Effect of Molecular Polarization on Bond-Length Alternation, Linear Polarizability, First and Second Hyperpolarizability in Donor–Acceptor Polyenes as a Function of Chain Length

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The linear (α) and nonlinear (β, γ) molecular polarizabilities of a series of donor–acceptor polyenes containing 3–8 π-bonds are studied using the semiempirical AM1 parametrization and finite-field (hyper)polarizability computations as a function molecular polarization and resulting changes in bond-length alternation. Plots of α, β, and γ versus bond length alternation had similar shapes (although different magnitudes) for each chain length. The changes in α, β, and γ with molecular length were fit to exponential functions (N^m) for various bond-length alternations. These values varied over a significant range depending upon the value of bond-length alternation chosen.

Introduction

Donor–acceptor polyenes are the prototypical organic chromophores that have been considered for their nonlinear optical (NLO) response. In attempting to understand the relationship between chemical structure and the linear and nonlinear optical properties of molecules, two relevant molecular parameters are typically varied: ground-state polarization (by varying the relative strengths of the donor and acceptor), and the molecular length. We have recently described a procedure that permits us to calculate α, β, and γ of donor–acceptor polyenes of the form $R_2N{-}(CH{=}CH)_n{-}CHO$ (**1**) through a range of bond-length alternation (BLA) corresponding to differing degrees of charge separation in the molecule (Figure 2, shown here for $n = 5$ and previously reported for $n = 4$).[1,2] Using this method, the molecule can be varied from a gas-phase form with little charge separation [the polyene limit] depicted by the resonance form on the left side of Figure 1, through a bond-length equivalent form in which both resonance forms make an approximately equal contribution [the cyanine limit], through a strongly charge-separated form [the zwitterionic limit] dominated by the resonance structure at the right side of Figure 1. Having established the basic validity of this approach, we now present results of a computational study that varies both BLA and molecular length. We point out that a physically accessible parameter, BLA, can be related to maxima and minima in the molecule's linear polarizability (α) and first- (β) and second molecular hyperpolarizability (γ) for molecules of differing length. In addition, we provide a more detailed description of the computational technique as well as several tests to help validate the procedure.

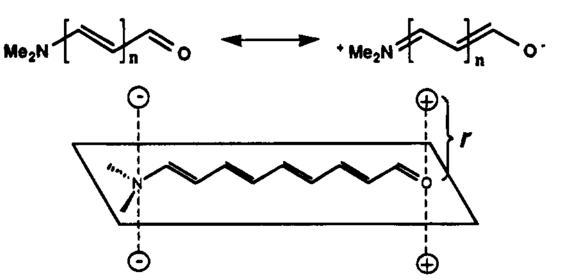

Figure 1. Neutral (top, left) and charge-separated (top, right) resonance structures that contribute to both the electronic and nuclear structure of the molecule and a depiction of the placement of the point charges (bottom). In the absence of an external perturbation, a computational geometry optimization is biased against charge separation and depicts the molecule almost solely as it is represented on the left. Point charges promote increased charge-separated character as they approach the molecule.

Results and Discussion

Using the semiempirical AM1 parameterization in the MOPAC package,[3,4] we examined donor–acceptor polyenes of the form **1** (R = Me, $n = 2{-}7$) under the influence of an external perturbation designed to vary the ground-state polarization and geometry. This perturbation was two positive and two negative point charges placed as is shown in Figure 1 and moved incrementally toward the molecules (from 40 to 4 Å). While the distances between the point charges and the molecule were held fixed, the molecular geometry was optimized. As the point charges were placed closer to the molecules, it was observed that the single bonds in the molecules became shorter (from ≈1.44 to ≈1.35 Å) and the double bonds became longer (from ≈1.35 to ≈1.44 Å). Although this entire range of bond lengths could not be spanned for the shorter polyenes under study ($n < 4$), the range corresponds to a change in bond-length alternation (defined as the difference between the average of the central $n - 2$ C=C bonds and

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the average of the central $n - 2$ C—C bonds in the molecules with the resonance structure shown at the left of Figure 1) from BLA ≈ -0.09 Å, represented predominantly by the charge-neutral (left) resonance structure in Figure 1 to BLA $\approx +0.09$ Å, represented predominantly by the charge-separated (right) resonance structure in Figure 1. At the same time, the ground-state dipole moments of the molecules increased smoothly.

Values for α, β, and γ for the polarized molecules were then calculated using a finite field subroutine.[5] Although polarization by point charges is different than charge stabilization by solvent (in particular, the largest fields applied in our calculations are considerably larger than the reaction fields for common solvents), this method qualitatively reproduces experimental trends in geometry and polarizabilities as a function of increasing ground-state polarization.[1,2,6–12] Several observations are made from Figure 2. (i) The value of α exhibits a peak at the cyanine limit. (ii) The value of β exhibits a positive peak between the polyene and the cyanine limits, crosses through zero at roughly the cyanine limit (at which point the difference between the dipole moment of the strongly allowed first excited state and the ground state is roughly zero[12]), and exhibits a negative peak between the cyanine and zwitterionic limits. (iii) Between the polyene and cyanine limits, the value of γ is initially positive and increases, reaching a peak. The value of γ then decreases, crosses through zero (at a BLA corresponding to that where β peaks), becomes negative, reaching a negative peak (with a maximized absolute value) at the cyanine limit. To first approximation, the region between the cyanine and zwitterionic limits mirrors that on the other half of the curve. (iv) The curves are roughly derivatives with respect to each other as is discussed in detail elsewhere.[11] For β and γ, solvent-dependent electric-field-induced second harmonic generation (EFISH) and third harmonic generation (THG) studies on a series of molecules of similar length and with ground-state polarizations that span almost the entire range of BLA depicted by these curves confirm the behavior predicted in Figure 2.[8,12] Furthermore, it has recently been shown that molecules with reduced BLA similar to that at the positive peak in the β curve have exceptionally high nonlinearities.[13] As discussed earlier,[1,2,6] all of these results are consistent with simplified perturbative expressions which approximate α, β, and γ based upon couplings, transition energies, and changes in dipole moments between the ground and one or two excited states of the molecule.[6,14–21] In addition, recent, similar computational studies using a sum-on-states approach,[22] using an anharmonic oscillator model,[23] and using a simplified two-level valence bond approach[24] predict essentially the same relationships as a function of ground-state polarization.

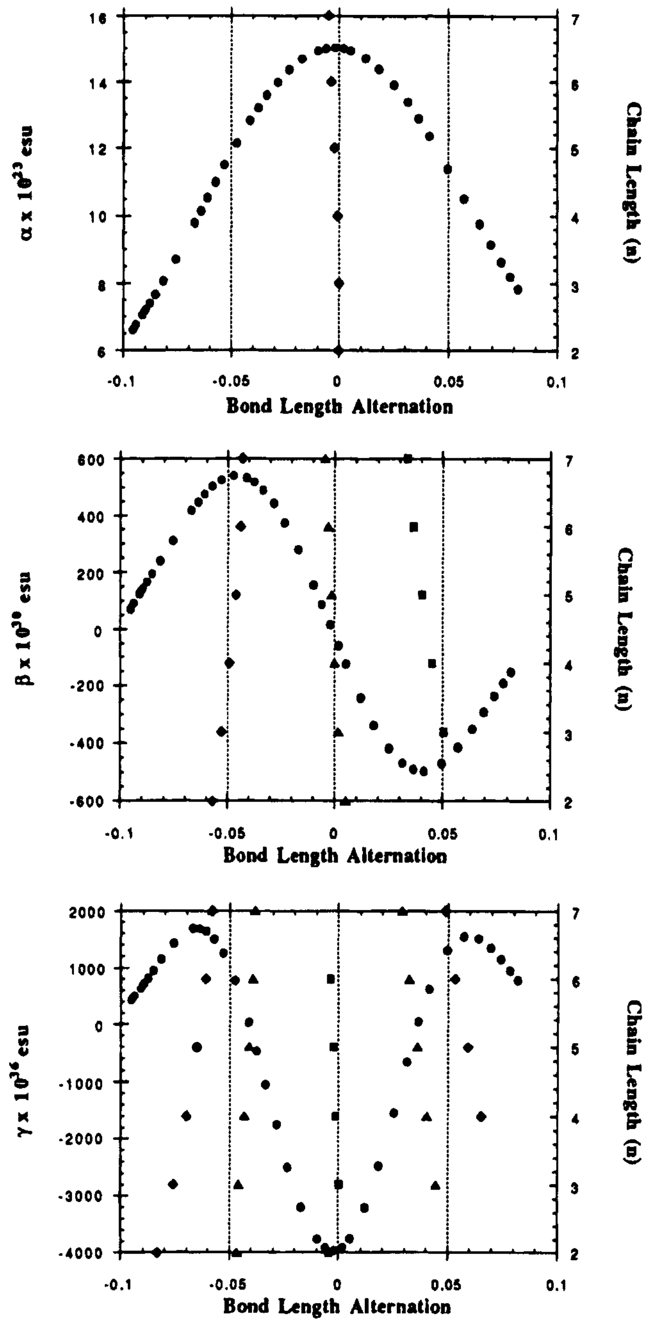

Figure 2. Correlation of molecular polarizability, α (top plot), first , β (center plot) and second, γ (bottom plot) hyperpolarizabilities (on the left axes), with bond length alternation (BLA, defined in the text) for $Me_2N-(CH=CH)_5-CHO$ (●). The bond length alternation at which α (top plot), β (center plot), and γ (bottom plot) are maximized (◆), are minimized (■) or cross through zero (▲, for a given of chain-length (n), where n is shown on the right axes. The shorter molecules could not be driven to the most charge-separated form (BLA $\gtrsim +0.025$), so not all maxima/minima could be reported. Likewise, the 7-double bond polyene could not be driven smoothly through the region of BLA = 0.

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Table 1. Summary of Exponents for α, β, and γ of Polyenes and Polarized Polyenes

quantity	geometry	m	N's used	compounds/method[b]
α	BLA = −0.09	1.33	3−8	this work
	maximum[a]	2.16	3−8	this work
	computational[25]	1.38	3−8	$H-(CH=CH)_n-H$, $N = n$ using the 6-31G + PD basis set w (SOS)
	computational[26]	1.31	3−8	$H-(CH=CH)_n-H$, $N = n$ using AM1/FF
β	BLA = −0.09	2.95	3−8	this work
	maximum[a]	4.51	3−8	this work
	BLA = −0.06	4.28	3−8	this work
	BLA = −0.05	4.49	3−8	this work
	BLA = −0.04	4.61	3−8	this work
	computational[27]	3.43	3−7	$Me_2N-(CH=CH)_n-NO_2$ $N = n + 1$ using CNDOVSB/SOS
	computational[27]	3.21[c]	3, 5, 7, 9	$Me_2N-(CH=CH)_n-CHO$ $N = n + 1$ using CNDOVSB/SOS
	computational[28]	3.52	3−6	$Me_2N-(CH=CH)_n-NO_2$, $N = n + 1$ using PPP/SOS
	experimental[32]	4.02	4−6	$Me_2N-Ph-(CH=CH)_n-CH=C(CN)_2$, $N = n + 4$, EFISH at 1.06 μm in chloroform
	experimental[32]	2.27	6−9	$Me_2N-Ph-(CH=CH)_n-Ph-NO_2$, $N = n + 5$, EFISH at 1.06 μm in chloroform
	experimental[39]	2.48	5, 8, 10, 12	$\mu\beta(0)$ values, julolidine−$(CH=CH)_n-CH=C(CN)_2$, $N = n + 4$, EFISH at 1.91 μm in chloroform or acetone
	experimental[39]	3.26	2, 5, 7, 9	$\mu\beta(0)$ values, benzodithia−$(CH=CH)_n-CHO$, $N = n + 1$, EFISH at 1.34 μm in chloroform or acetone
	experimental[7]	3.2	1−4	$Me_2N-(CH=CH)_n-CHO$, $N = n + 1$, EFISH at 1.91 μm in chloroform
	experimental[7]	5.4	2−5	$Me_2N-(CH=CH)_n-CH=C(CN)_2$, $N = n + 2$, EFISH at 1.91 μm in chloroform
γ	BLA = −0.09	4.400	3−8	this work
	maximum[a]	6.091	3−8	this work
	BLA = −0.08	5.111	3−8	this work
	BLA = −0.07	5.969	3−8	this work
	BLA = −0.06	6.727	3−8	this work
	minimum[a,d]	6.509	3−7	this work
	computational[25]	3.421	3−8	$H-(CH=CH)_n-H$, $N = n$ using the 6-31G + PD basis set w (SOS)
	computational[26]	4.004	3−8	$H-(CH=CH)_n-H$, $N = n$ using AM1/FF

[a] That bond-length alternation that maximizes/minimizes the quantity of interest. In the case of γ, the maxima refere to that for the least charge separated form (i.e., BLA < 0). [b] Computational results are for $\omega = 0$ (sum-over-states [SOS]) or static perturbing field (finite field [FF]). Experimental results for β are by EFISH = electric field-induced second harmonic generation. Definition of N is consistent throughout and is different from that used by other authors. Two double bonds are counted for a benzene ring and an additional double bond is counted for the bond in the acceptor. [c] For a curve containing only 3 points (N = 3, 5, 7), m = 3.281. [d] Curve fit is to $|\gamma_{\min}|$.

When evaluating the molecular length dependence of β, it is common to fit data to a function of the form $\beta(0) \propto N^m$.[25−28] Here, N is defined as the number of conjugated multiple bonds in the molecule (including the C=O bond, i.e., $N = n + 1$) so as to more accurately represent the real length of the molecule. The exponent, *m*, lends insight into the chain-length dependence of β. We have computed m for β for the molecules at various bond length alternations and for molecules at $\beta_{\max}$ (Table 1). The exponent *m* is also computed for α and γ. Exponents derived from data in the literature are also reported (for these cases N is defined as above, and therefore exponents may differ from those reported in the original work, due a the use of altnerative counting scheme for the conjugation length).[29] The exact bond-length alternation corresponding to a maximized β and γ varies somewhat with molecular length, and this value is graphically displayed as a function of chain length, *n*, in Figure 2. It is not expected that each member of this homologous series of molecules will have the same bond-length alternation in a given solvent, but the range of exponents for both constant bond-length alternation and for bond-length alternation corresponding to a maximized β or γ gives a range into which optimized molecules are expected to fall. In particular, it is expected that increasingly strong donors and acceptors will be required to reach a given BLA value as molecules become longer, reflecting the greater difficulty in separating charge over greater lengths. The exponents at or near the maxima or minima of the α, β, and γ, curves are larger than those computed for hyperpolarizabilities based upon bond-length alternate (gas-phase) geometries,[27,28] and, in the case of β, for those observed for molecules containing aromatic end groups.[7,30−32] For α, the data show that chromophores with minimal bond-length alternation (the cyanines) are optimized, a conclusion consistent with previous experimental determinations.[33] β is optimized at BLA = −0.05 ± 0.01 Å, and around this point, $m \approx 4.5$. We have synthesized simple donor−acceptor polyenes such as **1** (n = 0−3) as well as $R_2N-(CH=CH)_n-CHC(CN)_2$, **2** (n = 0−3), and find that the value for *m* for these molecules (measured by EFISH in $CHCl_3$) is 3.2 and 5.4, respectively.[34] As mentioned earlier, a series of vinylogous compounds (such as **2**) will not necessarily have the same BLA at different chain lengths. Therefore, it is possible to move closer to the maxima of the curve with increasing chain length, if BLA for a short compound in the series is too close to zero to optimize β and if |BLA| becomes larger with increasing length. This would result in higher exponents than would be predicted for any given bond-length alternation. Conversely, if the magnitude of BLA is greater than that required to optimize β in a positive sense, then for a given donor or acceptor, the exponent is expected to be lower than might be predicted based on short compounds within the series. The magnitude of γ is maximized in the cyanine limit but also shows a maximum at BLA = −0.07 ± 0.01 Å which may correspond to more stable molecules, particularly for longer chain lengths. The exponents corresponding to these extrema are again significantly greater than those predicted previously for polyenes.[25,26]

In conclusion, these results provide structure–property relationships for donor–acceptor polyenes, both as a function of molecular length and as a function of the ground-state polarization and resulting bond-length alternation in the molecules. In particular, we predict that molecules with a significantly lower magnitude bond-length alternation than is observed in polyenes and diphenyl-capped polyenes can have larger hyperpolarizabilities *as well as faster increases in hyperpolarizability with increasing chain length*. Thus, we suggest that cyanines with 0 Å of bond-length alternation and donor–acceptor polymethines with roughly ±0.07 Å of bond length alternation be considered for third-order NLO applications. Likewise, we suggest that donor–acceptor polymethines with roughly ±0.05 Å of bond-length alternation be considered for second-order electrooptic applications.

Description of the Computation

General. Geometry optimizations of **1** (R = Me, n = 2–7) were accomplished using the AM1 parametrization available in MOPAC 6.0.[3,4] Using a Z-matrix definition for the starting molecular geometries, the distances, angles, and dihedral angles between external point charges of opposite signs, and between two of the point charges (positive Sparkles) and the molecule (nitrogen atom) were fixed. To accomplish this task, the molecules were held planar during this procedure. Using a less convenient external point charge arrangement in which the point charges were placed in the molecular plane, it was shown that μ, α, β, and γ versus bond-length alternation were basically unchanged when the least planar molecule, **1** (n = 3), was alternately held planar and permitted to become nonplanar during geometry optimization. Likewise these two arrangements of the external point charges around the molecule (e.g. point charges in the molecular plane versus point charges perpendicular to the molecular plane) made little difference in μ, α, β, and γ when these quantities were plotted versus bond-length alternation. The detailed shape of the electric field will of course be dependent upon the arrangement of the external point charges (Figure 1). This point has been considered, and alternate arrangements of the point charges were employed. These included (a) four charges in the molecular plane, (b) eight charges arranged as dipoles perpendicular to the molecular plane, and (c) four charges at different distances from the donor and acceptor to account for donors and acceptors of different relative strengths. For all of these different arrangements, and even when the potential stabilization at one side of the molecule was 3 times that at the other (corresponding to a much weaker donor than acceptor and vice versa) the behavior of μ, α, β, and γ were essentially unchanged, and, in most cases, curves were superimposable when viewed versus bond length alternation. Again, it is not our intention to simulate the effect of a particular solvent or other medium upon a molecule with any given external point charge arrangement but rather to probe the electronic and geometric changes in the molecule, and its (hyper)polarizabilities as it becomes more polarized. In this case, these results merely indicate that the specific point charge arrangement used to polarize the molecule is not critical to observing these effects.

The point charges (Sparkles) were moved in steps from 40 to 4 Å from the ends of the molecule in the trajectory shown in Figure 1. The step increment became smaller as the point charges approached the molecule, and the change in electric field with a change in distance became larger, beginning with an increment of 10 Å (40, 30, 20 Å), followed by an increment of 1 Å (15 through 8 Å), and ending with an increment of 0.2 Å (8 through 4 Å) for n = 3–6. For n = 7, this last increment was varied as little as 0.0002 Å (between 6.8820 and 6.8840 Å) in an effort to map out the region around BLA = 0 Å. Despite the use of this small increment, this region was not mapped out. BLA jumped from −0.013 Å (for a Sparkle distance of 6.8840 Å) to +0.015 Å (for a Sparkle distance of 6.8838 Å). Reasons for the existence of this "forbidden region" in molecules of this length (and longer, results not presented here) are under consideration but may be related to charge localization in infinite polyenes[35,36] and long cyanine molecules.[37,38]

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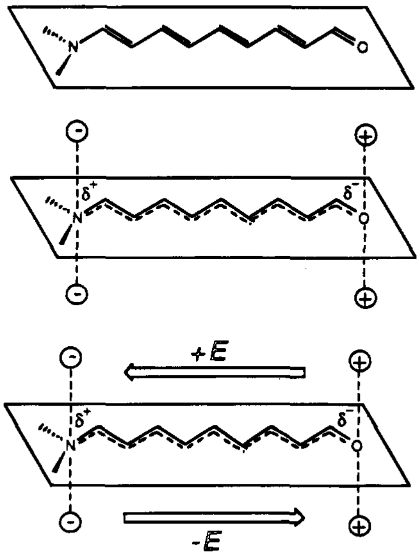

Figure 3. Molecule **1** [top] in the absence of an external electric field, [middle] exhibiting both nuclear and electronic polarization due to external point charges, and [bottom] exhibiting further electronic polarization (indicated by the arrows) as the result of the finite field procedure.

At each fixed Sparkle distance, the geometry was optimized, and μ, α, β, and γ were calculated in the presence of these point charges using the finite-field subroutine[5] available in MOPAC 6.0 using an SCF convergence criterion (SCFCRT) of 10^{-20} au as recommended by Kurtz.[5] All of these quantities are vectors or tensors, and, in most cases, average values are reported. These average values are $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$; $\beta_\mu = {}^3/_5(\beta\cdot\mu/|\mu L|)$ where $\beta\cdot\mu = \beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z$ and $\beta_i = \{\beta_{iii} + \beta_{ijj} + \beta_{ikk}\}$; and $\gamma = ({}^1/_5)[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2.0(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$. All reported values are obtained from the energy equations[5] ($E4$) in the finite field subroutine. Values obtained from the dipole equations[5] (DIP) differ by less than 1% of the $E4$ values.

It is important to note that although two explicit fields are applied to the molecule, the point charge field and the electric field within the finite field calculation, these fields have distinctly different effects on the molecule. In particular, the first field is permitted to influence both its geometric and electronic structure. Thus, at the start of the finite field computation, the molecule is in a new equilibrium geometry and electronic configuration, within which the hyperpolarizabilities are then calculated (Figure 3). By varying the strength of the electric field employed in the finite field routine, both numerical accuracy problems and electron configurational changes, observed for field strengths that are two small and large, respectively, were avoided (see below). Using point charges to polarize the electrons without permitting the molecular geometry to change results in a finite field calculation of a molecule in a nonequilibrium, polarized state. Likewise, removal of the point charges after geometry optimization but before the finite field procedure leaves nuclei in a position corresponding to a polarized molecule but removes the potential that stabilizes the polarization. Both of the above procedures were performed; however, for each case, since the nuclei and the electrons were not in equilibrium configurations, much larger applied fields were needed to polarize the molecule, as compared to applying a field and allowing the geometry to optimize. These results suggested to us that both the applied electric field and the position of the nuclei make important contributions to the polarization response and that the most reasonable procedure was to account for both effects.

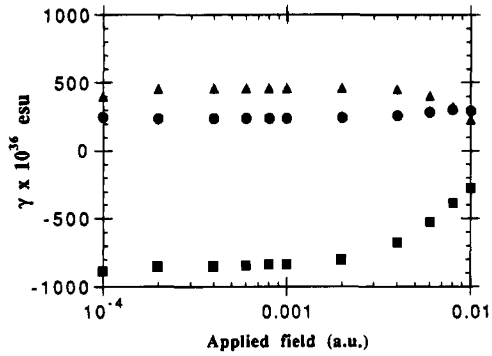

Figure 4. Sensitivity of γ (reported in Figure 2), calculated using energy equations[5] ($E4$) values from the finite field subroutine, *for* **1** *with [circles] no point charges, [triangles]* external point charges placed 10 Å from the molecule as in Figure 1 and [boxes] external point charges placed 6 Å from the molecule as in Figure 1. Over the range shown, the dipole equation values were comparable to those shown down to a field strength of 2×10^{-4} au, at which point they diverged.

Tests of the Finite Field Procedure. In the finite field procedure, the default strength of the perturbing electric field (10^{-3} au) was employed, and all values reported are those obtained using this base field strength. To test the validity of this field strength, it was varied to ensure that both numerical accuracy problems and electron configurational changes, observed for field strengths that are two small and large, respectively, were avoided.[5] Figure 4 shows the value of γ ($= {}^1/_5[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$) for **1** ($n = 4$) both in the presence and absence of the external point charges arranged as in Figure 1. This longer, more (hyper)polarizable molecule is much more sensitive to changes in applied field than were the smaller substituted benzenes reported earlier by Kurtz,[5] indicating that this test is worth performing for these molecules. However, the external point charges do not significantly change the sensitivity of the computed (hyper)polarizabilities to the applied field. This observation is consistent with the conclusion that the molecule is in an equilibrium nuclear and electronic configuration at the start of the finite field procedure.

Results at Nonequilibrium Configurations. Figure 5 shows β computed for **2** in what we rationalize as nonequilibrium configurations. In one case (Figure 5, top) the molecule was geometry optimized in the gas phase and external point charges were placed around the molecule only for the finite field calculations, corresponding to a computation in a nonequilibrium configuration. The value of β increases as the molecule is polarized and even maximizes at approximately the same induced dipole moment as that observed when the geometry is permitted to optimize. The absence of nuclear relaxation, however, limits the extent of molecular polarization. In the second case (Figure 5, bottom) the molecule was geometry optimized in the

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(39) Blanchard-Desce, M.; Bloy, V.; Lehn, J.-M.; Runser, C.; Barzoukas, M.; Fort, A.; Zyss, J. *Proc. SPIE* **1994**, *2143*, 20–29.

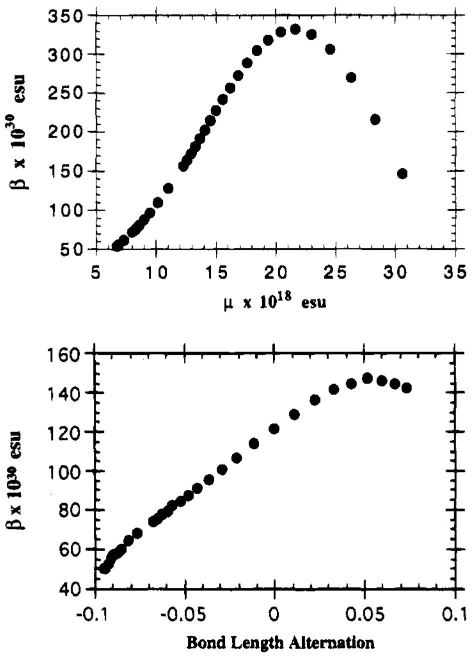

Figure 5. β calculated in two nonequilibrium scenarios for **2**. Top: plot of β versus μ where the molecule was geometry optimized in the gas phase and external point charges were placed around the molecule (as in Figure 1) only for the finite field calculations, corresponding to a computation in a nonequilibrium nuclear configuration. Bottom: plot of β versus bond-length alternation; the molecule was geometry optimized in the presence of the external point charges, and these were removed before the finite field calculation, corresponding to a nonequilibrium electronic configuration. β is plotted versus bond length alternation.

presence of the external point charges, and these were removed before the finite field calculation, corresponding to another nonequilibrium configuration. The molecule polarizes, as evidenced by an increase in dipole moment from 6 to >30 D over the range shown in the graph. This polarization again makes an incomplete contribution to the overall molecular polarization, evidenced by an even more sluggish response to the electric field applied in the first half of the procedure. Overall, it is our contention that both electronic and nuclear polarization make an important contribution to the configuration of the molecule, and both should be taken into account.

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