipole moment, μ , for a series of donor-acceptor **polyenes** with a large range of ground-state polarization, was measured in a variety of solvents by electric field induced second harmonic generation. The observed behavior of $\mu\beta$ as a function of ground-state polarization agrees well with theoretical predictions. In particular, as a function of increasing polarization, $\mu\beta$ was found to first increase, peak in a positive sense, decrease, pass through zero, become large and negative and eventually peak in a negative sense.

It has been suggested that optimizing the first hyperpolarizability, β , of donor-acceptor compounds requires a specific donor/acceptor strength for a given conjugated bridge.¹⁻³ For donor-acceptor **polyenes**, β can be maximized when an optimal degree of mixing between neutral and charge-separated canonical resonance forms exists.^{2,4} 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 and 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).⁴ For **unsubstituted polyenes**, or chromophores with weak donors/acceptors, the neutral canonical form is the dominant contributor to the ground state, resulting in large positive BLA. As the donor/acceptor strength increases, the charge-separated resonance structure contributes more to the ground state resulting in smaller BLA until both resonance forms contribute equally and the ground-state structure possesses essentially zero BLA analogous to a symmetrical **cyanine**.⁵ Increasing the ground-state polarization further results in the charge-separated canonical form dominating the ground-state structure, leading to negative BLA.

The relationship between β and BLA can be understood within the context of a two-state model⁶ in which the dominant component of the β tensor is given as:

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

where g (e) is the index of the ground (charge-transfer excited) state, μ and E are the dipole matrix element and transition energy between two subscripted states, respectively. It has been predicted^{1,7} 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 μ_{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. In this paper, molecular second-order nonlinear optical properties of a series of donor-acceptor polyenes have been evaluated by electric field induced second harmonic generation (EFISH) to test the structure-property relationships proposed in Figure 2.

Molecules 1-6 (Figure 1), synthesized using literature procedures,^{4,8-10} were examined since strong evidence exists that they cover approximately the BLA range A-E (Figure 2). For example, BLA values for **1** and **2**, determined by X-ray crystallography, are 0.05 Å and <0.02 Å respectively, suggesting that **1** lies in region A and **2** in region B.¹¹ X-ray crystallographic studies¹² 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 I), indicative of BLA changing sign as a function of solvent polarity.¹⁰ These data suggest that **3** and **4** fall in region C. Compounds **5** and **6** are negatively solvatochromic in all solvents used. Furthermore, the large $^1\text{H} - ^1\text{H}$ coupling constant (14.91 and 15.21 Hz for **5** and **6**, respectively, in CDCl_3) across the central carbon-carbon bond is consistent with a trans double bond as depicted in the zwitterionic form of **5** and **6** (Figure 1 right). These data imply that **5** falls in region D and that **6** falls in D in moderate polarity solvents and possibly region E in highly polar solvents. For a given molecule, BLA can be fine-tuned by varying solvent polarity since mixing of the neutral and charge-separated canonical forms is sensitive to this perturbation.^{10,11,14,15}

Non-resonant EFISH measurements of $\mu \cdot \beta$ were performed, at 1907 nm, on 1-6 in solvents of varying polarity using an apparatus and methodology described elsewhere.¹⁶ The $\mu \cdot \beta$ product and absorption maxima as a function of the normalized solvent polarity parameter $E_T(30)$ ³ are presented in Table I. The $\mu \cdot \beta$ product of **1** increases with solvent polarity, consistent with the hyperpolarizability trend expected given the large BLA from previous structure determinations.¹¹ The strength of the donor/acceptor pair is insufficient therefore to obtain the particular ground-state polarization or BLA required to optimize β in a positive sense. When the stronger dicyano moiety (**2**) replaces the aldehyde

acceptor, the contribution of the charge-separated canonical form to the ground state increases, BLA decreases and $\mu\cdot\beta$ exhibits a positive peak (region B of Figure 2). A positive peak in $\mu\cdot\beta$ has been reported previously for dimethylindoaniline.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 $\mu\cdot\beta$ *changes sign*, consistent with the structural assignment above of 3 and 4 being in region C. This sign change occurs as a result of solvent stabilization of the charge-separated canonical form tuning BLA through the **cyanine-limit**.¹⁰ This is the first observation of a sign change in $\mu\cdot\beta$ as a function of changing an external property, without tuning through a resonance. The values of λ_{max} for 4 are maximized when $\mu\cdot\beta$ 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 $\mu\cdot\beta$, with increasing solvent polarity, is observed consistent with the predicted behavior for region D. While there have been reports of negative $\mu\cdot\beta$ values¹⁷ and solvent-dependent negative $\mu\cdot\beta$ values,¹⁵ this is the first report of the *optimization* of $\mu\cdot\beta$ in a negative sense.

In summary, donor-acceptor **polyenes** of comparable conjugation length have been synthesized and their solvent-dependent, non-resonant hyperpolarizabilities probed by EFISH. Optimization in both a positive and negative sense as well as a sign change of $\mu\cdot\beta$ 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 the donor/acceptor strengths and solvent polarity. The trend of these geometry-dependent hyperpolarizabilities is fully consistent with the trend theoretically predicted.

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Supplementary Material:

¹H nuclear magnetic resonance spectroscopic and elemental analytical data for 3-6 and X-ray crystallographic data for 4 (40 pages). Ordering information is given on any current masthead page.

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Figure captions

Figure 1. Canonical charge-transfer resonance structures for the donor-acceptor **polyenes** investigated. Electron donor/acceptor strength in the neutral form increases from **1-6**. Et= C₂H₅ and Bu \equiv *n*-C₄H₉.

Figure 2. The dependence of the ground-state structure on μ_{ge}^2 (- - -), $1/E_{ge}^2$ (····), $\mu_{ee} - \mu_{gg}$ (— — —) and β (—) in arbitrary units for (CH₃)₂N-(CH=CH)₄-CHO. Ground-state polarization increases from regions A-E. The point at which both $(\mu_{ee} - \mu_{gg})$ and β are zero corresponds to the "cyanine-limit" of zero BLA (center of region C).

Table I. Solvent-dependent $\mu \cdot \beta$ (units of 10^{-48} esu) for molecules 1-6 (given *in* boldface). The estimated precision in the $\mu \cdot \beta$ values is $\pm 10\%$. The polarity of the solvents increase (the contribution of the charge-separated resonance structure to the ground-state geometry increases) from left to right. The normalized $E_T(30)^{13}$ values of the solvents are presented within parenthesis. The wavelength of maximum absorption (λ_{\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.

Molecule	Solvent						Region
	CCl ₄ (0.0525)	C ₆ H ₆ (0.1111)	CHCl ₃ (0.2593)	CH ₂ Cl ₂ (0.3086)	CH ₃ CN (0.4560)	CH ₃ NO ₂ (0.4815)	
1 $\mu \cdot \beta$	299	272	322	343	348	430	A
λ_{\max}	396	404	420	420	418	426	
2 $\mu \cdot \beta$	332	360	400	340	231	195	B
λ_{\max}	446	472	478	480	476	480	
3 $\mu \cdot \beta$	401	205	200	141	109	-65	C
λ_{\max}	498	504	510	508	502	506	
4 $\mu \cdot \beta$	276	264	-22	-60	-240	-316	C
λ_{\max}	526	532	536	534	524	526	
5 $\mu \cdot \beta$.	-180	-374	-414	.	-350	D
λ_{\max}	528	520	510	506	488	490	
6 $\mu \cdot \beta$.	.	-600	-770	-550	-363	D/E
λ_{\max}	548	538	526	520	496	496	

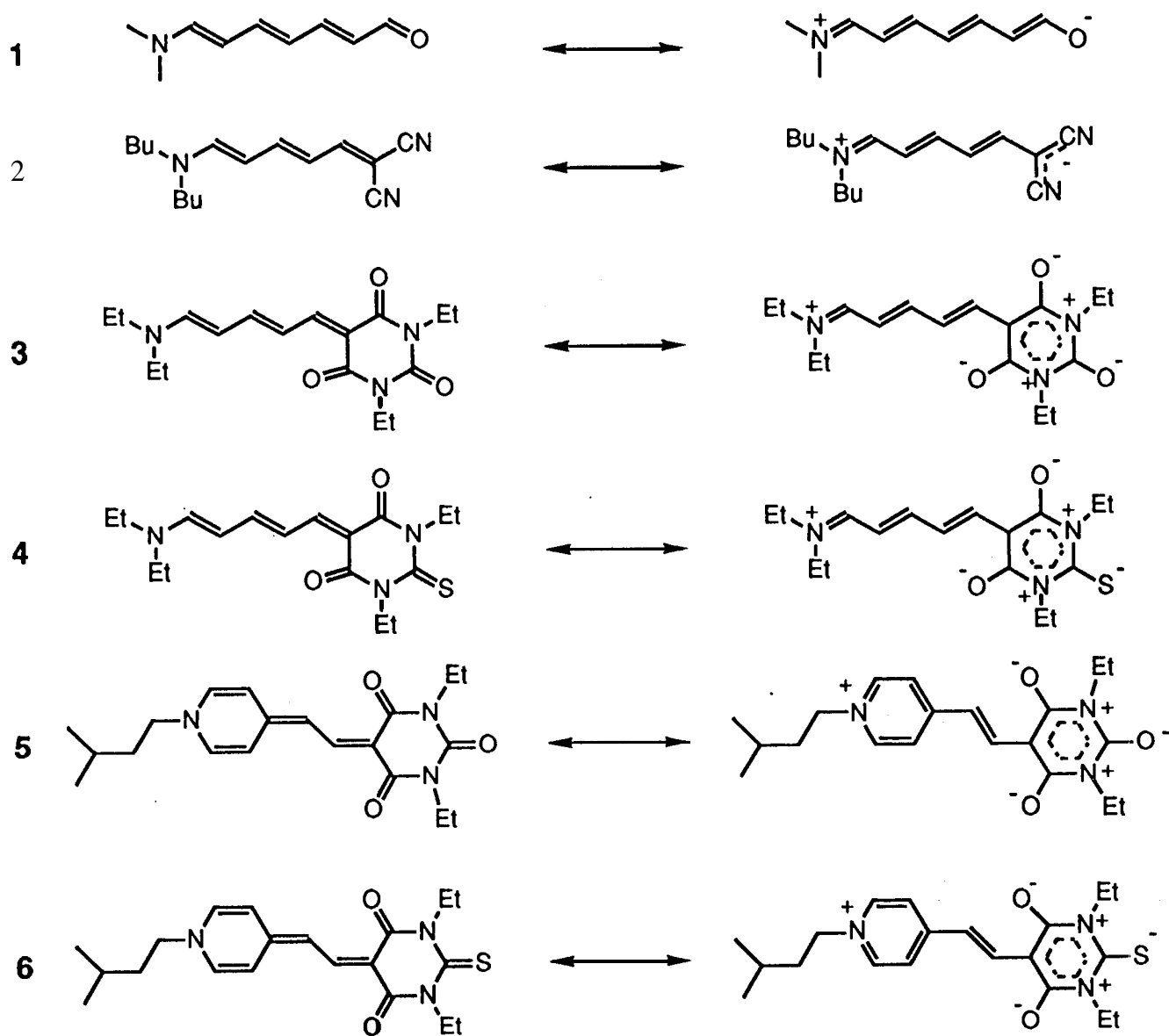


Figure 1: Bourhill et al.

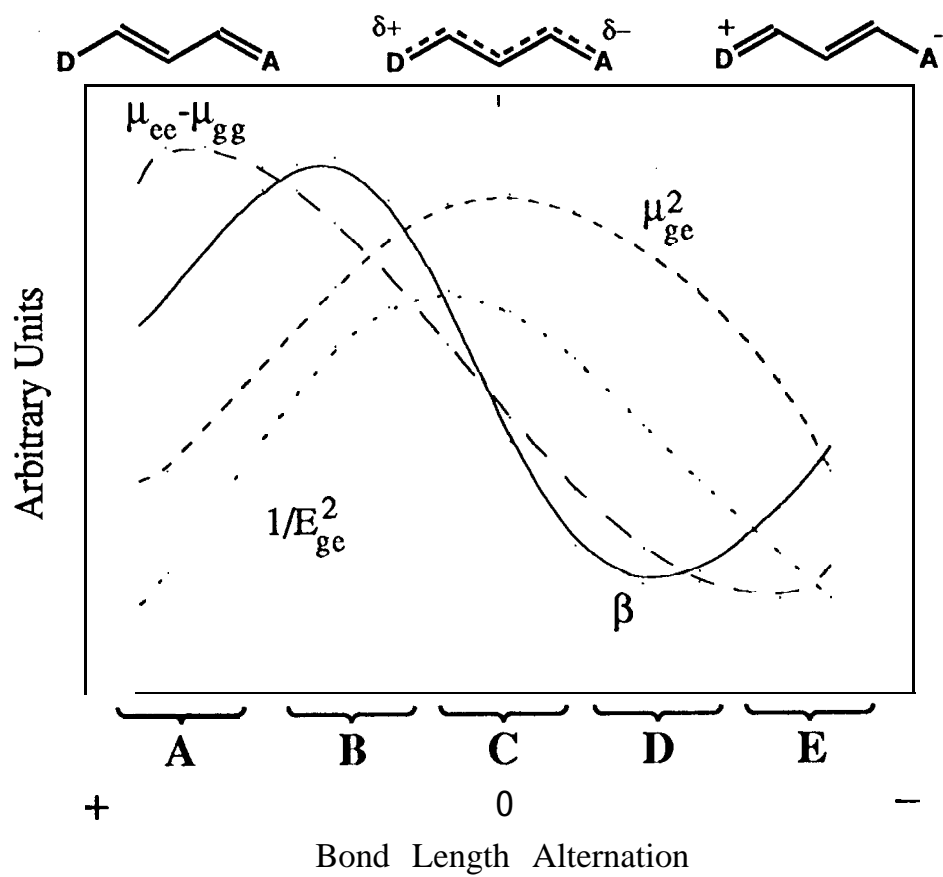


Figure 2: Bourhill et al.