

Nonlinear Optical Properties of Conjugated Molecules

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Due to their intrinsic orientational anisotropy and elevated polarizability n -conjugated polymers are widely perceived as promising materials for use in nonlinear optical devices. Advances in the development of practical systems have been impeded, however, by the difficulties in developing a realistic theoretical description of the experimental situation. In this paper we present several examples of theoretical progress towards this goal and discuss how the different effects contributing to the polarization response in the systems can be quantified.

I. Introduction

In the last fifteen years, n -conjugated polymers have become widely recognized as promising materials for the development of nonlinear optical devices^[1-3]. Specific features of these molecules, such as the intrinsic anisotropy of the polymeric chains and the high polarizability of the n -electron system, contribute to the manifestation of very large nonlinear optical parameters.

While it is true that general use of these materials in devices will have to wait until problems associated with thermal, environmental and mechanical stability are overcome, the wealth of possibilities offered by chemical modification holds the promise of fine tuning properties for the desired application^[4]. In this sense, the eventual development of a molecular based electronics controlling the flow and storage of information has been considered the ultimate step in circuit miniaturization^[5].

Before such developments can take place, however, we will need a much better understanding of the factors

that determine the polarization response of these systems. For this purpose theoretical investigation of the different effects contributing to the nonlinear behavior of the optical properties is essential. In this paper we will discuss several directions along which progress has been made in the investigation of these properties in conjugated systems, and discuss the relative importance of electronic (such as charge transfer) and geometric (e.g., conformational changes) contributions.

It is important at the outset to make clear that we still have a long way to go before quantitative theoretical predictions of the optical properties of conjugated polymers can be truly verified in experiments using real samples. First of all, theoretical calculations are usually made for a single perfect chain and so do not consider the contribution due to interaction among neighboring chains or the role of conformational defects. Real samples of conjugated polymers also have chain growth defects, such as local sp^3 hybridization (which reduces the average delocalization length of the π electrons), branching and topological kinks^[6]. Furthermore, in typical experiments the polymer chains will in general

not be perfectly oriented and, as a result, the polarization response along the longitudinal direction is likely to be reduced by orientational averaging in the macroscopic sample^[7]. Finally, while most of the theoretical calculations are devoted to the investigation of static (i.e. zero-frequency) polarizabilities, the polarization is generally measured at optical frequencies using laser excitation.

Although theory does not yet provide all the information desired, significant progress has been made in identifying general trends in the behavior of the polarization response and in providing insight with regard to the physical origin of the different factors contributing to it. A possible theoretical approach is to apply band structure techniques, such as the the Genkin and Mednitsin sum of states perturbation method^[8] to compute the polarization response directly for the infinite system^[9]. A different point of view is the one adopted in the present discussion in which we work with finite oligomers of the systems of interest and let the physical intuition to guide us as what should be the relevant factors controlling the polarizability of conjugated molecules. For a series of related molecules, the longitudinal (i.e. along the chain direction) component of the polarizability must grow with increasing chain sizes and become dominant. In fact, for small chains the longitudinal polarizability per repeat unit increases supralinearly with chain length, and eventually approaches a saturation limit where end effects cease to be important^[10–12]. At that point, further increase in the chain length adds equivalent repeat units to an essentially invariant environment within the central region.

Theoretical results at the semiempirical level have first revealed that the higher the order (in the perturbing field) of the polarization response examined, the longer are the chain sizes required for the saturation behavior to manifest itself^[10,11]. This general trend has also been observed in *ab initio* studies^[12,13]. Hopefully, the rate of convergence will be rapid enough to allow for accurate extrapolation of *ab initio* results. This is of fundamental importance since only an *ab initio* treatment can discriminate reliably between the vari-

ous contributions to the polarization and allow a systematic improvement of the computed results. The ever increasing availability of faster computers and more efficient *ab initio* quantum chemistry programs make the outlook hopeful in this regard. This optimistic perspective is reinforced by the possibility of development of special techniques for this particular problem (some of which will be discussed below) which can make simpler the understanding of the relevant parameters controlling the polarizability response of conjugated chains.

In the next Section we will discuss several case studies of the polarization response of conjugated molecules and show that for the prototype conjugated polymer, *trans*-polyacetylene, t-PA, a comprehensive picture is beginning to emerge. It should be noted, in this connection, that t-PA is the worst case yet studied as far as convergence to the infinite chain limit is concerned.

II. Case studies

A few selected examples will show how valuable information can be obtained from semiempirical calculations. However, they will also illustrate the importance of carrying out a comprehensive *ab initio* investigation whenever possible.

A. Regular chains of t-PA

Due to its simple structural formula (Fig. 1a) t-PA has been used as the prototype for the theoretical investigation of conjugated polymers. A few years ago it was established on the basis of semiempirical and *ab initio* calculations^[10,11] that the second hyperpolarizability per repeat unit, γ_{zzzz}/N , converges slowly with chain length on the linear polyenes $C_{2N}H_{2N+2}$. In fact, we have now found using *ab initio* RHF/6-31G calculations, that the curve (Fig. 2) of γ_{zzzz}/N vs. N has an inflection point at about $C_{26}H_{28}$, which marks the onset of the saturation regime^[13]. This means that previous extrapolation of results through $C_{22}H_{24}$ cannot yield a reliable infinite chain value. More dependable extrapolations can be carried out, however, on the basis of current treatment of the polyenes through $C_{44}H_{46}$. For this purpose we use a least square fit to a $1/N$ power series expansion and vary the maximum power as well

as the number of points and the largest polyene considered. In this way we can establish that the limiting infinite chain values of 1.65×10^2 a.u. for α_{zz}/N and 6.80×10^6 a.u. for γ_{zzzz}/N are well determined. It is worth observing, however, that for the $C_{44}H_{46}$ oligomer the ratio $\gamma_{zzzz}^{N=22}/\gamma_{zzzz}^{N \rightarrow \infty}$ is still only about 0.44.

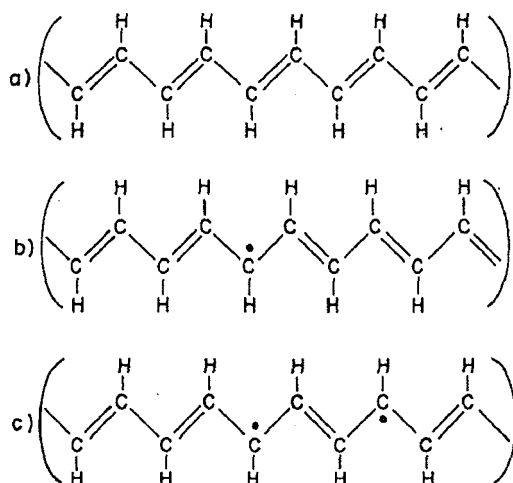


Figure 1: Polyenic chains: (a) regular structure, (b) with a single soliton, and (c) with a polaron type of defect.

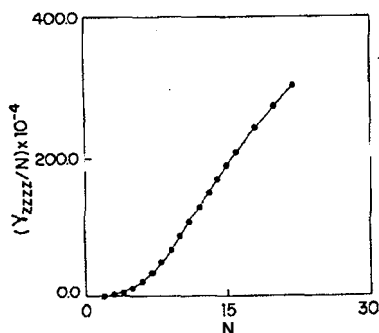


Figure 2: Restricted Hartree-Fock longitudinal hyperpolarizabilities per repeat unit in atomic units, for the $C_{2N}H_{2N+2}$ linear polyenes, calculated (Ref. 13) using a 6-31G basis set at the optimized geometry.

A similar rate of convergence is observed when correlation effects determined from second order Moller-Plesset perturbation theory (MP2) are included. However, due to what may be a fortuitous coincidence, the ratio between the MP2 property value and the corresponding Hartree-Fock result converges rapidly. As a matter of fact, the ratio for γ_{zzzz}/N is completely converged beyond $N = 6$, while α_{zz}/N is readily extrapolated using $N = 4 - 9$. From the limiting ratios (0.854 ± 0.004 a.u. and 2.84 ± 0.02 for α_{zz}/N

and γ_{zzzz}/N , respectively), the infinite chain polarizabilities per repeat unit, including correlation, can be estimated as $(\alpha_{zz}^{\text{total}}/N)_{N \rightarrow \infty} = 1.41 \times 10^2$ a.u. and $(\gamma_{zzzz}^{\text{total}}/N)_{N \rightarrow \infty} = 1.93 \times 10^7$ a.u.. It is interesting to note that correlation affects the linear and nonlinear polarizabilities very differently. While the estimated ratio is somewhat smaller than 1 for α_{zz}/N , it is on the order of 3 for γ_{zzzz}/N . The origin of this difference is not well understood.

B. Role of defects and interchain interactions in *trans*-polyacetylene

Conformational defects are known to play a determining role in transport properties of conjugated polymers^[14-16]. Topological kinks arise naturally as a consequence of the polymerization process but they can also be induced by chemical doping or photolytically when a laser beam of appropriate frequency is applied to the material^[17,18]. Since their presence is an inherent feature of most conjugated polymers samples, it is of interest to examine how their presence can affect the nonlinear optical properties.

It is well known that the polarizability of regular polyenes is extremely dependent on the degree of bond alternancy along the chain^[19]. These conjugation defects, either of soliton or polaron nature (see Figs 1b-1c), alter the geometry of the chain only in the neighborhood of the defect site. A pioneering study of the evolution of the polarizability response per repeat unit of neutral polyenic chains $C_{2N}H_{2N+2}$ of different geometries (regular chains and chains with a central soliton or polaron) was performed^[10] for the range $N < 10$ using a Perturbative Expansion of the Density Matrix (PEDM) calculation^[20] with the Pariser-Parr-Pople level of hamiltonian approximation^[21]. For these short chains, while the linear polarizability seems to indicate a saturation of the response per repeat unit at $N \sim 8$, the second hyperpolarizability is still increasing exponentially as aN^b . In general terms, a qualitatively good fitting of the calculated values was obtained by this power law. The corresponding results (Table I), which were adapted from those of Ref. 10, indicate that the effect of conformational change is greater for

TABLE I. PEDM results^a for α_{zz}/N and γ_{zzzz}/N in neutral linear polyene chains $C_{2N}H_{2N+2}$.

chain structure	α_{zz}		γ_{zzzz}	
	a	b	a	b
regular polyene	4.63	0.75	52.0	3.25
solitoni	4.81	0.77	146	3.05
polaron	6.53	0.78	42.0	3.60

^a Ref. 10; all calculations were done using standard bond lengths and bond angles.

TABLE II. PEDM results^a for α_{zz}/N and γ_{zzzz}/N of charged linear polyenic chains $C_{2N}H_{2N+2}$.

chain structure	α_{zz}		γ_{zzzz}	
	a	b	a	b
charged soliton	3.41	1.19	-7.0	3.79
singly charged polaron	1.85	1.56	-2.66	5.57
bipolaron	1.94	1.42	0.247	5.04

^a Ref. 10; all calculations were done using standard bond lengths and bond angles.

the hyperpolarizability.

Besides being associated with geometric changes, conjugation defects also participate as active sites for charge transfer between polymeric chains and dopants^[17–13]. In Table II we present results^[10] for the polarizabilities per repeat unit for short polyene oligomers carrying soliton and polaron defects in different charge states. The distinct evolution pattern for each of these quantities reveals the importance that charge transfer can have in the polarization response of conjugated systems. Of course, the above conclusions which were attained through a semiempirical study need to be certified more thoroughly by an equivalent *ab initio* investigation.

Although the relationship between static polarizabilities and dynamic susceptibilities is not a direct and simple one, one can take the above results as qualitative indication of a similar behavior for the dynamical optical response of conjugated polymers. It is well known that defects with a time decay of the order of 20ps can be photoproduced in conjugated polymer samples by a properly tuned laser beam^[22]. Then a simple optical device can be envisioned in which an external laser

pulse is used to switch the polarization response of the polymeric sample between the pristine and induced defect values.

In order to compare theoretical with experimental values of the nonlinear polarization, it is important to take into consideration interchain interactions. The importance of such interaction is currently a matter of sharp debate^[23–25]. Using small polyene chains and the X-ray geometry of Kalilert et al.^[26], a series of *ab initio* 6-31G basis set calculations was initiated^[27] to shed light on this effect for γ_{zzzz}/N . Thus far, we have found that interchain interactions result in a steady decrease of γ_{zzzz}/N as one, and then, two nearest neighbors are included. With two nearest neighbors (the maximum considered) the reduction is about 50% (regardless of relative orientation) at either the Hartree-Fock or correlated level of treatment. This result appears to be relatively independent of chain length. Since there are six nearest neighbors to be accounted for in a polyacetylene fibril the total effect could be very large. Finally, the change in geometry due to interchain coupling is small and has an insignificant effect on γ_{zzzz} .

C. Conjugated polymers with heteroatoms

In addition to polyacetylene, other conjugated polymers such as polypyrrole and polyaniline can present high electrical conductivity once doped^[17]. While solitons can exist for polyacetylene, in these other conjugated chains conformational defects of similar structure would not have the necessary mobility to account for the charge transport mechanism. An extension of the idea of mobile defects as the active charge carrier had to be advanced to explain the wealth of experimental data readily collected about the transport properties of these materials^[15].

The main question here resides in the fact that while solitons are conformational defects associated with a half period mismatch of the conjugation pattern of the chain, they must be connected to isoenergetic chains at each side to become mobiles. Once a conjugation defect is present in a conjugated chain which contains heteroatoms, this symmetry between the *rhs* and the *lhs* is broken (Fig. 3). The only way to restore the original al-

ternation pattern is to admit the existence of combined defects (known as polarons) formally corresponding to a bonding state resulting from the attractive interaction between two solitons^[15]; the polarons only locally alter the geometry of the system and can therefore be mobile along the chain. Single and doubly charged polarons (bipolarons) are assumed to be responsible for the charge transport in those polymers^[17].

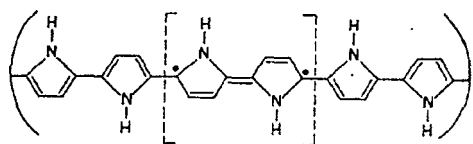


Figure 3: Example of a mobile defect in a non-degenerate conjugated chain: polaron in polypyrrole.

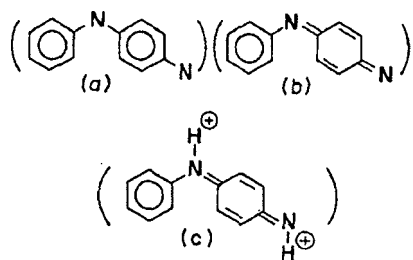


Figure 4: Different forms of polyaniline monomers: (a) leucoemeraldine, (b) pernigraniline, and (c) protonated pernigraniline.

Of these, polyaniline seems to be a special case, since its conductivity is also dependent on the pH of the medium. Accordingly to the electrochemical potential applied to the working electrode, polyaniline can alter its structure among different forms (Fig. 4), each one with a characteristic conjugation pattern. It has been determined that the conductivity of these different forms can be significantly different^[28-29].

The PEDM method at the PPP hamiltonian level of approximation was used in preliminary investigation of the static nonlinear optical properties of oligomers of polyaniline in its different forms^[30]. The results, shown in Table III, reveal that once again conformational changes (and charge state) play a critical role in determining the polarizabilities of conjugated systems and that this effect is much more important for the nonlinear response. These results suggest that an

interesting experiment would be to determine the nonlinear susceptibilities of polyaniline *in situ*: while the polymer is deposited on a transparent conducting glass electrode, the electrochemical potential of the cell is slowly cycled to take the polymer through all of its intermediate forms^[31] with a concomitant change in its nonlinear optical properties.

For these polymers of more complex unit cell, the distinction between geometric and electronic effects on the nonlinear optical properties is less evident. It would then be desirable to start an *ab initio* study of the corresponding polarizabilities, to put on a more quantitative basis the relative importance of the different effects contributing to the polarization response. Initial steps in this direction have been taken for the case of polypyrrole^[32]: using an *ab initio* Hartree-Fock treatment for a 6-31G basis set, the linear polarizability and the second hyperpolarizability per repeat unit, α_{zz}/N and γ_{zzzz}/N , respectively, were examined for the oligomers $(C_4H_2 - NH)_nH_2$ with $n = 1 - 9$. For these short oligomers it is not possible yet to observe the onset of the saturation regime, and power laws of the type aN^b seem to fit reasonably well the data. On the other hand, it is interesting to note that as found for the polyacetylene oligomers the ratio α^{MP2}/α^{HF} and γ^{MP2}/γ^{HF} seem to converge more rapidly than either of the individual quantities, to the respective values of 0.96 and 1.39.

D. Retinal derivatives

A final example will illustrate more clearly the importance of charge transfer and geometric rearrangements on the polarizabilities of conjugated molecules. Retinal and its derivatives (Fig. 5) are molecules associated with the fundamental processes of vision and photoperception in biological species ranging from bacteria to humans. In the so called *primary* event of vision in animals, for example, the absorbed photon induces the *cis* to *trans* isomerization of the 11-protonated Schiff base (PSB).

TABLE III. PEDM results^a for the longitudinal components of the linear and nonlinear polarizabilities of leucoemeraldine (LE), pernigraniline (PG) and protonated pernigraniline (PPG) oligomers relative to the corresponding values of the LE dimer. The first line corresponds to the polarizabilities of the LE dimer in atomic units.

		α_{zz}	β_{zzz}	γ_{zzzz}
LE	dimer	0.104210 ³	0.260710 ³	0.728810 ⁵
LE	tetramer	2.29	1.23	4.32
	hexamer	3.32	0.94	6.44
PG	dimer	2.79	-26.3	7.71
	tetramer	13.6	-123.	252.
	hexamer	33.2	-1,450.	3,160
PPG	dimer	3.11	-31.0	8.74
	tetramer	15.4	-143.	312.
	hexamer	37.9	-1,710.	3,760

^a Ref. 29

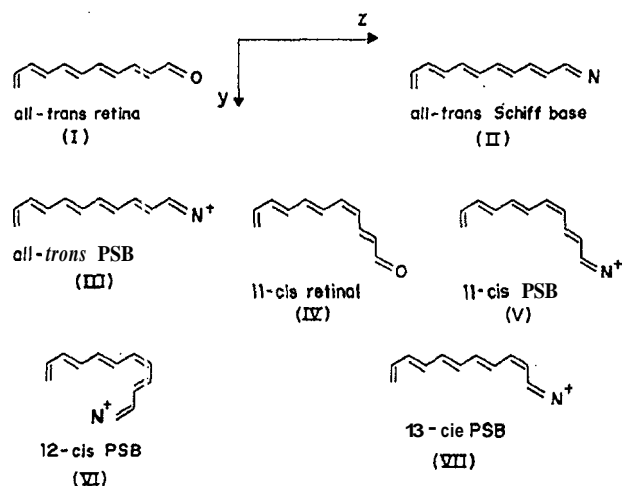


Figure 5: Model of retinal analogs.

In the retinal family we have once again present the two important effects of geometry rearrangement (associated with fotoinduced isomerization) and charge transfer to the chain (made evident in the comparison of equivalent regular and nitrogen substituted retinal molecules). A preliminary semiempirical study of the polarizabilities of retinal derivatives^[33] has revealed a systematic change of the polarizability components of retinal analogs upon isomerization, in a clear manifestation of "geometric" effects. On the other hand, at this level of approximation much smaller changes were predicted when the terminal nitrogen atom was protonated or substituted for oxygen (the "electronic" effect).

To corroborate such conclusions an *ab initio* study of this problem was recently completed^[34]. It was found

that while the right trend of behavior upon isomerization was predicted by the semiempirical calculation, the lack of reliable geometry optimizations inherent to these methods did not allow a correct description of the changes associated with the protonation of the terminal heteroatom. The corresponding results (Table IV) indicate an enhancement of the longitudinal (z-axis) and perpendicular in-plane (y-axis) components of the first nonlinear polarizability, β . As anticipated, in the retinal series of analogs we find a remarkable example of the geometric and electronic effects on the polarizability response. The eventual confirmation of these predictions in an experiment will depend on the possibility of preparation of very organized samples in which the orientational averaging effects could be reduced to a minimum.

III. Conclusion

In this work we have discussed the problems one faces in the comparison of theoretical results for the nonlinear optical properties of conjugated polymers with experimentally determined values. While in real samples one probes the collective response of several different forms under dynamical conditions, most theoretical calculations are performed for isolated chains of well defined geometry. To reduce the gap between theory and experiment would be desirable on the experimental side to use samples of higher degree of crys-

TABLE IV. Ratio of the *ab initio* polarizabilities^a of different retinal analogs relative to those of *all-trans* retinal. The last line correspond to the polarizabilities of *all-trans* retinal in atomic units. Structures I-VII are those of Fig.5.

	α_{zz}	β_{zzz}	γ_{zzzz}	γ_{yyyy}
II/I	1.03	0.52	1.03	1.23
III/I	1.60	5.27	0.73	1.24
IV/I	0.84	0.29	0.50	2.49
V/I	1.15	2.55	0.78	-19.7
VI/I	0.90	2.37	0.64	-49.9
VII/I	1.42	4.33	0.97	-0.26
I	0.36×10^3	-0.27×10^4	0.88×10^6	-0.14×10^4

^a Ref. 33

tallinity. On the other hand, significant progress in the theoretical understanding of the problem can be made by a systematic investigation of the factors controlling the polarizability response of these systems. The several examples discussed in the present work illustrate recent effort made along the latter approach.

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