

# Experimental demonstration of the relationship between the second- and third-order polarizabilities of conjugated donor-acceptor molecules

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## ABSTRACT

The dependence of the second- and third-order polarizabilities ( $\beta$  and  $\gamma$ ) on ground-state polarization was measured for a series of donor-acceptor polyenes using electric field induced second harmonic generation and third harmonic generation, respectively. The changes in ground-state polarization, associated with the donor/acceptor strength or solvent polarity, were probed by x-ray crystallography, <sup>1</sup>H-NMR, electronic absorption and Raman spectroscopies. The observed behavior of  $\beta$  and  $\gamma$  as a function of ground-state polarization agrees well with theoretical predictions. In particular, positive and negative peaks, as well as sign changes, were observed for both  $\beta$  and  $\gamma$ . The dependences for  $\beta$  and  $\gamma$  are consistent with a derivative relationship between them. In addition, the third-order polarizability of a series of molecules possessing zero bond length alternation was found to be negative, in agreement with predictions based on the relationship between the polarizabilities and ground-state geometry.

## 2. INTRODUCTION

Recent studies<sup>1,2</sup> have suggested that optimizing the polarizabilities of donor-acceptor polyenes requires a specific degree of mixing between neutral and charge-separated resonance structures. The degree of mixing is related to the donor/acceptor strength and can be correlated with the ground-state polarization (i.e. the dipole moment) and a molecular parameter, bond length alternation (BLA), defined as the difference between the average single and double carbon-carbon bond lengths in the polymethine chain. Figure 1 illustrates how chemical modifications can systematically tune the bond length alternation by varying the degree of mixing between neutral and charge-separated structures. For unsubstituted polyenes, or chromophores with weak donors/acceptors, **A**, the ground-state structure resembles that of the neutral resonance form resulting in large positive BLA.<sup>3</sup> Increasing the mixing between the two limiting resonance forms by utilizing the stronger dicyanovinyl acceptor, **B**, results in increased ground-state polarization and smaller BLA.<sup>3</sup> Complete mixing of the limiting resonance forms results in essentially zero BLA, as for symmetrical cyanines, **C**.<sup>4</sup> In neutral donor/acceptor systems, increasing the donor and/or acceptor strength further, **D**, results in the charge-separated resonance form being the dominant contributor to the ground state, resulting in negative BLA.<sup>5</sup>

For a particular chromophore, the degree of BLA can be fine-tuned by utilizing solvents of varying polarity since the degree of mixing between neutral and charge-separated resonance structures is known to be sensitive to this perturbation.<sup>3,6,7</sup> Since polar solvents can stabilize the charge-separated structure to a larger extent than nonpolar solvents, the ground-state polarization of a donor-acceptor molecule can thus be increased by utilizing increasingly polar solvents, since this increases the contribution of the charge-separated form to the ground-state geometry.



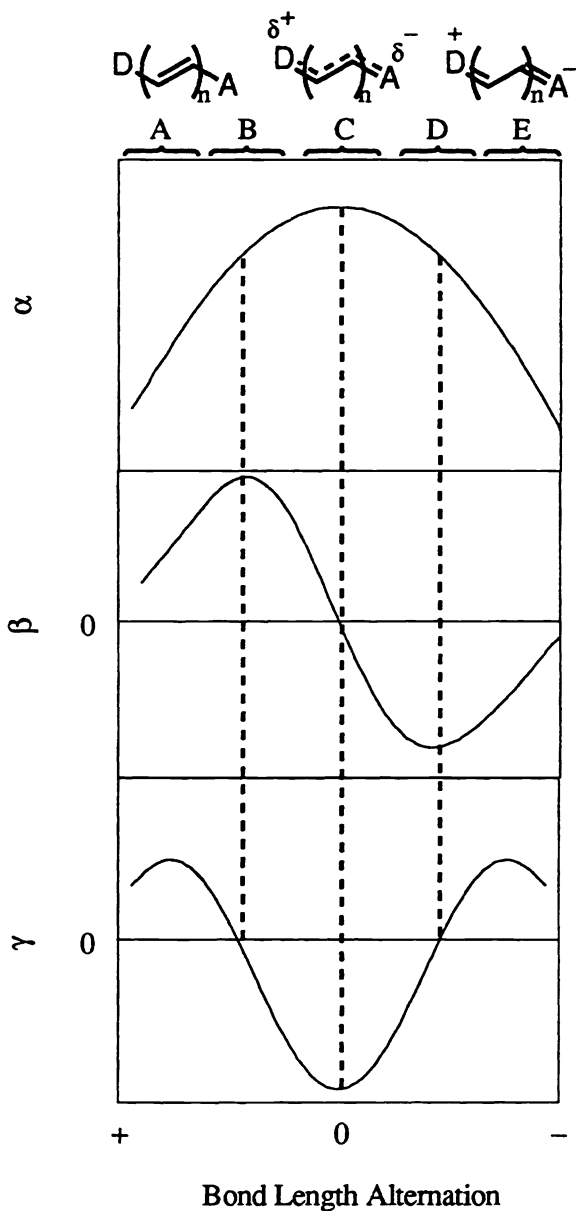


Figure 2. Schematic illustration of the predicted dependence of  $\alpha$ ,  $\beta$  and  $\gamma$  on bond length alternation. The ground-state polarization increases from A to E.

The first-order polarizability,  $\alpha$ , is dependent on two terms,  $(1/E_{ge})$  and  $\mu_{ge}$ , which both peak<sup>1</sup> at the cyanine-limit of zero bond length alternation (Figure 3), explaining the dependence of  $\alpha$  on BLA in Figure 2. The two-level model<sup>9</sup> for  $\beta$  is similar to an  $\alpha$ -term scaled by a factor of  $(\mu_{ee}-\mu_{gg})/E_{ge}$ . The difference in dipole moment between the ground and excited state,  $(\mu_{ee}-\mu_{gg})$ , exhibits positive and negative peaks at BLA values corresponding to regions A and E respectively (Figure 3).<sup>1,2,8,10</sup> Thus  $\beta$ , as a function of increasing ground-state polarization, starts positive, increases, peaks in a positive sense, decreases, crosses through zero at the limit of zero BLA, becomes large and negative, peaks in a negative sense and eventually decreases in magnitude (Figure 3).<sup>1,2,8,10</sup>  $\beta$  displays positive and negative peaks closer to the zero BLA limit (i.e. regions B and D, respectively) than the  $(\mu_{ee}-\mu_{gg})$  peaks (Figure 3) since  $(1/E_{ge})$  and  $\mu_{ge}$  peak at the zero BLA limit.

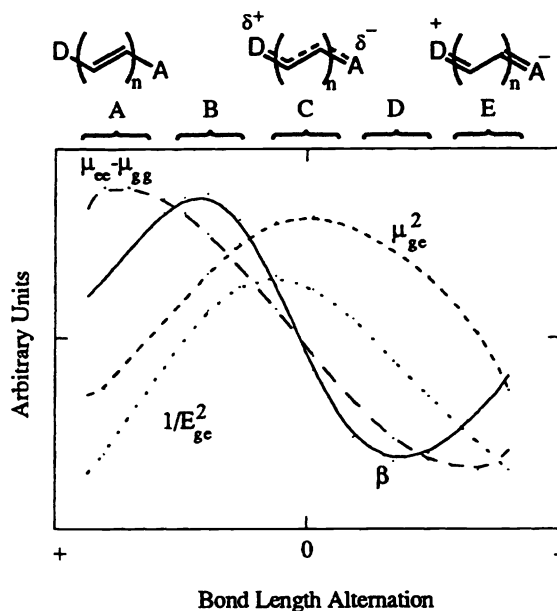


Figure 3. Dependence of  $(\mu_{ge})^2$ ,  $(1/E_{ge})^2$ ,  $(\mu_{ee}-\mu_{gg})$  and  $\beta$  on the ground-state structure. The ground-state polarization increases from A to E. The point where  $(\mu_{ee}-\mu_{gg})$  and  $\beta$  are zero corresponds to the bond-equivalent cyanine-limit of zero bond length alternation. The curves were calculated<sup>8</sup> for  $\text{Me}_2\text{N}-(\text{CH}=\text{CH})_4-\text{CHO}$ , geometry-optimized in the presence of a static electric field (used to modify the geometry from the highly bond-alternate polyene-limit (region A), through the bond-equivalent cyanine-limit (region C) to the bond-alternate charge-separated polyene-limit (region E)), at the semiempirical INDO level using a sum-over-states approach in combination with an INDO-configuration interaction technique that includes full single and limited double configuration excitations.

The three-level model<sup>11-13</sup> for the third-order polarizability,  $\gamma$ , consists of a negative,  $\alpha^2$ -like term, N1, a two-photon term, P1, and a  $\beta$ -like term, P2. For chromophores with large positive BLA, such as unsubstituted polyenes, the P2 term is negligible due to small  $(\mu_{ee}-\mu_{gg})$  and the P1 term dominates N1 resulting in positive  $\gamma$  (Figure 2).<sup>7,11</sup> By increasing the ground-state polarization and thus decreasing BLA, the P2 term, like  $\beta$  (Figures 2 and 3), starts to increase and hence  $\gamma$  increases. However, increasing the ground-state polarization toward the cyanine-limit (region C) also increases  $|\text{N1}|$  and therefore a positive peak in the  $\gamma$  curve is evident at larger magnitudes of BLA than the peak in the  $\beta$ -like P2 term. Upon further polarization, P2 peaks in a positive sense and starts to decrease and  $|\text{N1}|$  continues to increase and thus  $\gamma$  decreases in magnitude until  $|\text{N1}| = \text{P1} + \text{P2}$  and  $\gamma$  is zero.<sup>7,8</sup> At the bond-equivalent cyanine-limit (region C), the P2 term is zero since  $(\mu_{ee}-\mu_{gg})$  is zero. The  $\gamma$  curve exhibits a negative peak at this point since both  $|\text{N1}|$  and P1 peak but  $|\text{N1}| > |\text{P1}|$ .<sup>7,8</sup> To a first approximation, the behavior of  $\gamma$  in the region of negative BLA mirrors that in the positive BLA region (Figure 2).

The observation that  $\alpha$ ,  $\beta$  and  $\gamma$  appear to be related by a derivative-like relationship can be understood by considering a Taylor series expansion of the dipole moment,

$$\mu = \mu_0 + \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \dots \quad (4)$$

where

$$\alpha = \left. \frac{\partial \mu}{\partial E} \right|_0 \quad \beta = \left. \frac{\partial^2 \mu}{\partial E^2} \right|_0 \quad \gamma = \left. \frac{\partial^3 \mu}{\partial E^3} \right|_0 \quad (5)$$

so that

$$\beta = \left. \frac{\partial \alpha}{\partial E} \right|_0 \quad \gamma = \left. \frac{\partial \beta}{\partial E} \right|_0 \quad (6)$$

Now if we consider a molecule to be polarized by a strong field,  $F$ , that can modify the degree of bond length alternation associated with the molecule, the dipole moment will depend on  $F$  in some characteristic way,

$$\mu = \mu(F) \quad (7)$$

for which a single Taylor series with constant coefficients is not a sufficient description. Qualitatively, we would expect, and AM-1,<sup>2</sup> INDO<sup>8</sup> and valence bond calculations<sup>14</sup> show: (i) that for weak fields, such that the BLA is polyene-like,  $\mu$  will be small and weakly dependent on field; (ii) that when the field is large, such that the structure is close to the bond-alternate charge-separated polyene-limit,  $\mu$  will be large and weakly dependent on field; (iii) that for moderate fields,  $\mu$  will be intermediate and will vary most rapidly with field, i.e. the rate of change of the BLA with field is largest at the cyanine-limit.

At any particular value of  $F$ , say  $F'$ , we can expand  $\mu$  in a Taylor series, and thus

$$\alpha = \left. \frac{\partial \mu}{\partial F} \right|_{F'} \quad \beta = \left. \frac{\partial \alpha}{\partial F} \right|_{F'} \quad \gamma = \left. \frac{\partial \beta}{\partial F} \right|_{F'} \quad (8)$$

Therefore the functions  $\alpha(F)$ ,  $\beta(F)$  and  $\gamma(F)$  will be given by

$$\alpha(F) = \frac{\partial \mu(F)}{\partial F} \quad \beta(F) = \frac{\partial \alpha(F)}{\partial F} \quad \gamma(F) = \frac{\partial \beta(F)}{\partial F} \quad (9)$$

leading to derivative relationships between a given polarizability and the lower-order polarizability. Keeping in mind that the ground-state polarization, and hence BLA, is a function of the field strength, i.e.  $BLA = BLA(F)$ , that if we want to map the polarizabilities as a function of BLA, that the change of variables is nonlinear, i.e.

$$\alpha = \frac{\partial \mu}{\partial F} \frac{\partial F}{\partial BLA} \quad (10)$$

since BLA is a nonlinear function of  $F$ . This leads to a change of the shape of the  $\alpha$ ,  $\beta$  and  $\gamma$  curves versus BLA compared to those versus  $F$ . Nonetheless, the relation of the peaks and zero crossings of the different polarizabilities, e.g. the peak of  $\alpha$  and the zero crossing of  $\beta$ , are preserved and we will use these special points to test experimentally the validity of these relationships.

#### 4. MODEL COMPOUNDS AND DEGREES OF BLA

The molecules (Figure 4) studied to test the predicted structure-property relationships were chosen since strong evidence exists that they approximately cover the BLA range A-E in Figure 2.<sup>10</sup> The bond length alternation values were coarsely changed by utilizing donors and acceptors of varying strength and fine-tuned using solvent polarity. Bond length alternations, determined from x-ray crystallography, of unsubstituted polyenes and **3**, containing the weak formyl acceptor, have been reported previously<sup>3,15</sup> and allow an assignment of 1-3 to region A. This assignment is consistent with the positive solvatochromism displayed by **3** in all solvents used (Table I).

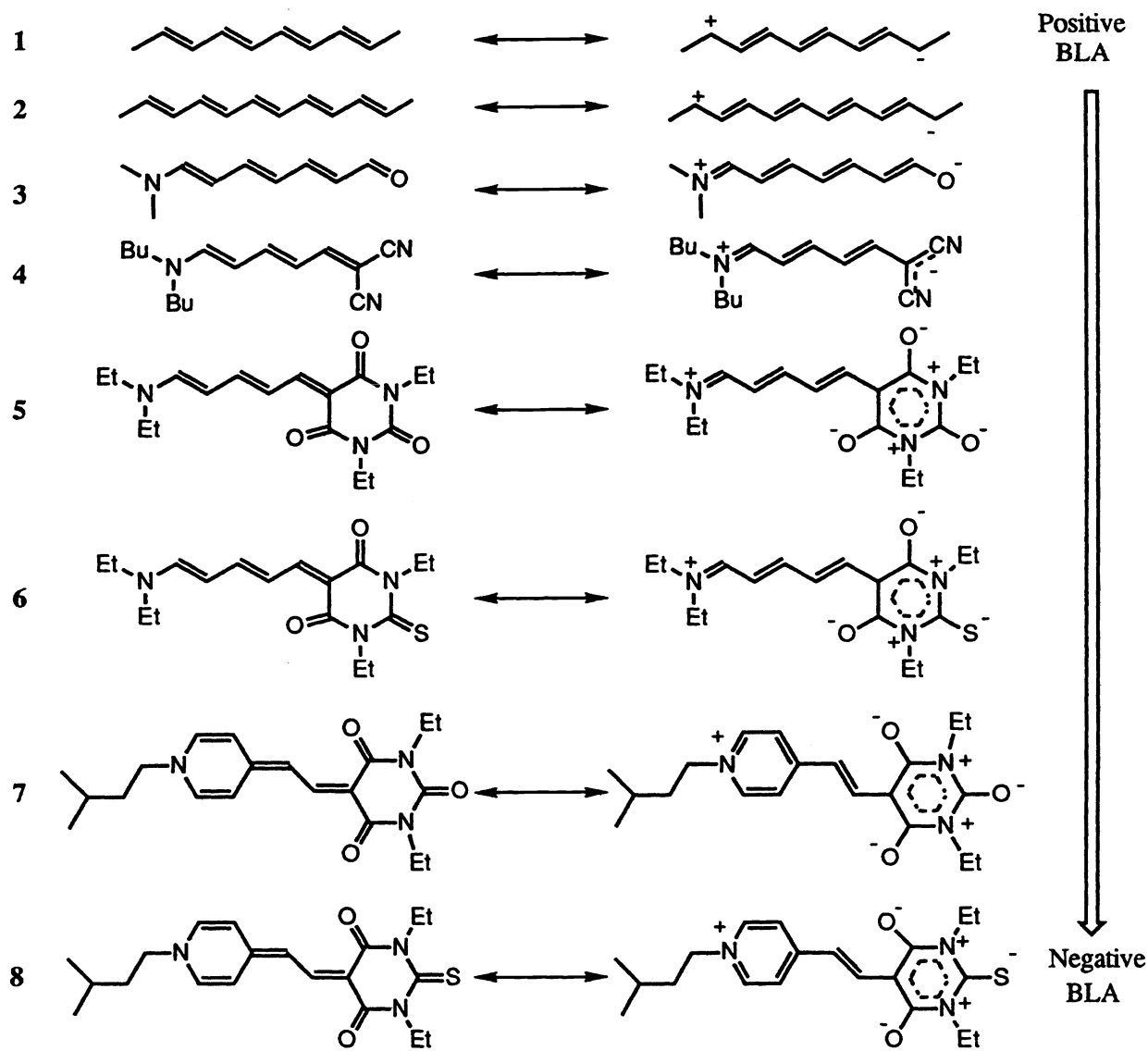


Figure 4. Canonical resonance structures for the donor-acceptor polyenes investigated. Electron donor/acceptor strength increases from 3 to 8. Et  $\equiv$  C<sub>2</sub>H<sub>5</sub> and Bu  $\equiv$  n-C<sub>4</sub>H<sub>9</sub>.

Compound 4 with the stronger dicyanovinyl acceptor possesses a bond length alternation of  $+0.015\text{\AA}$  in the solid state, assigning this molecule to region B. Interestingly, this small BLA value suggests that in polar solvents the ground-state geometry is cyanine-like whereas in nonpolar solvents, due to a decreased contribution of the charge-separated state, the ground-state structure is more similar to an unsubstituted polyene. These solvent-dependent geometry changes on a related molecule (B, Figure 1) were probed by non-resonant Raman spectroscopy (Figure 5).<sup>3</sup> The Raman spectrum of the unsubstituted polyene, (Figure 5a), exhibits two main bands, those due to the C-C ( $1150\text{ cm}^{-1}$ ) and C=C modes ( $1600\text{ cm}^{-1}$ ). The Raman spectrum of the bond-equivalent cyanine, (Figure 5d), exhibits increased activity at intermediate frequencies consistent with the loss of discrete C-C and C=C character. As predicted, the Raman spectrum of the dicyanovinyl moiety in nonpolar solvents (CHCl<sub>3</sub>, Figure 5b) is qualitatively similar to that of the polyene whereas the spectrum in polar solvents (CH<sub>3</sub>CN, Figure 5c) is qualitatively similar to that of the cyanine. The positive solvatochromism displayed by 4 in all solvents used (Table I) is consistent with the structural assignment of region B.

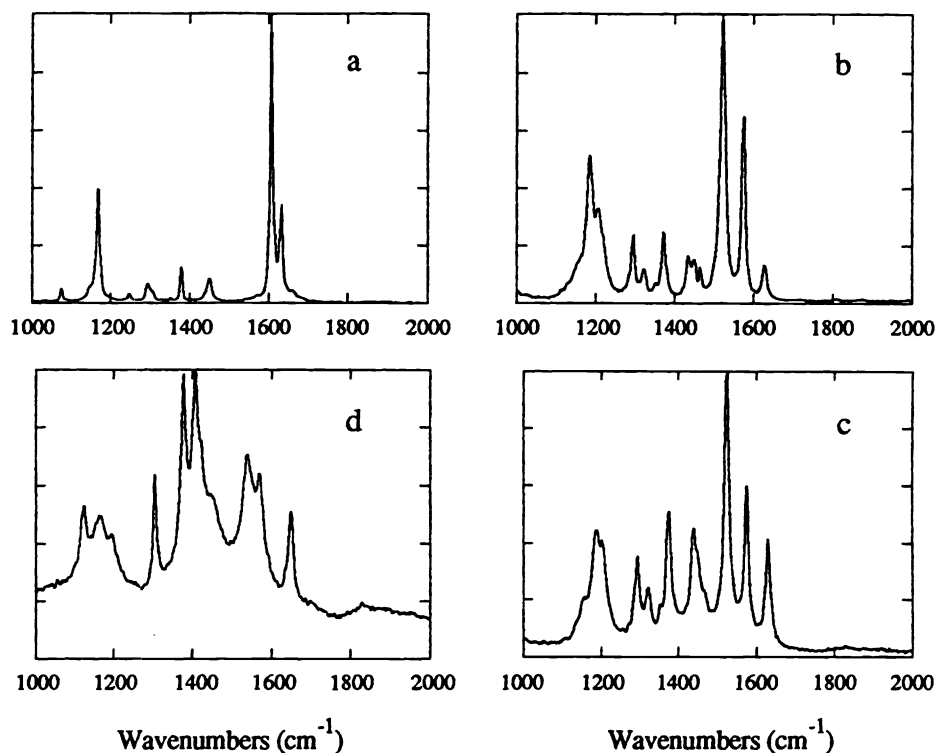


Figure 5. Raman spectra for (a) The polyene decatetraene (1, Figure 4) in the solid state; (b) B (Figure 1) in  $\text{CHCl}_3$ ; (c) B (Figure 1) in  $\text{CH}_3\text{CN}$ ; (d) A cyanine (C, Figure 1), in  $\text{CH}_3\text{CN}$ .<sup>3</sup> The counterion for the cyanine was perchlorate.

The ground-state polarization can be increased (bond length alternation decreased) further by utilizing the barbituric and thiobarbituric acid acceptors, 5 and 6 respectively. In fact, BLA for 6 in the solid state is  $-0.014\text{\AA}$  (Figure 1), which indicates that the ground-state geometry is biased slightly towards the charge-separated canonical resonance form. Both 5 and 6 display positive solvatochromism in nonpolar solvents, whereas negative solvatochromism is displayed for 5 in highly polar solvents and 6 in moderate polarity solvents, consistent with 5 being in region B/C and 6 in region C.

Molecules 7 and 8 display negative solvatochromism in all solvents used. Furthermore, the large  $^1\text{H}-^1\text{H}$  coupling constants (Figure 6) across the central carbon-carbon bond are consistent with a trans double bond (as depicted in the zwitterionic form in Figure 4, right) assigning 7 and 8 to regions C/D and D/E respectively. These coupling constants increase with increasing solvent polarity, consistent with an evolution of the ground-state geometry towards a more charge-separated structure.

The product of the ground-state dipole moment,  $\mu$ , and the second-order polarizability,  $\beta$ , was determined by solvent-dependent, electric field induced second harmonic generation (EFISH) measurements at 1907 nm using apparatus and methodology described elsewhere.<sup>17</sup> The third-order polarizability,  $\gamma$ , was determined by solvent-dependent third harmonic generation (THG) measurements at 1907 nm. A description of the experimental apparatus and data reduction scheme has been reported previously.<sup>18</sup>

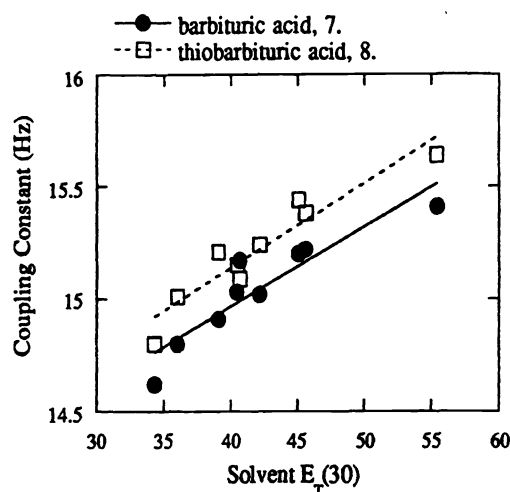


Figure 6. The  $^1\text{H}$ - $^1\text{H}$  coupling constants for 7 and 8 as a function of solvent polarity.<sup>16</sup> The trend of increasing coupling constant with increasing solvent polarity is indicative of an evolution towards a more charge-separated ground state (Figure 4, right).

## 5. RESULTS AND DISCUSSION

The solvent-dependent polarizabilities for the molecules in Figure 4 are presented in Table I. Molecules 1 and 2 display positive  $\gamma$  values consistent with those expected given the large positive bond length alternation values from previous structure determinations.<sup>15</sup> The increase of  $\gamma$  with increasing conjugation length has been noted by other authors.<sup>19</sup> Molecule 3, with the weak formyl acceptor, displays an increasing  $\mu\cdot\beta$  product and a positive peak in  $\gamma$  with increasing solvent polarity. This behavior is consistent with that expected for the structural assignment above of 3 in region A (Figure 2). The increase in  $\gamma$  for the donor-acceptor polyene, 3, over that of the symmetrical unsubstituted polyenes 1 and 2 has been noted previously<sup>11</sup> and is due to the lowering of symmetry with the result that the P2 term (equation 3) contributes positively to  $\gamma$ .

Compound 4 with the stronger dicyanovinyl moiety displays a positive peak in  $\mu\cdot\beta$  and a sign change in  $\gamma$ . In fact, the  $\mu\cdot\beta$  peak and the zero crossing of  $\gamma$  occur simultaneously, consistent with the derivative-like relationship predicted in Figure 2 and with the structural assignment of 4 in region B.

Molecules 5 and 6 display decreasing  $\mu\cdot\beta$  products with increasing solvent polarity. For 5 in the most polar solvent and for 6 in moderate polarity solvents,  $\mu\cdot\beta$  changes sign, consistent with the ground-state geometry being tuned through the cyanine-limit of zero bond length alternation. The  $\gamma$  values for 5 become large and negative with increasing solvent polarity with some evidence that  $\gamma$  peaks in a negative sense in the most polar solvents. Molecule 6 displays a clear negative  $\gamma$  peak in moderate polarity solvents. The zero crossing of the  $\mu\cdot\beta$  curve for both 5 and 6 coincides with the negative  $\gamma$  peak, consistent with the proposed structure-property relationships. Additionally, to the extent to which  $\alpha$  can be represented by  $(1/E_{ge})$ ,  $\alpha$  is maximized at the zero crossing of  $\mu\cdot\beta$ , again consistent with the predicted trend (Figure 2).

By increasing the ground-state polarization further, as with molecules 7 and 8, there is some evidence that the degree of mixing required to maximize  $\mu\cdot\beta$  in a negative sense has been achieved.<sup>10</sup> A zero-crossing in  $\gamma$  for 7 in nonpolar solvents is observed as well as evidence of  $\gamma$  approaching a positive peak for 8 in the most polar solvents. The zero crossing of  $\gamma$  however does not coincide with the negative peak in  $\mu\cdot\beta$ . This may be explained by the large ground-state dipole moment shifting the peak in  $\mu\cdot\beta$  to lie closer to the  $\gamma$  peak than would the  $\beta$  peak.

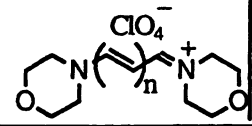
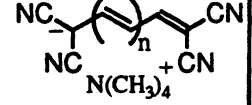
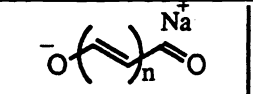


Table I. Maximum absorption wavelength ( $\lambda_{\max}$ , units of nm), solvent-dependent  $\mu\beta$  (units of  $10^{-48}$  esu) and  $\gamma$  (units of  $10^{-36}$  esu) for 1-8. The estimated precision in  $\mu\beta$  and  $\gamma$  is  $\pm 15\%$ . The polarity of the solvents increase (the contribution of the charge-separated structure to the ground-state geometry increases) from left to right. Normalized  $E_T(30)$  values<sup>16</sup> of the solvents are presented within parentheses. Insolubility precluded the determination of the polarizabilities in certain solvents. The  $\mu\beta$  values were determined assuming that the contribution to the EFISH signal from the third-order polarizability,  $\gamma$ , is negligible. This leads to an error in the  $\mu\beta$  values of  $< 15\%$ , except when the magnitude of the  $\mu\beta$  values is  $< 70 \times 10^{-48}$  esu where the error can approach 70%. However, no change in the  $\mu\beta$  trends, from those reported below, is observed when the  $\gamma$  contribution is included.

Molecule	Solvent								Region
	CCl <sub>4</sub> (0.052)	C <sub>6</sub> H <sub>6</sub> (0.111)	1,4-Dioxane (0.164)	CHCl <sub>3</sub> (0.259)	CH <sub>2</sub> Cl <sub>2</sub> (0.309)	CH <sub>3</sub> CN (0.456)	CH <sub>3</sub> NO <sub>2</sub> (0.482)	CH <sub>3</sub> OH (0.762)	
1 $\lambda_{\max}$	-	300	300	-	300	-	-	-	A
$\mu\beta$	-	-	-	-	-	-	-	-	
$\gamma$	-	34	25	-	27	-	-	-	
2 $\lambda_{\max}$	-	328	350	-	330	-	-	-	A
$\mu\beta$	-	-	-	-	-	-	-	-	
$\gamma$	-	60	70	-	72	-	-	-	
3 $\lambda_{\max}$	396	404	402	420	420	418	426	440	A
$\mu\beta$	299	272	-	322	343	348	430	-	
$\gamma$	-	-	40	95	105	113	113	73	
4 $\lambda_{\max}$	446	472	468	478	480	476	480	476	B
$\mu\beta$	332	360	-	400	340	231	195	-	
$\gamma$	40	15	-25	-42	-50	-120	-117	-135	
5 $\lambda_{\max}$	498	504	502	510	508	502	506	500	B/C
$\mu\beta$	401	205	-	200	141	109	-65	-	
$\gamma$	-	-20	-100	-135	-145	-205	-220	-166	
6 $\lambda_{\max}$	526	532	528	536	534	524	526	520	C
$\mu\beta$	276	264	-	-22	-60	-240	-316	-	
$\gamma$	-	-85	-170	-195	-175	-130	-125	-10	
7 $\lambda_{\max}$	528	520	510	510	506	488	490	468	C/D
$\mu\beta$	-	-180	-	-374	-414	-	-350	-	
$\gamma$	-	-	-25	15	30	79	73	150	
8 $\lambda_{\max}$	548	538	526	526	520	496	496	482	D/E
$\mu\beta$	-	-	-	-600	-770	-550	-363	-	
$\gamma$	-	-	-	130	167	228	227	291	

The structure-property relationships proposed in Figure 2 can be further tested by examining the third-order polarizability of molecules possessing zero bond length alternation, for example cyanines and oxonols. The results for a series of these chromophores are presented in Table II where it can be seen that, with the exception of the shortest chromophores, the  $\gamma$  values are negative as predicted.

Table II.  $\gamma$  values (units of  $10^{-36}$  esu) and maximum absorption wavelengths ( $\lambda_{\max}$ , units of nm) for molecules possessing zero bond length alternation. The estimated precision in  $\gamma$  is  $\pm 15\%$ , except in the case where the magnitude of  $\gamma < 3 \times 10^{-36}$  esu when the estimated error in  $\gamma$  is  $\pm 5 \times 10^{-36}$  esu.

Molecule	n	$\lambda_{\max}$	$\gamma$
	1	318	+ 3
	2	416	- 40
	3	516	- 370
	1	438	- 45
	2	538	- 500
	1	266	+ 3
	2	362	- 7

## 6. SUMMARY

Donor-acceptor polyenes of comparable conjugation length have been synthesized and their solvent-dependent hyperpolarizabilities probed by EFISH and THG measurements at 1907 nm. Optimization in both a positive and negative sense, as well as sign changes in  $\mu\text{-}\beta$  and  $\gamma$  were observed. These observations were explained by molecular structure changes (probed by x-ray crystallography,  $^1\text{H-NMR}$ , electronic absorption and Raman spectroscopies) 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 the geometry-dependent hyperpolarizabilities is fully consistent with the trends predicted using geometry-optimized electric-field-dependent AM1 and INDO-CI calculations and with the prediction that the polarizabilities are related by a derivative relationship. A separate series of ionic molecules possessing zero bond length alternation were found to exhibit negative third-order polarizabilities, also in agreement with the proposed structure-property relationships.

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