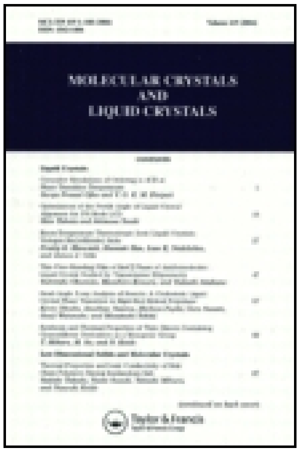

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Polyacetylenes: From Conduction Properties to Nonlinear Optics

J. L. Bredas [a], J. M. Toussaint [a] & F. Meyers [a]
[a] Service de Chimie des Matériaux Nouveaux, Université de Mons, Département des Matériaux et Procédés, avenue Maistriau 21, B-7000, MONS, BELGIUM

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POLYACETYLENES: FROM CONDUCTION PROPERTIES TO NONLINEAR OPTICS

J.L. BREDAS, J.M. TOUSSAINT, AND F. MEYERS

Service de Chimie des Matériaux Nouveaux, Département des Matériaux et Procédés, Université de Mons, avenue Maistriau 21, B-7000 MONS (BELGIUM)

Abstract We investigate two series of all-trans polyacetylene oligomers, i.e. linear polyenes. In the first case, we focus on unsubstituted polyenes and examine the geometry relaxation process in S_1, which is the first singlet, one photon optically-allowed, B_u excited state. Calculations are performed at various levels of sophistication, from a simple Su-Schrieffer-Heeger (Hückel-like) Hamiltonian up to Pariser-Parr-Pople single CI and Restricted Hartree-Fock ab initio Hamiltonians. It is found that explicit consideration of the electron-lattice coupling is essential to the description of the geometry relaxation in S_1, which takes the form of a two-soliton configuration. Such a configuration cannot be described by the bond order-bond length relationships that have traditionally been used in this context. Influence on the nonlinear optical properties is discussed. In the second case, we study the electronic structure and second-order polarizability (ß) of a series of push-pull polyenes, benzodithiapolyenals. These compounds have recently been reported to present among the largest µ.ß values ever measured. The theoretical results allow for a complete understanding of the properties of these systems.

INTRODUCTION

Since the discovery that polyacetylene can be made highly conductive through doping with electron donors or acceptors,[1] extensive theoretical and experimental works have been devoted to this polymer. These have for example led recently to the synthesis of a new type of polyacetylene which exhibits conductivities after doping as high as that of copper.[2,3]

Most of the peculiar electrical, optical, and magnetic properties appearing upon doping of polyacetylene have been rationalized by invoking the formation of nonlinear elementary excitations of soliton-type.[4,5] Solitons in all-trans polyacetylene are topological kinks that produce a reversal of the bond alternation pattern (see Figure 1). It takes about seven to ten bonds (i.e., 15 to 20 carbon atoms) for the bond alternation reversal to be complete. The presence of solitons on a polyacetylene chain also affects the polymer electronic structure: localized electronic states associated to solitons appear around midgap and thus produce novel subgap optical transitions that can be detected on doping.

FIGURE 1. Reversal of the bond alternation pattern induced by the presence of a soliton along a polyacetylene chain.

Following the pioneering work of Sauteret et al,[6] it has been realized that conjugated polymers inherently possess very high nonlinear optical responses.[7,8] It has been recently pointed out that the influence of electron-lattice coupling and e.g. of the presence of nonlinear elementary excitations such as solitons could also be significant for the nonlinear optical properties.[9-13] In all-trans polyacetylene, photoexcitation produces electron-hole pairs that are found to decay very rapidly (in 10^{-13} sec.) into pairs of separated, positively and negatively charged, solitons[14-16] (in agreement with the early theoretical predictions of Su and Schrieffer[17]). It is important to note that such a process results in an efficient charge separation mechanism, a feature essential to provide large optical nonlinearities.[18] In the off-resonance regime, instantons (i.e., virtual soliton-antisoliton pairs)[19] have been suggested to yield enhanced optical nonlinearities with respect to a purely rigid lattice situation.[8-10]

In short polyenes, spectroscopic studies indicate that strong geometry relaxations can take place in the first B_u one-photon optically-allowed excited state.[20] These geometry relaxations are traditionally modeled theoretically using Bond Order/Bond Length (BOBL) relationships.[21] In this framework, the geometry relaxations are calculated to become smaller as the chain length increases and tend to be negligible for chains containing over 15-20 carbon atoms.[22-24] Such an evolution is, however, inconsistent with the situation appearing in long chains (i.e., polyacetylene) where the first B_u state strongly relaxes to produce a pair of charged solitons, as mentioned above.[14,15,25]

Therefore, in this paper, we review the calculations we have performed in order to remove the inconsistency between the traditional understanding of the $1B_u$ relaxation process in short polyenes and the perception of the situation prevailing in all-trans polyacetylene. First, we investigate the relaxation process in the $1B_u$ excited state of polyene chains by means of the methodology of Su, Schrieffer, and Heeger,[4] as adapted by Brédas et al.[26] We make use of a Hückel Hamiltonian with bond-length dependent transfer integrals and σ-bond compressibility. We study chains ranging from 10 to 58 carbon atoms in order to understand the evolution when going from short to long polyene chains. Second, calculations are carried out at a much higher level of sophistication (combined Restricted Hartree-Fock ab initio / Pariser-Parr-Pople Configuration Interaction level) for three polyene molecules: hexatriene (C_6H_8), decapentaene ($C_{10}H_{12}$), and tetradecaheptaene ($C_{14}H_{16}$). Finally, we report on ab initio calculations of the electronic structure and second-order polarizability of a series of push-pull polyene molecules, based on benzodithiapolyenals. Our motivation is that such compounds have recently been shown to present among the largest $\mu.\beta$ values ever measured.

Su-Schrieffer-Heeger Hamiltonian Approach

In order to be in a position, on the one hand, to examine the evolution in going from short to long polyenes and, on the other hand, to make the comparison to polyacetylene, we have chosen to work first at the Su-Schrieffer-Heeger Hamiltonian level. This corresponds to a Hückel technique with bond-length dependent transfer integrals and σ-bond compressibility.[4]

We have kept the parameters originally optimized for polyacetylene by Su, Schrieffer, and Heeger[4] and applied them to polyene chains ranging in size from 10 to 58 carbon atoms.[11] These parameters lead to: (i) a degree of bond length alternation of 0.14 Å in the ground state (single bond equal to 1.47 Å and double bond equal to 1.33 Å), (ii) a (somewhat underestimated) bandgap of 1.4 eV in trans-polyacetylene, and (iii) a creation energy of 0.89 eV for a pair of totally separated solitons.[11]

We have searched the configuration space to find the geometry allowing the lowest $1B_u$ excited state total energy. Two types of situation have been mostly investigated:

(i) We have allowed for geometries similar to those obtained with traditional BOBL relationships in the framework of Pariser-Parr-Pople (PPP) calculations including configuration interaction.[27] The amplitude and the extent of the relaxation are both optimized.

(ii) We have searched for geometries resulting in the formation of a soliton pair (two-soliton geometries). Both the distance between the defects and the soliton widths are optimized.

The results corresponding to the two-soliton geometries are given in Table I for chains containing from 10 to 58 carbon atoms.

In the longest polyene chain we have investigated (58 carbon atoms), we observe results identical to those obtained for the infinite polyacetylene chain.[4,26] The $1B_u$ excited-state geometry relaxes to form a pair of solitons (with a creation energy of 0.922 eV), which lowers the $1B_u$ excited state total energy by 38% relative to the vertical excitation energy. The solitons are calculated to be optimally located on sites 19 and 40, i.e., they are as distant from one another as from the chain ends. Each soliton is found to extend over about 15 carbons, as in trans-polyacetylene.[4]

TABLE I Evolution as function of chain length of: (i) the vertical excitation energy (in eV) to the first B_u excited state, δE_{vert}; (ii) the corresponding relaxed excitation energy (in eV), δE_{rel}; (iii) the relative total energy lowering (in %) due to the relaxation of the ^1B_u excited state; (iv) the optimal soliton width, 2l (in number of sites); (v) the optimized site locations of the soliton defects, n_1 and n_2; and (vi) the HOMO-LUMO separation (in eV) in the relaxed geometry.

n	δE_{vert}	δE_{rel}	%	2l	n_1,n_2	HOMO-LUMO
58	1.477	0.922	37.6	15	19,40	0.14
46	1.515	0.939	38.0	11	15,32	0.20
38	1.557	0.983	36.9	11	11,28	0.20
26	1.682	1.105	34.3	7	9,18	0.30
22	1.760	1.178	33.1	7	7,16	0.55
18	1.876	1.340	28.6	3	5,14	0.70
14	2.064	1.541	25.3	3	5,10	0.98
10	2.400	1.853	22.8	3	3,8	1.16

As the chain length decreases, the total energy lowering due to the relaxation of the $1B_u$ excited state becomes smaller. However, even in the case of decapentaene, this energy lowering due to a soliton pair formation still amounts to 23% of the vertical transition energy.

Very importantly, the relaxation energies obtained for excited-state geometries corresponding to the use of BOBL relationships are calculated to be 0.2-0.3 eV smaller than in the two-soliton formation situation. The major result of our Hückel calculations is thus to find that, as shorter chains are considered, the relaxation effects in the $1B_u$ excited state are qualitatively similar to those in trans-polyacetylene. Even in the shortest chains, the $1B_u$ excited state is found to relax optimally in such a way as to produce a pair of solitons. In order to be accommodated in shorter chains, the solitons shrink in size: their width decreases from $2l=15$ for trans-polyacetylene, to $2l=11$ for chains containing between 30 and 50 carbon atoms, $2l=7$ for chains between 20 and 30 carbon atoms, and $2l=3$ in chains containing less than 20 carbons. In all cases, the solitons tend to adopt locations separating them equally from one another and from the chain ends. The evolution between short and long polyene chains is thus found to be fully coherent.

It is important to stress that the two-soliton formation in the $1B_u$ excited state of polyenes appears to agree better with experimental data than does the situation where the $1B_u$ excited state geometry is described in terms of BOBL relationships. In the former case, the average bond-length variations between the $1B_u$ excited state and the ground state are calculated to be 0.070 and 0.087 Å for the double and single bonds, respectively. In the latter case, the corresponding values are 0.043 and 0.047 Å.[24] These results are to be compared with the experimental estimates of Granville et al.[20] which provide average variations of 0.085 and 0.081 Å for double and single bonds, respectively. Furthermore, the relaxation energy experimentally measured in the $1B_u$ state of decapentaene (at 77 K) is on the order 0.8 eV.[20] Such a relaxation represents 20% of the vertical excitation energy.[20] Within the two-soliton configuration, the relaxation is calculated to be about 23% of the vertical transition energy, while it is only 10-12% in the BOBL-derived $1B_u$ excited state.[24]

The overall picture obtained within the simple Su-Schrieffer-Heeger Hamiltonian is that there exists a smooth evolution of the relaxation of the $1B_u$ excited-state geometry in going from short polyenes to polyacetylene. This evolution is consistent with the strong geometry relaxations experimentally observed in short polyenes (e.g. decapentaene) as well as polyacetylene. In all cases, the relaxation is such as to produce a pair of soliton defects on the chain. Note that a relaxation tending to produce a two-soliton geometry is not unlike the ionic valence-bond pictures used to describe the $1B_u$ excited state.[27]

It is however important to address the question of the $1B_u$ excited-state relaxation using a more sophisticated Hamiltonian taking explicitly into account the effects of electron-electron interactions and electron correlation. The calculations have therefore been extended on short polyenes, using a combined PPP Configuration Interaction and Hartree-Fock ab initio approach.

PPP-CI/RHF ab initio Approach

It is usually the case that PPP Hamiltonians are suitably parameterized to reproduce excited state transition energies. However, they do not provide reliable geometry optimizations in terms of total energy differences. On the other hand, if ab initio techniques (which can afford good total energy differences) can be used quite easily to optimize ground-state geometries, they soon prove to be too costly when applied to optimize excited-state geometries of systems containing over one hundred basis functions.

Therefore, we have seeked to combine these two techniques in order to be able to perform calculations on relatively large molecules and to assess more reliably the trends in the first B_u excited state geometry.[12] We have thus considered: (i) geometry optimizations at the Restricted Hartree-Fock (RHF) 3-21G split valence basis set level,[28] which allows for a correct sketch of the ground-state potential energy curve; and (ii) PPP Configuration Interaction (CI) calculations including single excitations from the ground-state reference framework and based on the various 3-21G optimized geometries. The PPP program and parameters we have used can be found in Ref. 29. The parameters are chosen in such a way as to provide a degree of bond-length alternation in the ground state almost identical to that calculated at the RHF 3-21G level, see below. Although it does not predict a correct ordering of the excited states, a single CI approach is known to describe adequately the first B_u excited state.[22,23,27]

Combining the ground state total energies with the PPP vertical transition energies, leads to the relative excited-state total energies corresponding to various geometrical situations.

We have considered three linear polyene molecules: hexa-1,3,5-triene (C_6H_8), deca-1,3,5,7,9-pentaene ($C_{10}H_{12}$), and tetradeca-1,3,5,7,9,11,13-heptaene ($C_{14}H_{16}$).

The RHF ab initio calculations are performed in the ground state for three different geometry situations:[12]

(i) In the first case, we carry out a full (i.e., all bond lengths and valence angles) 3-21G optimization of the ground state geometry assuming coplanar conformations.

(ii) In the second case, we consider the geometry corresponding to the relaxed $1B_u$ excited-state, obtained using BOBL relationships with the PPP Hamiltonian.[24] All bond angles are optimized at the ab initio 3-21G level, while the carbon-carbon bond lengths are kept at their PPP B_u-state values and the carbon-hydrogen bond lengths are set at their optimal ab initio ground-state values.

(iii) In the third case, we partly optimize the geometry corresponding to the formation of a pair of solitons, as obtained at the Hückel/SSH Hamiltonian level described previously. Here, we force the two carbon-carbon bonds surrounding the soliton centers to be of equal lengths. The values of these bond lengths and those of the bonds towards the ends of the molecules are optimized. The carbon-carbon bonds located between the solitons are chosen to be identical to the single and double bonds appearing in the 3-21G optimized ground-sate geometry. All the bond angles are fully optimized, while the carbon-hydrogen bonds are fixed at the ab initio ground-sate optimal values.

In Table II, we present the ground-state geometries of hexatriene, decapentaene, and tetradecaheptaene, as optimized at the RHF ab initio 3-21G level. The decapentaene PPP values[24] are also indicated. The PPP values are obtained by using the following bond order (l_{pq})/bond length (R_{pq}, in Å) relationship: $R_{pq} = 1.51 - 0.19\ l_{pq}$

TABLE II Optimized RHF/3-21G carbon-carbon bond lengths (in Å) for the ground state of hexatriene (column A), decapentaene (column B), and tetradecaheptaene (column C). The numbers between parentheses for decapentaene refer to the PPP Hamiltonian-optimized values.[21] The atoms are labeled starting from one end of the molecule.

	A	B	C
R(C1-C2)	1.322	1.322 (1.325)	1.322
R(C2-C3)	1.462	1.461 (1.465)	1.461
R(C3-C4)	1.327	1.329 (1.330)	1.329
R(C4-C5)		1.456 (1.463)	1.455
R(C5-C6)		1.330 (1.332)	1.331
R(C6-C7)			1.454
R(C7-C8)			1.331

The evolution of the degree of bond-length alternation along the polyene chains obtained on the basis of BOBL relationships are depicted in Figure 2. It is clearly observed that in this framework the geometry relaxation in the first singlet B_u excited state strongly decreases with increasing chain length. In hexatriene, all bonds are significantly affected by the excitation; in the middle of the molecule, the sign of bond dimerization reverses. This is only slightly the case in decapentaene, where the two central bonds are almost equal and the bond alternation for the outer bonds reaches +0.09 Å. In tetradecaheptaene, however, the sign of the bond alternation remains positive all along the molecule, indicating no single bond-double bond character reversal. (Note that by convention, we consider the sign of the bond alternation to be positive when it is the same as in the ground state).

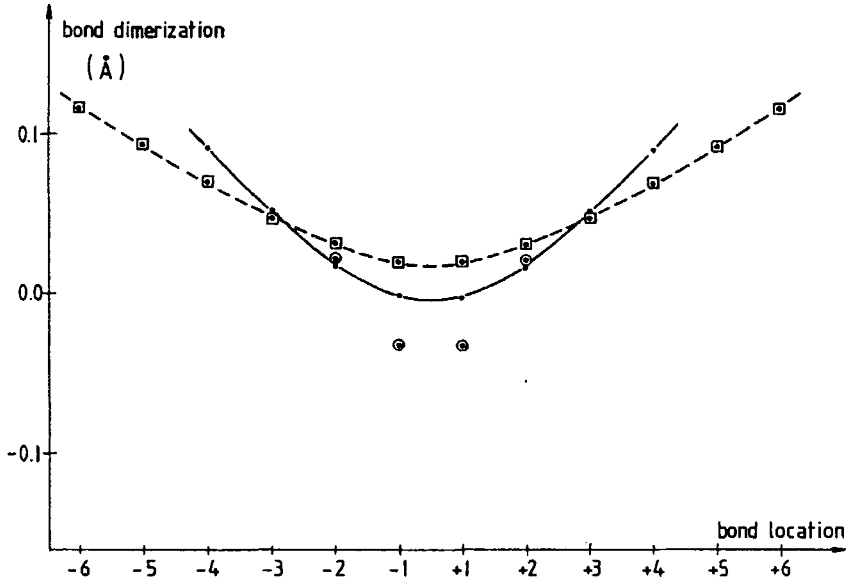


FIGURE 2. Illustration of the evolution of the bond dimerization value (in Å) along the molecules of hexatriene (double circles), decapentaene (closed circles, solid line), and tetradecaheptaene (squares, dashed line), in the BOBL-derived relaxed geometry for the first B_u excited state. The sign of the dimerization is by convention taken to be positive if it is the same as in the ground state. The bonds are labeled starting from the central bond of the molecule.

In Figure 3, we present the results obtained when considering the possibility of formation of a soliton-antisoliton pair as the $1B_u$ state relaxes. A comparison of Figures 2 and 3 illustrates that the two-soliton geometry leads to bond length modifications relative to the BOBL-derived geometries, which are smaller in the hexatriene case but much larger in the longer chains. We note that for hexatriene, it is actually rather misleading to speak in terms of the formation of a two-soliton configuration since the soliton and the antisoliton are localized on adjacent sites. Hexatriene is therefore too short a chain to provide for a complete bond alternation reversal in the middle of the molecule when applying the soliton formalism. Such a reversal, however, clearly occurs in decapentaene and tetradecaheptaene. In decapentaene, the average bond-length modification with respect to the optimal ground-state geometry is 0.073 Å. We stress again that, relative to the 0.08 Å experimental estimate of Granville et al. for the relaxed B_u state,[20] this value is in much better agreement than that provided by BOBL relationships (on the order of 0.04 Å, i.e. twice smaller than the experimental value).

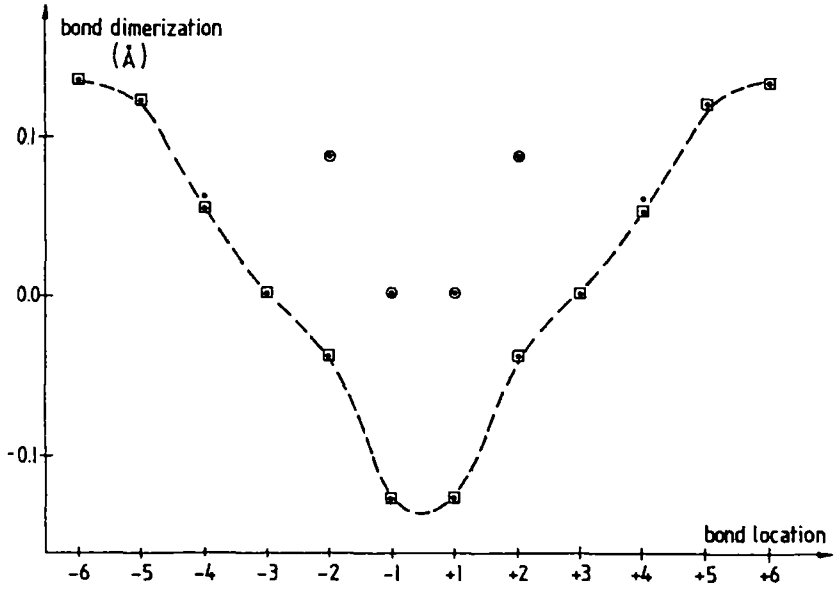


FIGURE 3. Illustration of the evolution of the bond dimerization value (in Å) along the molecules of hexatriene (double circles), decapentaene (closed circles and dashed line), and tetradecaheptaene (squares, dashed line), in the two-soliton relaxed geometry for the first B_u excited state. The sign of the dimerization is by convention taken to be positive if it is the same as in the ground state. The bonds are labeled starting from the central bond of the molecule.

In Table III, we list for the three kinds of investigated geometries: (i) the relative total energies in the ground state, as obtained at the Hartree-Fock ab initio 3-21G level; (ii) the vertical transition energies to the first optically-allowed singlet B_u state, as calculated at the PPP-CI level; and (iii) the relative total energies in the $1B_u$ excited state, obtained by simply summing the first two terms.

TABLE III Comparison of the energies involved in hexatriene, decapentaene, and tetradecaheptaene for the three geometry situations investigated in this work: (A) relative RHF ab initio total energies in the ground state (the fully optimized RHF ab initio 3-21G value being taken as reference); (B) PPP-CI vertical transition energies to the first singlet B_u state; (C) relative total energies in the first singlet B_u state (calculated by summing the first two terms). All energies are given in eV.

	A	B	C
hexatriene			
ab initio ground state	0.00	5.86	5.86
BOBL	0.63	4.14	4.77
two-soliton	0.27	4.83	5.10
decapentaene			
ab initio ground state	0.00	5.03	5.03
BOBL	0.51	3.56	4.07
two-soliton	1.19	2.93	4.12
tetradecaheptaene			
ab initio ground state	0.00	4.65	4.65
BOBL	0.43	3.37	3.80
two-soliton	1.08	2.65	3.73

What we need to compare for our purpose are the relative total energies in the excited state. For all three molecules, we find as expected that a strong relaxation takes place in the excited state, i.e. the geometry which is found to be optimal for the ground state does not constitute the optimal geometry in the B_u excited state. In hexatriene, the B_u relaxed geometry derived from BOBL relationships is significantly favored (by about 0.3 eV) over that corresponding to the two-soliton geometry. However, as discussed above, in the case of hexatriene, the BOBL configuration provides for a stronger geometry relaxation and a two-soliton configuration is not truly achieved. In decapentaene, the two-soliton geometry becomes very close in energy (within 0.05 eV) with respect to the BOBL geometry for the excited state. In both configurations, the relaxation relative to a vertical process is found to be on the order of 0.9 eV, a value in excellent agreement with the 0.84 eV value which is experimentally measured.[20] Importantly, in the case of tetradecaheptaene, the two-soliton geometry corresponds to the most stable situation for the excited-state, being about 0.07 eV lower in energy than the BOBL geometry. The gain in stability of the two-soliton configuration with respect to the BOBL configuration as chain length increases is fully consistent with the experimental observation on the photogeneration of soliton pairs in the first $1B_u$ excited state of polyacetylene. In long chains, a BOBL-derived configuration would in contrast lead to negligible relaxation.

An interesting feature is uncovered when: (i) observing in Figures 2 and 3 the evolution in bond length alternation for decapentaene and tetradecaheptaene; and (ii) comparing it to the geometry relaxation process due to a photogenerated electron-hole pair in polyacetylene (see Figure 2a of Ref. 19). From this observation, we suggest that the configuration given by BOBL relationships corresponds to the early stage of the process of electron-hole separation into a pair of solitons whereas the two-soliton configuration relates to the final stage of the separation process. This separation is actually induced through the explicit coupling of the electronic structure to the lattice, an ingredient which is absent from the BOBL approach.

The results obtained from the combined RHF ab initio/PPP-CI approach thus confirm that in linear polyenes containing at least ten carbon atoms, the electron-lattice coupling plays a significant role in the relaxation of the first B_u excited state. We stress that the fast relaxation of the $1B_u$ state related to the decay of a photoinduced electron-hole pair into a pair of charged solitons has been invoked to be an important factor in the large nonlinear optical response of polyacetylene.[3-10,19] Such a decay indeed provides a very effective charge separation mechanism which is essential to large hyperpolarizabilities.[5,7,16]

Our work thus suggests that going beyond frozen geometry models of the polarizabilities and hyperpolarizabilities by incorporating electron-lattice coupling could also prove to be essential to describe properly the optical nonlinearities in short and intermediate-sized polyenes,[30,31] as well as in other oligomers where electron-lattice coupling effects are known to be important (polypyrroles, polythiophenes,...).

From the experimental standpoint, we note that the two-soliton geometry relaxation leads to the appearance of new electronic states in the gap.[11] It would be therefore most interesting to carry out photoinduced absorption experiments in the subpicosecond regime since such measurements constitute an ideal means to probe the energies and fast time evolution of the new optical absorptions that would result from such a relaxation in linear polyenes.

ELECTRONIC STRUCTURE AND SECOND-ORDER POLARIZABILITY OF BENZODITHIAPOLYENALS

Recently, Lehn and co-workers[32] have succeeded in synthesizing two series of push-pull polyene molecules containing up to 8 double bonds in the polyene segment: benzodithiapolyenals (BDTP's) and dimethylanilinopolyenals (DMAP's), see Figure 4. Through EFISHG (Electric-Field Induced Second-Harmonic Generation) measurements, Barzoukas et al.[33] have shown that the longest of these compounds possess among the largest $\mu.\beta$ values that have ever been reported, on the order of 7000-9000 x 10^{-48} esu at 1.34 µm, leading to a static value of about

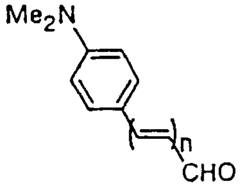
3000 x 10^{-48} esu. The value of μ.ß as a function of the length of the polyene segment is experimentally observed to evolve as $n^{2.4}$, where n is the number of double bonds in the polyene segment.[33] Interestingly, no saturation effect is obtained even after eight double bonds.

A simple model, detailed in Ref. 34, suggests that μ should evolve as $n^{1.5}$, in which case ß would almost have a square dependence on the number of double bonds. We have tried to check on that dependence by performing RHF ab initio 3-21G calculations of the electronic structure and second-order polarizability ß, on the benzodithiapolyenal series. We chose to focus our attention on the BDTP compounds because we wished to rationalize the lower μß values (relative to the dimethylanilinopolyenal series) measured for the shortest chains, in particular that containing only one double bond in the polyenic segment. The μß(0) is indeed ≈20 x 10^{-48} esu for the BDTP compound with one double bond, to be compared to μß(0) of ≈200 x 10^{-48} esu for the corresponding DMAP molecule.

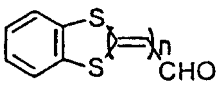
Full geometry optimizations have been carried out at the 3-21G level on the BDTP molecules containing up to four double bonds as well as on a series of dithiolylidenepolyenal (DTLP) molecules where the DBTP benzene rings are simply replaced by a double bond (connecting the carbons located in α from the sulfurs), see Figure 4. It was indeed observed that the molecular properties we are interested in (dipole moment, hyperpolarizability) are almost unaffected by that replacement. We therefore decided to pursue the theoretical works on the dithiolylidenepolyenal compounds since they allow us to perform ß calculations on molecules containing up to 3 double bonds in the polyene segment. The ground state dipole moments for the dithiolylidenepolyenals are given in Table IV. We observe that the dipole moment actually evolves very little with the length of the polyene segment. This can be understood on the basis that the charges induced by the donor (dithiolylidene group) on the one hand, and the acceptor (carbonyl) group on the other hand, are calculated to remain very localized and do not spread over the polyene segment. The μ evolution is found to go as $n^{0.1}$

TABLE IV RHF ab initio 3-21G dipole moments μ (in Debye) for the optimized geometries of dithiolylidenepolyenal molecules containing from (n=) 0 to 4 double bonds in the polyenic segment. The static second-order polarizabilities β (in 10^{-30} esu) and μ.β terms (in 10^{-48} esu) are provided for molecules with up to three double bonds.

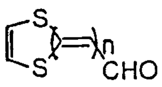
	μ	β(o)	μ.β(0)
n=0	4.04	-3.57	-14.42
n=1	5.12	2.47	12.63
n=2	5.52	21.18	116.95
n=3	5.79	50.61	292.81
n=4	6.39	-	-



DMAP



BDTP



DTLP

Figure 4. Geometric structures of the dimethylanilinopolyenal (DMAP), benzodithiapolyenal (BDTP), and dithiolylidenepolyenal (DTLP) molecules.

In Table IV, we also present the 3-21G ab initio static second-order polarizabilities, β(0), as well as the μ.β(0) terms. Two important remarks can be made.

First, the theoretical μ.β(0) are in excellent agreement with the values that can be interpolated from the EFISHG measurements of Barzoukas et al. (see Figure 2 of Ref. 33). This lends much confidence in our theoretical approach. The DTLP μ.β(0) calculated values evolve as $n^{2.6}$, in excellent agreement to the experimental data on BDTP's.

Second, we observe that the ß value switches sign in going from the n=0 to the n=1 DTLP molecule. As will be detailed elsewhere,[35] the origin of this effect is due to the fact that in the n=0 compound, the most intense optical transition involves the promotion of an electron from the HOMO molecular orbital to the (LUMO+1) molecular orbital which is localized on the dithiolylidene part of the molecule. For n=1, the HOMO-LUMO transition becomes the most intense, the LUMO being, on the contrary, localized on the polyenal part of the molecule. As the length of the polyenic segment increases, the (LUMO+1) MO remains at the same energy level; on the other hand, the LUMO keeps stabilizing and accounts more and more predominantly for the charge transfer in the excited state. On the basis of this simple two-level analysis, the change in sign of ß can be easily rationalized.

Furthermore, this effect also explains the low µ.ß values in the BDTP and DTLP molecules with small polyenic segments, relative to the corresponding DMAP molecules. In the latter case, the benzene rings are located along the charge-transfer path, thereby effectively increasing the conjugated length of the polyenic segment and providing a greater separation of charges upon excitation. In the former case, the benzene ring of the BDTP molecules or the double bond that replaces it in the DTLP molecules, are located in a direction opposite to the charge-transfer path, thereby counteracting an efficient charge transfer in the smaller molecules.

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