

Electronic Structure and Nonlinear Optical Properties of Push-Pull Polyenes: Theoretical Investigation of Benzodithia Polyenals and Dithiolene Polyenals

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Abstract: We report the results of ab initio Hartree-Fock calculations on the geometric and electronic structure and first-order (α) and second-order (β) molecular polarizabilities of a series of push-pull polyene molecules. The acceptor is in all cases an aldehyde group while the donor is either a benzodithia, a dithiolene, or a dithiolane group. The benzodithia polyenal compounds have recently been shown to present among the largest μ - β values ever measured. Theoretical results are found to be in excellent agreement with experimental data. They provide a detailed microscopic understanding of the evolution of the electronic and optical properties as a function of the length of the polyenic segment. While dipole moments and polarizabilities are only weakly sensitive to the conjugation path length, β values evolve over 2 orders of magnitude, thus strikingly pointing out the relevance of higher order nonlinear susceptibilities to account in more detail for electronic polarization related features of conjugated molecules. A detailed analysis of the angular deviation between the dipole moment μ and the vector component β of the first-order hyperpolarizability clearly illustrates the necessity to complement EFISHG measurements by theoretical computations in order to reach the modulus of tensor β . Large values of β , otherwise hidden by solution measurements, may then eventually be unraveled.

I. Introduction

The interest in nonlinear optical organic materials has grown tremendously in the past decade.¹⁻⁷ Important applications are envisioned, namely, toward integrated optical devices exploiting such phenomena as second-harmonic generation (SHG), frequency up and down conversion, optical parametric amplification and oscillation, electrooptic modulation, or optical bistability. Besides, higher order wave-mixing processes hold the potential of probing anisotropic polarization phenomena as well as electronic excited states that would be respectively either rounded-off or inaccessible in classical linear spectroscopy. These possibilities are particularly appealing in the case of conjugated organic linear or cyclic molecules where a variety of electronic excitations have been shown to participate in linear and nonlinear processes, their precise identification requiring an adequate confrontation of experimental data with theoretical approaches such as proposed here. Organic materials displaying enhanced second-order nonlinear optical effects appear to be especially promising candidates for such applications. These materials generally contain organic molecules with a π -conjugated pathway capped at one end by an acceptor group and at the other end by a donor group. A prototypical example is *p*-nitroaniline, which displays a static second-order polarizability (or first-order hyperpolarizability) extrapolated at zero frequency $\beta_{(0)}$ on the order of 9×10^{-30} esu.⁷

It has been experimentally established that the value of β strongly increases as the length of the conjugated pathway between the donor and the acceptor is extended.^{7,8} Obviously, the nature of the conjugated segment also plays a major role, and polyenes appear to be among the most efficient paths in this context.^{7,8} Extension of the conjugated segment usually goes in parallel with a reduction in the energies of the lowest optical transitions and leads to colored compounds which are strongly absorbing. Such low band gap materials may however be applied in electrooptic modulation and parametric amplification or emission provided, in the latter cases, that the pump is sufficiently removed from the cutoff wavelength.⁹ Electrooptic (Pockels) effect-related applications can be envisioned since the Pockels effect takes place at a single optical frequency and does not generate additional optical frequencies which would otherwise get absorbed via a linear mechanism. Furthermore, low band gap materials can be expected

to satisfy the requirements for parametric amplification or emission if the first visible absorption peak is separated from the next one by a low-absorption gap allowing for the propagation of a phase-matched harmonic wave.¹⁰

Recently, Lehn and co-workers¹¹ have synthesized two series of push-pull polyene molecules in which the acceptor group is an aldehyde functionality and the donor is either a dimethylaniline group or a benzodithia group. These molecules are sketched in Figure 1. Molecules containing polyene segments with up to 8 carbon-carbon double bonds were produced.¹¹ The second-order nonlinear optical properties of these compounds have been measured in solution by Barzoukas et al.¹² using the well-documented electric-field-induced second-harmonic generation (EFISHG) technique. The results of these measurements, which are illustrated in Figure 2, are especially interesting since they indicate the following: (i) These push-pull polyenes display among the

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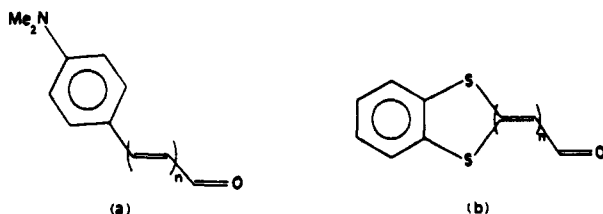


Figure 1. Sketch of the push-pull polyene molecules recently synthesized by Lehn and co-workers:^{10,11} (a) dimethylanilino polyenals; (b) benzodithia polyenals (n goes up to 8).

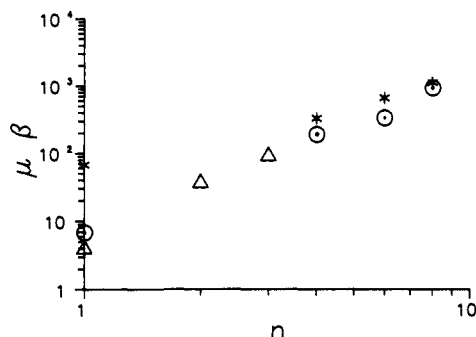


Figure 2. Results of the EFISHG measurements¹² on push-pull polyene molecules: evolution of the static $\mu\beta$ value as a function of the number (n) of double bonds in the polyenic segment. The circles [asterisks] refer to the benzodithia [dimethylanilino] polyenals. In addition, our calculated values for the dithiolenes are indicated by triangles. (Note that in order to take account of the different convention used for β in ref 12, the experimental values have been divided by a factor 3).

largest $\mu\beta$ values that have been reported so far (values reaching magnitudes up to 50 times larger than that of *p*-nitroaniline are obtained). This means that through adequate crystal engineering and subsequent (however hypothetical) molecular alignment along the polar axes, $\chi^{(2)}$ magnitudes 50 times superior to that in *N*-(4-nitrophenyl)-L-prolinol (NPP)¹³ could in principle be achieved. A more likely option in view of the difficulty of crystallizing long dipolar one-dimensional systems rests in their incorporation, either as dopants or covalently bonded side- or main-chain groups, in subsequently poled polymeric backbones.¹⁴ (ii) There is no sign of saturation appearing up to the longest systems studied (8 double bonds in the conjugated segment). Two other aspects are worth mentioning. First, for the shorter molecules, the dimethylanilino donor appears to be more effective than the benzodithia donor, while both donors lead to very similar $\mu\beta$ values in the longer molecules. Second, the evolution of $\mu\beta$ as a function of the number of double bonds, n , in the polyenic segment, is observed to go as $n^{2.1}$.

In order to gain a detailed understanding of the most interesting nonlinear optical properties presented by the dimethylanilino polyenal and benzodithia polyenal compounds, we have undertaken a complete theoretical characterization of their geometric structure, electronic properties, and first-order and second-order polarizabilities. The methodology we have followed is outlined in section II. We describe the results of the geometry optimizations in section III. Section IV is devoted to a discussion of the ground-state electronic properties such as dipole moments and charge distributions as well as of the nature of the lowest lying optical transitions. The first-order and second-order polarizabilities are presented in section V. The main conclusions of this work are summarized in the last section.

II. Methodology

All the calculations reported here, except for the investigation of the lowest optical transitions, have been carried out at the restricted Hartree-Fock (RHF) *ab initio* level. The molecules under study are closely

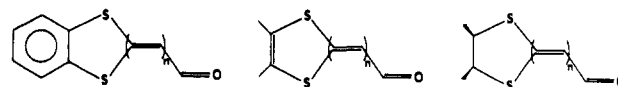


Figure 3. Sketch of the families of polyenal molecules considered in this work: (a) benzodithia polyenals, (b) dithiolenes polyenals, and (c) dithiolane polyenals. (The corresponding polyene compounds we have investigated simply lack the terminal aldehyde CHO group.)

related to the benzodithia polyenal series synthesized by Lehn and co-workers.¹¹ However, due to the size of these compounds, we have considered various simplifications. First, we have not taken into account the methyl groups that actually substitute some of the carbons of the polyenic segment (e.g., there are two methyl groups in the $n = 4$ molecule and four in the $n = 8$ molecule¹¹); the main purpose of these substituents is to add environmental stability to the polyenic segment, but they are obviously not interfering significantly with the conjugated system, making the computational cost of a full structure needlessly expensive. Second, though we have carried out a number of calculations taking explicitly into account the benzodithia group, we have also investigated molecules where the donor group has a simpler structure, the benzene being replaced by a double bond; this corresponds to a dithiolenes donor. Differences between the relative efficiencies of these two donors will be discussed in detail. Furthermore, we have studied a few compounds where the double bond of the dithiolenes group is saturated, leading to a dithiolane functionality. In addition, molecules which lack the acceptor group have also been investigated. The families of polyenal molecules investigated in the present work are displayed in Figure 3.

The geometry optimizations have been performed at the 3-21G split-valence basis set level¹⁵ with the GAUSSIAN-88 set of programs.¹⁶ All bond angles and all carbon-carbon and carbon-sulfur bond lengths were fully optimized, under the assumption of a coplanar structure. The carbon-hydrogen bond lengths were set at 1.075 Å, i.e., the average value they take in a conjugated system optimized at the 3-21G level.^{17a} Because of the limitations related to the size of the benzodithia group, the carbon-carbon bond lengths within the benzene rings were kept at 1.3846 Å, i.e., the 3-21G-optimized bond length in benzene.^{17b}

Furthermore, we found that the influence of the polyenic segment on the donor group geometry does not result in any significant departure from the local C_{2v} symmetry of the donor group. Therefore, the persistence of such a local symmetry was always assumed.

The static polarizability and hyperpolarizability tensor components have been calculated at the RHF/3-21G level with the HONDO-8 set of programs,¹⁸ on the basis of the 3-21G-optimized geometries, according to the methodology of Hurst et al.¹⁹ In the case of the shortest ($n = 1$) benzodithia, dithiolenes, and dithiolane polyenals, we have also carried out calculations including polarization or diffuse polarization basis functions in order to check the basis set dependence of our results. As will be shown in section V, we find that the 3-21G basis set (which is exclusively applied for the larger molecules) offers a reliable tool for the evolution of β , especially since our interest is in establishing trends between series of molecules rather than in predicting absolute (hyper)polarizability values.

The α and β components are calculated analytically via electric field derivatives of the Hartree-Fock self-consistent-field total energy, following a coupled-perturbed Hartree-Fock approach:¹⁹⁻²¹

$$E = E^{(0)} - \mu_i^{(0)} F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \dots$$

where the subscripts, which identify the tensor components, are summed over the Cartesian axes; $E^{(0)}$ is the unperturbed total energy; F_i is the component of the field in the i direction; $\mu^{(0)}$ is the permanent dipole

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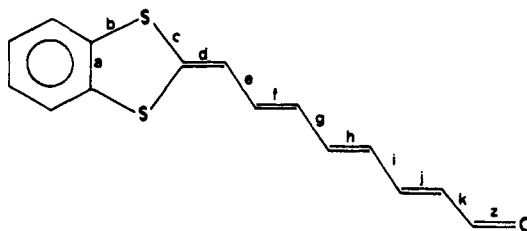
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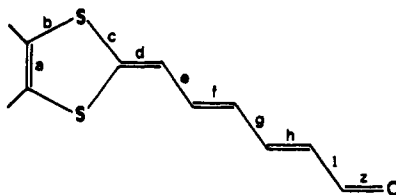
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Table I. 3-21G-Optimized Bond Lengths (Å) in Benzodithia Polyenes ($n = 1, 2, 4$), Benzodithia Polyenals ($n = 0, 1, 2, 4$), Hexatriene, and Octatetraene^a

n	b	c	d	e	f	g	h	i	j	k	z
Benzodithia Polyenes											
1	1.819	1.830	1.309								
2	1.817	1.830	1.316	1.462	1.321						
4	1.817	1.829	1.318	1.456	1.329	1.456	1.329	1.461	1.322		
Benzodithia Polyenals											
0	1.812	1.856									1.184
1	1.816	1.823	1.317	1.466							1.211
2	1.817	1.825	1.320	1.453	1.326	1.466					1.211
4	1.817	1.827	1.319	1.454	1.330	1.454	1.331	1.453	1.327	1.465	1.212
Hexatriene											
			1.322	1.462	1.327	1.462	1.322				
Octatetraene											
			1.322	1.461	1.328	1.457	1.328	1.461	1.322		
			(1.336)	(1.451)	(1.327)	(1.451)	(1.327)	(1.451)	(1.336)		

^a Bond length a is fixed to 1.3846 Å. In the case of octatetraene, the bond lengths determined from X-ray diffraction measurements²⁷ are indicated between parentheses.

Table II. 3-21G-Optimized Bond Lengths (Å) in Dithiolenes Polyenes ($n = 1, 2$) and Dithiolenes Polyenals ($n = 0-3$)

n	a	b	c	d	e	f	g	h	i	z
Polyenes										
1	1.310	1.812	1.838	1.309						
2	1.309	1.811	1.837	1.317	1.462	1.320				
Polyenals										
0	1.312	1.803	1.869							1.183
1	1.309	1.810	1.832	1.317	1.467					1.211
2	1.309	1.810	1.832	1.320	1.453	1.326	1.466			1.211
3	1.309	1.810	1.833	1.320	1.454	1.330	1.453	1.326	1.465	1.212

moment of the molecule; and α and β are the static first- and second-order dipole polarizability tensors.

It is important to stress that, in linear polyenes, a Hartree-Fock approach does not provide the correct ordering of the lowest lying excited states. Hartree-Fock leads to S_1 being the $1B_u$ excited state and S_2 the $2A_g$ excited state, while the reverse is found experimentally.²² Correlation effects need to be taken into account to provide the correct relative location of these states.²² However, this Hartree-Fock deficiency has no influence on the description of the (hyper)polarizabilities since the $2A_g$ state has small transition dipole moments with other states (even at the correlation level) and does not play any significant role in the nonlinear optical response of linear polyenes.^{23,24}

In the rest of this paper, we quote the total dipole moments μ in debyes. The average polarizabilities $\langle\alpha\rangle$ are expressed in electrostatic units, esu, or angstroms cubed (with 1 atomic unit of first-order polarizability equal to 0.1482×10^{-24} esu = 0.1482 \AA^3):

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The β hyperpolarizabilities are expressed in terms of (with 1 atomic unit of second-order polarizability equal to 0.8633×10^{-32} esu):

$$\beta_\mu = \frac{\beta \cdot \mu}{\|\mu\|} = \frac{\sum_{ij} \beta_{ij} \mu_i}{(\sum_i \mu_i^2)^{1/2}} \quad \|\beta\| = \frac{\beta_\mu}{\cos \theta}$$

where θ is the angle present between the β and μ vectors.

The energies of the highest occupied and lowest unoccupied molecular orbitals are calculated using the valence effective Hamiltonian technique²⁵ on the basis of the 3-21G-optimized geometries. This nonempirical pseudopotential method is known to yield good estimates for the ionization potentials and electron affinities in conjugated molecules. Our objective here is to obtain a qualitative understanding of the nature of the one-electron levels involved in the lowest electronic transitions. In addition, we have also carried out intermediate neglect of differential overlap²⁶ (INDO) calculations, including configuration interaction among

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all singly excited π levels (INDO/SCI), in order to evaluate the energies and transition intensities for the lowest lying excited states. A few calculations including doubly excited states (INDO/SDCI), thus allowing correlation with the ground state, have also been performed (the double excited configurations are built by considering the upper six occupied levels and the lower six unoccupied levels).

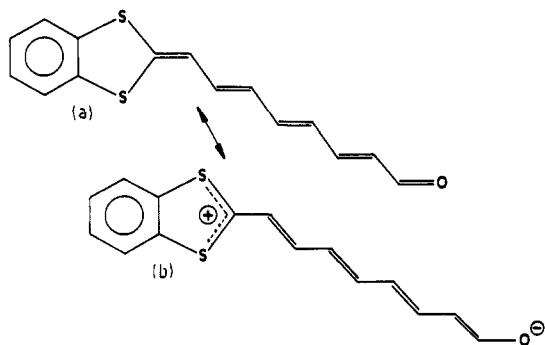
III. Geometric Structures

In order to precisely determine the influence of the donor and acceptor groups on the geometry of the polyenic segments, we have also optimized the geometry of 1,3,5-hexatriene and 1,3,5,7-octatetraene. In Tables I–III, we present the main optimized geometry parameters for (i) the benzodithia polyenes ($n = 1, 2, 4$) and polyenals ($n = 0, 1, 2, 4$), (ii) dithiolenes polyenes ($n = 1, 2$) and polyenals ($n = 0-3$), and (iii) dithiolane polyene ($n = 1$) and polyenal ($n = 1$), respectively. The results for hexatriene and octatetraene are given in Table I, where we also provide the experimental carbon-carbon bond lengths for octatetraene, as determined from X-ray diffraction measurements.²⁷

From Table I, it is seen that the 3-21G-calculated bond lengths for octatetraene are in excellent agreement with X-ray data of Baughman et al.²⁷ The only qualitative discrepancy is to be found in the fact that the inner double bonds are calculated to be slightly longer than the outer double bonds, as should be expected from conjugation effects, while the X-ray data indicate the opposite trend. However, Baughman et al.²⁷ pointed out that the difference they measured for the double bonds was statistically not significant.

From the results on benzodithia polyenes, we observe that the influence of the benzodithia group on the polyenic segment is small and limited to the adjacent double bond and single bond. In the $n = 4$ compound, these two bonds slightly shorten by ~ 0.004 Å; in the middle of the polyenic segment, the degree of bond-length alternation (i.e., the difference between the length of a double bond and that of an adjacent single bond) goes down very slightly to 0.127 Å from the 0.129-Å octatetraene value, which does not constitute a significant decrease. The situation is hardly changed in the push-pull benzodithia polyenal molecules. For instance, the degree of bond-length alternation in the middle of the polyenic segment in the $n = 4$ compound is 0.123 Å, which is only 0.006 Å smaller than in octatetraene. It might be pointed out that the CHO acceptor group affects in a stronger way the double and single bonds of the polyenic segment immediately connected to it. Indeed, the double bond linked to the CHO group increases by 0.005 Å (up to 1.327 Å from 1.322 Å in octatetraene) and the next single bond shortens by 0.008 Å (down to 1.453 Å from 1.461 Å). However, this is simply due to the fact that these two bonds of the polyenic segment are no longer located at the end of the molecule due to the extension of the conjugation provided by the C=O double bond.

From the geometry standpoint, the contribution from resonance form b (sketched below) to the molecular structure of benzodithia



polyenals is thus found to be negligible (a result which is confirmed by INDO/SDCI calculations). By and large, the same conclusions

Table III. 3-21G-Optimized Bond Lengths (Å) in Dithiolane Polyene ($n = 1$) and Dithiolane Polyenal ($n = 1$)

	a	b	c	d	e	z
dithiolane polyene	1.542	1.893	1.822	1.310		
dithiolane polyenal	1.540	1.892	1.816	1.318	1.466	1.212

Table IV. 3-21G Average First-Order Polarizabilities (α) (Å³ or 10⁻²⁴ esu), Dipole Moments μ (D), $\mu\cdot\beta$ Values (10⁻⁴⁸ esu), and Second-Order Polarizabilities β_μ and $\|\beta\|$ (10⁻³⁰ esu) for the Molecules Investigated in This Work^a

n	$\langle\alpha\rangle$	μ	$\mu\cdot\beta$	$\cos\theta$	β_μ	$\ \beta\ $
Benzodithia Polyene						
1	14.73	1.40	-1.93	-1.0	-1.38	1.38
2		1.30				
4		1.18				
Dithiolenes Polyene						
1	9.28	1.02	-0.12	-1.0	-0.12	0.12
2	13.33	0.91	1.43	0.95	1.58	1.67
Benzodithia Polyenals						
0	13.20	4.79	-7.50	-1.0	-1.57	1.57
1	17.12	5.76	0.26	0.04	0.05	1.11
2		6.10				
4		6.45				
Dithiolenes Polyenals						
0	8.04	4.04	-4.81	-1.0	-1.19	1.19
1	11.40	5.12	4.19	0.72	0.82	1.14
2	16.15	5.52	38.98	0.94	7.06	7.52
3	21.79	5.79	97.60	0.96	16.87	17.63
Dithiolane Polyenal						
1	11.94	6.27	7.06	0.76	1.12	1.47

^a We also include the values of $\cos\theta$, where θ is the angle present between the β and μ vectors.

apply when we investigate the dithiolenes and dithiolane compounds. We note that, in the dithiolenes molecules, the sulfur-carbon bonds [not] connected to the polyene path are calculated to be ~ 0.01 Å [shorter] longer than in the corresponding benzodithia systems, without this affecting the polyenic segment. In the dithiolanes, the C-S bonds connected to the single C-C bond elongate significantly up to 1.89 Å, while the other C-S bonds are slightly shorter (by 0.007–0.009 Å) than in the corresponding benzodithia compounds. (Note that C-S bond lengths are always overestimated by ~ 0.1 Å at the 3-21G level.¹⁵)

IV. Charge Distributions, Dipole Moments, and Electronic Transitions

The atomic charge distributions described in this section are calculated from a Mulliken population analysis, with the hydrogen contributions summed into the carbons they are covalently bonded to. Due to the arbitrariness involved in such an analysis, only the qualitative trends among the related series of molecules we investigate will be emphasized. The 3-21G atomic charges calculated in this way are collected for some representative compounds in Figure 4 and the dipole moments in Table IV.

In the benzodithia polyene compounds, we observe that the dipole moment is rather low and decreases as the length of the polyenic segment increases (from $\mu = 1.40$ D for $n = 1$ to $\mu = 1.18$ D for $n = 4$). The charge distribution within the donor group is key to the understanding of this decrease. The sulfur atoms are highly positive while the carbon atoms connected to them carry a large negative charge, in particular the carbon atom starting the polyenic segment (see Figure 4). As a result, the dipole has its negative pole toward the polyenic segment and its positive pole toward the benzene ring. However, the external part of the polyene

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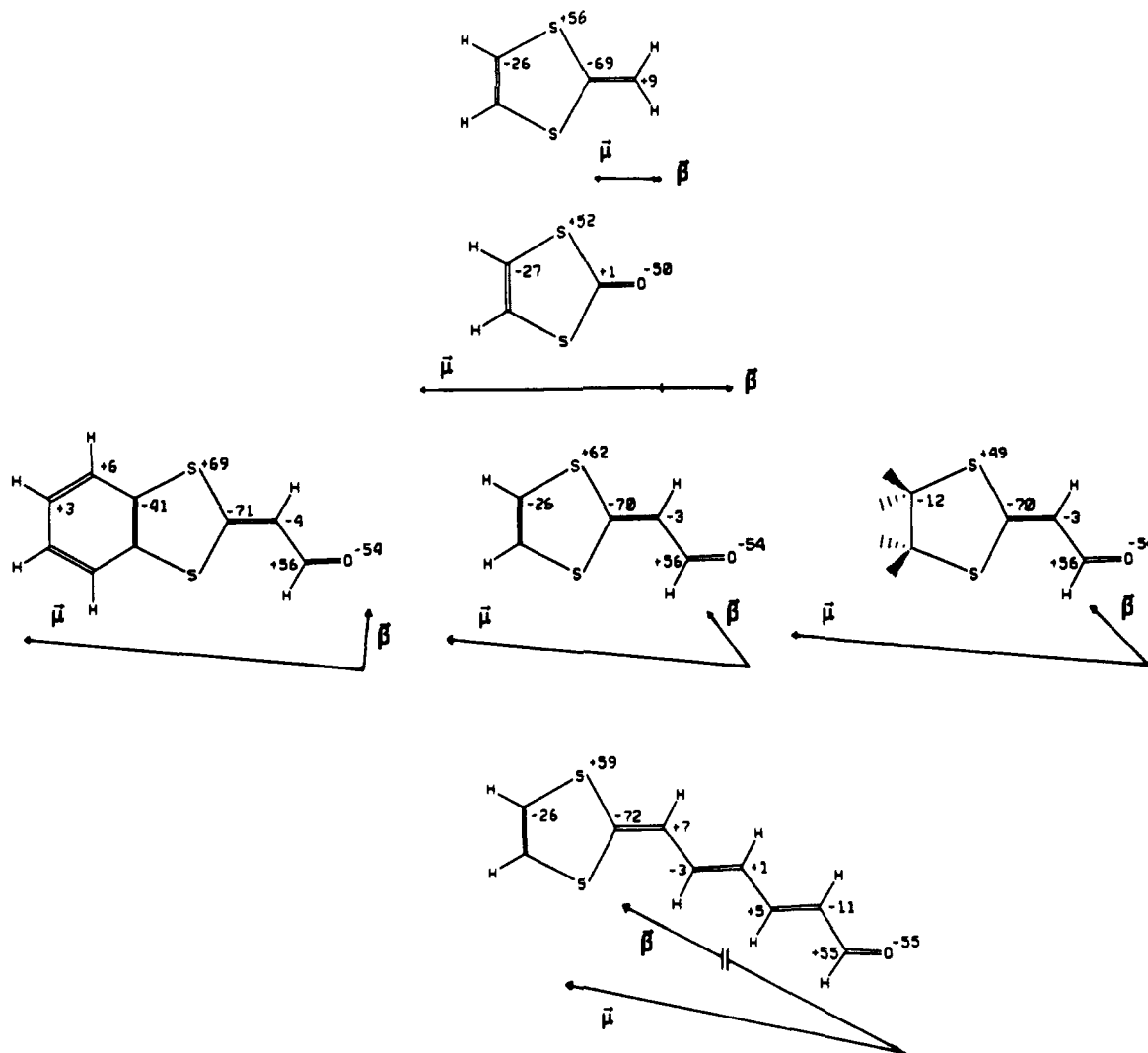


Figure 4. 3-21G atomic charges ($10^{-2} |e|$ units) of some representative molecules, with sketches of the relative orientations of the dipole moment μ and second-order polarizability β vectors.

segment carries a slightly positive charge. When the polyene segment extends, the positive charge carried by its external part spreads over a broader range, a feature which decreases the net dipole moment.

In the corresponding polyenal molecules, the dipole moment is significantly larger by about 4.5–6.5 D. This is easily understood as the polarization of the C=O bond itself considerably increases the negative pole at that end of the molecule as compared to the unsubstituted polyene end. Accordingly, the dipole moment now increases with the extension of the polyene path. It should be pointed out that the aldehyde group does not much affect the atomic charges that are localized along the polyenic segment. Only the two carbons immediately adjacent to the CHO group do get slightly polarized. This result is fully consistent with the very small geometry modifications imposed by the push and pull groups to the polyene segment.

A major result of our calculations is that we observe that, in the ground state, *there is negligible charge transfer all the way from the donor to the acceptor*. In other words, both the donor group and the acceptor group remain globally neutral and only induce a small polarization around them. This confirms the negligible contribution to the ground state from resonance form b sketched in the previous section. As a result, the evolution of the ground-state dipole moment value as a function of the number of double bonds in the polyene path is extremely weak.

As in the case of the geometry, the situation in the dithiolenes and dithiolane compounds parallels that in the benzodithia molecules. The dipole moments in the dithiolenes are roughly 0.5 D lower and those in the dithiolanes ~ 0.5 D larger than in

the corresponding benzodithia derivatives, as a result of the slight charge rearrangements at the extremity of the donor group (see Figure 4 and Table IV).

We have also found it of interest to obtain a qualitative insight into the first optical transitions arising in these push-pull polyenes, in order to have a better understanding of the low-lying excited states playing a role in the polarizabilities. In the polyene molecules with $n = 1$ and the polyenal molecules with $n = 0$, the point group symmetry is C_{2v} (by convention, the long [short] axis of the molecules corresponds to the Z- [Y-] axis and YZ defines the molecular plane). The π molecular orbitals belong to the a_2 and b_1 irreducible representations. Transitions among π levels of the same symmetry are polarized along the Z-axis (which, in the case of the push-pull molecules, corresponds to the charge-transfer axis); transitions from a_2 to b_1 or vice versa are polarized along the Y-axis. In the longer molecules, the C_{2v} symmetry is almost preserved and can still provide a reasonable framework for the discussion.

The evolution of the highest two occupied and lowest two unoccupied one-electron π levels, as calculated by VEH, is illustrated in Figure 5 for some of the benzodithia polyene and benzodithia polyenal compounds. We first discuss the benzodithia polyene $n = 1$ system. The HOMO-1 and LUMO levels possess a_2 symmetry, i.e., they are antisymmetric with respect to the XZ mirror plane. As a result, there is no contribution to these levels coming from the polyenic (or polyenal) segment. This remains valid even when the polyene (or polyenal) segment gets more extended so that these a_2 levels always appear at the same energies (-9.15 and -3.35 eV) and are fully localized within the benzo-

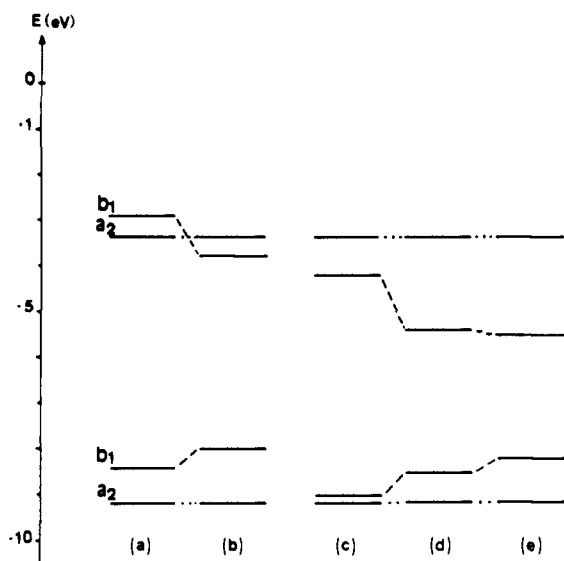


Figure 5. Evolution of the VEH-calculated energies (eV) for the highest two occupied and lowest two unoccupied molecular orbitals in benzodithia polyene ($n = 1, 2$) compounds (labeled a and b, respectively) and benzodithia polyenal ($n = 0, 1, 2$) compounds (labeled c-e, respectively).

dithia group. The HOMO and LUMO+1 levels have b_1 symmetry and contributions from all the π atomic orbitals of the molecule. When examining the electronic transitions, we find that both the HOMO to LUMO and HOMO to LUMO+1 transition (which are Y - and Z -polarized, respectively) actually lead to a charge transfer from the dithia polyene part of the molecule toward the benzene part. As a result, *there is a change in the direction of the dipole moment of the corresponding excited states with respect to the ground state.* This analysis is fully confirmed at the INDO/SCI level of calculations: the lowest two excited states, which are dominated respectively by the HOMO to LUMO and HOMO to LUMO+1 transitions, have dipole moments of -6.16 and -5.97 D, to be compared to the $+1.65$ -D INDO value in the ground state.

In the $n = 2$ benzodithia polyene system, the a_2 levels do not move relative to their locations in the $n = 1$ compound for the reason mentioned above, while the b_1 levels undergo a strong evolution as they possess large contributions from the polyenic segment. The HOMO level shifts upward by ~ 0.3 eV, and the first unoccupied b_1 level shifts downward by 0.4 eV, thereby becoming the LUMO level. As the LUMO level is mostly localized within the polyene segment, the HOMO to LUMO transition (which possesses the largest oscillator strength) leads to a charge transfer from the benzodithia group toward the polyene segment. This leads to a dipole moment in the corresponding excited state which is larger than in the ground state and in the same direction. At the INDO/SCI level, the dipole moment component along the long axis of the molecule evolves from $+1.64$ D in the ground state to $+8.79$ D in the lowest excited state, which is fully dominated by the HOMO to LUMO transition.

In the benzodithia polyenal molecules, the presence of the oxygen atom does not affect the a_2 levels but leads to a strong stabilization of the b_1 levels with respect to the benzodithia polyene systems. In the $n = 0$ compound, the HOMO and LUMO levels have both b_1 symmetry. The evolution when the polyenic segment is extended is globally the same as for the benzodithia polyenes.

Once again, the same picture holds for the dithiolene and dithiolane compounds. There is, however, one major difference: the transitions which imply a charge transfer from the polyene segment to the donor-group extremity of the molecule get weaker as one goes from the benzodithia to the dithiolene and from the dithiolene to the dithiolane. This is easily understood as the capacity of that extremity to capture π charge is reduced when passing from benzene to a double bond and to a single bond. This feature has to be borne in mind when we discuss the second-order polarizabilities in the next section.

Table V. Basis Set Dependence of the $\langle\alpha\rangle$ (10^{-24} esu) and $\|\beta\|$ (10^{-30} esu) Values for the $n = 1$ Benzodithia Polyenal, Dithiolene Polyenal, and Dithiolane Polyenal Compounds^a

	3-21G	DZP	DZP diffuse
Benzodithia Polyenal			
$\langle\alpha\rangle$	17.12	19.02	21.26
$\ \beta\ $	1.11	1.45	1.38
Dithiolene Polyenal			
$\langle\alpha\rangle$	11.40	12.49	14.33
$\ \beta\ $	1.14	1.61	1.12
Dithiolane Polyenal			
$\langle\alpha\rangle$	11.94	13.04	14.75
$\ \beta\ $	1.50	1.78	1.27

^aThe basis sets under consideration are 3-21G,¹⁵ DZP,^{18,28} and DZP, where the polarization functions are diffuse (see text).

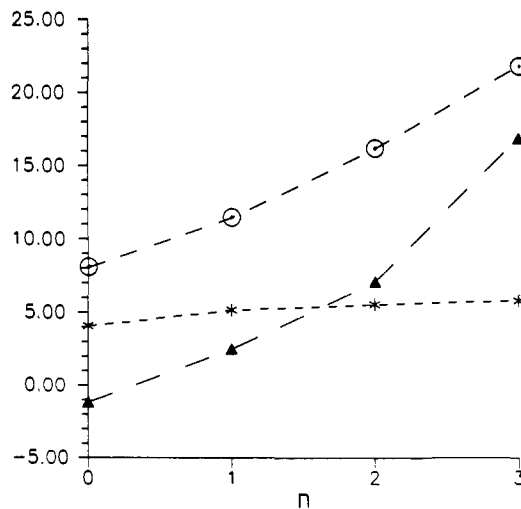


Figure 6. Evolution as a function of the number of double bonds (n) in the polyenic segment, of the calculated dipole moments μ (D; asterisks), average first-order polarizabilities $\langle\alpha\rangle$ (\AA^3 ; circles), and second-order polarizabilities β_μ (10^{-30} esu; filled triangles) for the dithiolene polyenals.

Finally, it is interesting to note that the INDO/SDCI calculations indicate that the evolution, as a function of polyene segment length, of the dipole moment in the first (charge-transfer) excited state is very weak. For instance, for the $n = 1-3$ dithiolene polyenal molecules, the dipole moments in the first excited state are 15.4 ($n = 1$), 16.9 ($n = 2$), and 17.7 D ($n = 3$). This is due to the fact that the charge transfer from the donor to the acceptor decreases with chain length; for these three molecules, the INDO/SDCI net charges carried by the CHO acceptor group in the excited state evolve from -0.48 $|e|$ ($n = 1$) to -0.40 $|e|$ ($n = 2$) and -0.36 $|e|$ ($n = 3$).

V. First-Order and Second-Order Polarizabilities

In Table IV, we present the 3-21G-calculated average first-order polarizabilities, $\langle\alpha\rangle$, together with the products $\mu\beta$, the β_μ values, and the intrinsic $\|\beta\|$ values. The β_μ values correspond to the projection of the vector part of the second-order polarizability onto the dipole axis; therefore, we also indicate the angle, θ , present between the μ and β vectors. The following molecules have been investigated: the $n = 0$ benzodithia polyenes, the $n = 0-1$ dithiolene polyenes, the $n = 0-1$ benzodithia polyenals, the $n = 0-3$ dithiolene polyenals, and the $n = 1$ dithiolane polyenal. Table V illustrates the basis set dependence of the $\langle\alpha\rangle$ and $\|\beta\|$ values for the three $n = 1$ polyenal molecules. Figure 6 depicts the very different evolutions of μ , $\langle\alpha\rangle$, and β_μ as a function of n , to be discussed below.

From Table V, we observe that the $\langle\alpha\rangle$ and $\|\beta\|$ values do not change significantly when we switch from a 3-21G basis set to a double- ζ basis set including polarization functions (DZP basis set^{18,28}) or diffuse polarization functions (same basis set as DZP

but $\zeta_{\text{Cd}} = 0.20$; $\zeta_{\text{Od}} = 0.20$; $\zeta_{\text{Sd}} = 0.15$; $\zeta_{\text{Hp}} = 0.10$). The absolute $\langle \alpha \rangle$ values slightly increase but the relative values are not changed. For $\|\beta\|$, we observe a small increase in going from 3-21G to DZP, followed by a small decrease (which will be rationalized below) when the polarization functions are made diffuse; the absolute values are so similar for all three compounds that the basis set modifications lead to variations in the relative values that are hardly significant. The 3-21G results thus appear reliable and will be discussed in the rest of this paper.

The average first-order polarizabilities are calculated to be all of the same order of magnitude; see Table IV. The benzodithia compounds have $\langle \alpha \rangle$ values that are $\sim 50\%$ larger than for the corresponding dithiolenes, which reflects the contribution of the benzene ring. For the sake of comparison, we note that the average polarizability calculated for *p*-nitroaniline with the same 3-21G basis set is 10.5 \AA^3 , i.e., a value intermediate between those for the $n = 0$ and $n = 1$ dithiolenes (8.0 and 11.4 \AA^3 , respectively). From the $\langle \alpha \rangle$ values obtained for the $n = 1$ -3 dithiolenes, we observe that the evolution of $\langle \alpha \rangle$ as a function of the number of double bonds in the polyenic segment is rather weak and goes approximately as $n^{0.6}$ (Figure 6). This is significantly smaller than what is calculated at the ab initio level for unsubstituted polyene molecules where $\langle \alpha \rangle = n^{1.7}$.²⁹

We now turn to the discussion of the hyperpolarizabilities. The first observation is that the values of $\mu\text{-}\beta$ or β_μ can differ by over 2 orders of magnitude among the different compounds investigated in this work. Second, for the compounds where there is only one C=C or C=O double bond attached to the benzodithia or dithiolenes group, the hyperpolarizabilities have a negative sign. See the opposite signs of the μ and β vectors illustrated for these molecules in Figure 4. Following the two-state model, this observation is indicative of a change in the direction of the dipole moment when going from the ground state to the main (charge-transfer) excited state. This feature is consistent with the discussion provided in the previous section about the charge transfer taking place upon electronic excitation in the shortest molecules. As the polyene segment extends, the $\mu\text{-}\beta$ and β_μ values become positive, which implies that the dipole moments in the ground and excited states have the same direction.

It is interesting to compare the 3-21G β_μ values calculated for the $n = 1$ polyenal systems. The β_μ goes from $+0.05 \times 10^{-30}$ esu in the benzodithia compound to $+0.8 \times 10^{-30}$ and $+1.1 \times 10^{-30}$ esu in the dithiolenes and dithiolane compounds, respectively. These results can be understood in the following way. In all the benzodithia, dithiolenes, and dithiolane groups, the donors are the sulfur atoms. The presence of conjugated carbons to the other side of the sulfurs with respect to the conjugated polyenic path connecting the sulfurs to the acceptor groups actually counteracts the efficiency of the push-pull system and much more strongly so in the benzodithia group than in the dithiolenes group. (We note that this effect is emphasized when we use diffuse polarization functions, which explains the decrease in the $\|\beta\|$ values when going from a DZP to a DZP diffuse basis set; see Table V.) It is striking to observe in Figure 4 that, in the benzodithia molecule, the 3-21G μ and β vectors are almost perpendicular to one another ($\theta = 87.6^\circ$); the θ angle goes down to 44.0° and 40.2° in the dithiolenes and dithiolane molecules, respectively. When the polyenic segment becomes longer, the relative influence of the benzene ring or the double bond to the other side of the sulfurs considerably weakens and we should expect the three donors to lead to very similar β values. Furthermore, we also see from Figure 4 that the θ angle between the μ and β vectors decreases when the polyenic segment extends ($\theta = 16.7^\circ$ for the $n = 3$ dithiolenes molecule).

This analysis allows us to rationalize the experimental observation mentioned in the introduction¹² that, in the short compounds, the dimethylanilino donor appears to be much more effective than the benzodithia donor while both groups provide

similar $\mu\text{-}\beta$ values in the longer molecules. We note that, in the dimethylanilino group, the benzene ring is located along the conjugated path in-between the donor and the acceptor, thereby effectively increasing the conjugation length by an amount corresponding approximately to 1.5 double bonds; it is not located outside of the donor-acceptor conjugated path as in the benzodithia group.

In the dithiolenes polyenals, the extension of the polyenic segment from $n = 0$ to $n = 3$ results in a strong increase of the calculated $\mu\text{-}\beta$ values, which are found to be in good agreement with the static $\mu\text{-}\beta$ experimental data for the benzodithia polyenals, illustrated in Figure 2. The $\mu\text{-}\beta$ values are calculated to evolve roughly as $n^{2.9}$ (the μ and β evolutions being individually displayed in Figure 6). The experimental evolution of $\mu\text{-}\beta$ is actually less strongly dependent on n ($\mu\text{-}\beta \approx n^{2.4}$ (ref 12) or $\mu\text{-}\beta \approx n^{2.1}$ (ref 30)). This discrepancy can come from a number of factors, among them the possible limitations of our computational procedure, which does not include correlation effects or the influence of the solvent (we recall that the EFISHG measurements are performed in solution). Furthermore, we should point out that, in equivalent EFISHG measurements on α -*p*-methoxyphenyl- ω -*p*-nitrophenyl polyenes with $n = 1$ -5, Huijts and Hesselink³¹ have recently reported a $\mu\text{-}\beta$ evolution as $n^{3.0}$ while earlier data published by Dulcic et al.³² provide an evolution as $n^{2.1}$; this stresses the difficulty in assessing precise power law dependences on n when one is dealing with rather limited sets of experimental or theoretical points. In any case, the fact that the power law is strongly superlinear indicates that the lengths of all the oligomers investigated in this paper are well below the saturation regime in which the power dependencies turn into linear ones. Note that the saturation regime is reached much more quickly in *p*-phenylene oligomers.^{34,35}

The $n = 3$ dithiolenes polyenal molecule can be compared directly to *p*-nitroaniline since, in both cases, the conjugated path between the donor and the acceptor contains 6 π electrons. The polyenal molecule is calculated to present a β_μ value which is over 2 times larger than in *p*-nitroaniline (16.9×10^{-30} vs 7.9×10^{-30} esu³⁵). This fully illustrates the larger efficiency of polyenes over phenylenes in terms of second-order polarizabilities, a feature which is by now well documented.^{7,8,33,34,38}

A major motivation for theoretical estimations of β values comes from two intrinsic limitations of the EFISHG measurements:

(i) The second-harmonic nonlinear polarization generated in a solution under the combined influence of the squared fundamental laser field and the poling voltage actually depends on both first-order and second-order nonlinear processes. The former one is of mixed orientational and electronic origins and is proportional to $\mu\text{-}\beta/kT$, while the latter relates to the scalar part of γ and is of purely electronic origin. As shown in ref 30, it is possible to disentangle the two contributions by performing additional third-harmonic generation measurements at different wavelengths and further relate the THG $\gamma(-3\omega;\omega,\omega,\omega)$ value to the corresponding EFISHG $\gamma(-2\omega;\omega,\omega,0)$ value by an adequate two- or three-level dispersion model. Although the contribution of the cubic nonlinearity to the EFISHG overall susceptibility has been found to be on the order of 20% at most for the longer polyenes

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($n = 8$), it is convenient to have, as done here, a direct evaluation method of β which is free of higher order contamination.

(ii) The second problem has to do with the evaluation of the deviation angle between μ and β . If one is interested in poled polymers¹⁴ where the nonlinearity originated from oriented chromophores, the SHG or electrooptic coefficient is a higher order Langevin function of $\mu \cdot \beta$, which reflects the statistical ordering of the medium. Knowledge of $\mu \cdot \beta$ is essential but is hardly sufficient if one is interested in the actual magnitude of β in order to guide further molecular optimization studies. As shown in this work, possibly high values of β might lead to low $\mu \cdot \beta$ values when the deviation angle θ comes close to 90° . It is therefore essential to have direct access to θ values, such as provided here by theoretical estimations. (In this context, the synthesis and nonlinear optical characterization of the $n = 1$ benzodithia polyenal compound where $\theta \approx 90^\circ$ would be of interest.)

VI. Synopsis

We have presented a detailed theoretical study of a series of benzodithia polyenal molecules and related compounds, which present among the largest molecular second-order polarizabilities ever measured.

Our calculations have addressed a variety of properties of these molecules: geometric structure, charge distributions, dipole moment, electronic transitions, and first-order and second-order polarizabilities. From our results, we can draw the following conclusions.

The geometric structure of the polyenic segment is not affected in any significant way by the presence of the donor and acceptor groups. The ground-state charge distributions indicate that charge polarization occurs *within* the donor and acceptor groups with little linkage via the polyene segments. As a result, it can be stated that, in the ground state, *there is negligible charge transfer all the way from the donor to the acceptor*, a behavior which has also been brought to light both experimentally³⁶ and theoretically,³⁷ in the case of push-pull diphenyl polyynes. Accordingly, the ground-state dipole moment of the dithia polyenal compounds is calculated to be very weakly dependent on the number of double bonds in the conjugated path.

The average first-order polarizabilities are found to be of the same order of magnitude in all the compounds we have investigated ($(10-20) \times 10^{-24}$ esu) and are comparable to the value calculated for *p*-nitroaniline. In the dithiolenepolyenals, $\langle \alpha \rangle$ evolves as $n^{0.6}$. In marked contrast to the $\langle \alpha \rangle$ values, the $\mu \cdot \beta$ values range over

2 orders of magnitude. Very good agreement is obtained with the experimental data.

In the molecules presenting only one C=C or C=O double bond attached to the donor group, the second-order polarizability possesses a negative sign. This originates from the fact that the lowest dominant optical transitions involve a charge transfer from the polyene or polyenal segment toward the donor-group extremity of the molecule. Since this feature disappears in the longer molecules, it explains the experimental observation that the dimethylanilino and benzodithia polyenals gradually tend toward the same $\mu \cdot \beta$ values, as the polyene path extends. This is also clearly illustrated by the analysis of the deviation angle θ between μ and β in the different compounds.

The $\mu \cdot \beta$ values are calculated to evolve as $n^{2.9}$, while the experimental $\mu \cdot \beta$ evolution has been recently reported to be about $n^{2.4} - n^{2.1}$. This strongly superlinear dependency indicates that the lengths of even the longest push-pull polyene oligomers referred to in this work are still well below the saturation regime.

In summary, we believe that the combinations of theoretical calculations, such as those performed here, are very useful in order to provide a detailed interpretation of experimental data on organic molecules with large hyperpolarizabilities and gain further insight into the electronic mechanism underlying and eventually enhancing such processes.

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Registry No. Benzodithiapolyene ($n = 1$), 139199-94-3; benzodithiapolyene ($n = 2$), 139199-95-4; benzodithiapolyene ($n = 4$), 139199-96-5; benzodithiapolyenal ($n = 0$), 139199-97-6; benzodithiapolyenal ($n = 1$), 87815-67-6; benzodithiapolyenal ($n = 2$), 139199-98-7; benzodithiapolyenal ($n = 4$), 139199-99-8; hexatriene, 2235-12-3; octatetraene, 1482-91-3; dithiolenepolyene ($n = 1$), 139200-00-3; dithiolenepolyene ($n = 2$), 139200-01-4; dithiolenepolyenal ($n = 0$), 133950-38-6; dithiolenepolyenal ($n = 1$), 88313-06-8; dithiolenepolyenal ($n = 2$), 133940-07-5; dithiolenepolyenal ($n = 3$), 133940-08-6; dithiolanepolyene ($n = 1$), 76368-26-8; dithiolanepolyenal ($n = 1$), 139200-02-5.