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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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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 model[6] in which the dominant component of the β tensor is given as:

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

where $g(e)$ is the index of the ground (charge-transfer excited) state and 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, and 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.

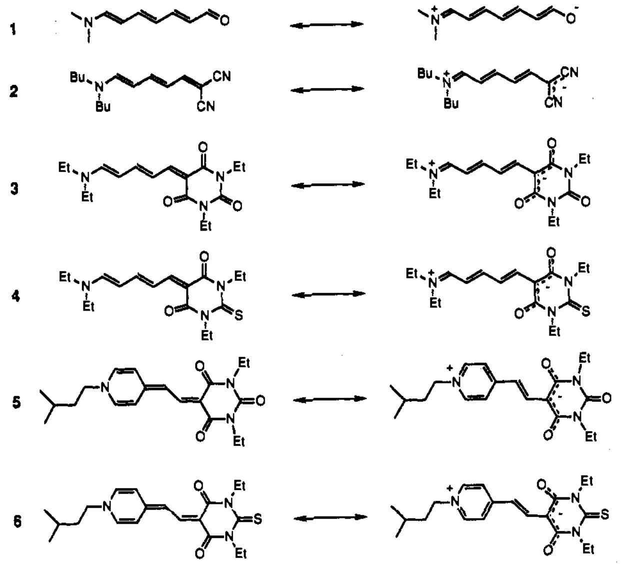

Figure 1. Canonical charge-transfer resonance structures for the donor–acceptor polyenes investigated. Et ≡ C_2H_5 and Bu ≡ n-C_4H_9.

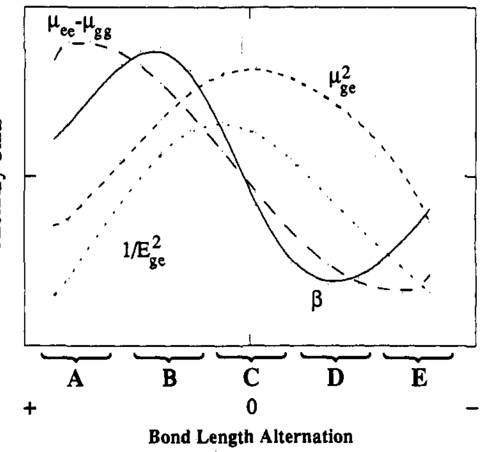

Figure 2. Dependence of μ_{ge}^2 (- - -), $1/E_{ge}^2$ (···), $\mu_{ee} - \mu_{gg}$ (— — —), and β (—) on the ground-state structure for $(CH_3)_2N$-$(CH{=}CH)_4$-CHO.

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

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Table 1. Solvent-Dependent $\mu\cdot\beta(0)$ (units of 10^{-48} esu) Values for Molecules **1–6** (given in boldface) and the Corresponding Wavelengths of Maximum Absorption (λ_{max}, units of nm) of the Chromophores[a]

		Solvent						
molecule		CCl_4 (0.0525)	C_6H_6 (0.1111)	$CHCl_3$ (0,2593)	CH_2Cl_2 (0.3086)	CH_3CN (0.4560)	CH_3NO_2 (0.4815)	region
1	$\mu\cdot\beta(0)$	**236**	**213**	**247**	**263**	**268**	**327**	A
	λ_{max}	396	404	420	420	418	426	
2	$\mu\cdot\beta(0)$	**245**	**255**	**281**	**238**	**162**	**136**	B
	λ_{max}	446	472	478	480	476	480	
3	$\mu\cdot\beta(0)$	**272**	**137**	**133**	**94**	**73**	**–43**	B/C
	λ_{max}	498	504	510	508	502	506	
4	$\mu\cdot\beta(0)$	**177**	**168**	**–14**	**–38**	**–155**	**–203**	C
	λ_{max}	526	532	536	534	524	526	
5	$\mu\cdot\beta(0)$		**–117**	**–248**	**–276**		**–240**	C/D
	λ_{max}	528	520	510	506	488	490	
6	$\mu\cdot\beta(0)$			**–386**	**–500**	**–374**	**–247**	D/E
	λ_{max}	548	538	526	520	496	496	

[a] The estimated precision in the $\mu\cdot\beta(0)$ values is ±15%. The polarities of the solvents increase from left to right. The normalized $E_T(30)$[13] values of the solvents are presented within parentheses. The $\mu\cdot\beta(0)$ values were calculated assuming that the contribution to the EFISH signal from the third-order polarizability, γ, is negligible. However, no change in the $\mu\cdot\beta(0)$ trends from those reported here is observed when the γ contribution is included.

example, BLA values for **1** and **2**, determined by X-ray crystallography, are 0.05 and <0.02 Å, respectively, suggesting that **1** lies in region A and **2** in region B.[11] X-ray crystallographic studies[12] 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.[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 ^1H–^1H 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]

Nonresonant 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 $\mu\cdot\beta(0)$ product and absorption maxima as a function of the normalized solvent polarity parameter $E_T(30)$[13] are presented in Table 1 (the dispersion-corrected $\mu\cdot\beta(0)$ values were obtained using the standard two-level correction[6]). In the discussion below, it is important to note that the key comparisons are not among the absolute magnitudes of the $\mu\cdot\beta(0)$ values for the different compounds but rather how the values for each compound change in the different solvents. It is this behavior that allows us to map out the *shape* of the $\mu\cdot\beta(0)$ curve. The $\mu\cdot\beta(0)$ 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 $\beta(0)$ 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 $\mu\cdot\beta(0)$ exhibits a positive peak (region B of Figure 2). Increasing the acceptor strength further by utilizing the diethylbarbituric (**3**) and diethylthiobarbituric acid (**4**) moieties results in decreasing $\mu\cdot\beta(0)$ product with increasing solvent polarity. In fact, for **3** in the most polar solvent and **4** in nonpolar solvents $\mu\cdot\beta(0)$ *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] The values of λ_{max} for **4** are maximized when $\mu\cdot\beta(0)$ 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 $\mu\cdot\beta(0)$, with increasing solvent polarity, is observed, consistent with the predicted behavior for region D. While there have been reports of negative $\mu\cdot\beta(0)$ values[17] and solvent-dependent negative $\mu\cdot\beta(0)$ values,[15] this is the first report of the *optimization* of $\mu\cdot\beta(0)$ in a negative sense. Optimization of $\mu\cdot\beta(0)$ in either a positive or a negative sense is of interest for poled polymer applications where the macroscopic nonlinearity scales with this product.

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Supplementary Material Available: ^1H nuclear magnetic resonance spectroscopic and elemental analytical data for **3–6** and X-ray crystallographic data for **4** (26 pages); listing of observed and calculated structure factors (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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