

Use of Vibrational Spectra for the Determination of First-Order Molecular Hyperpolarizabilities of Push–Pull Polyenes as Function of Structural Parameters

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ABSTRACT: Experimental data on the nonlinear optical molecular hyperpolarizabilities of push–pull polyenes (measured with the vibrational method recently proposed) are presented and discussed. The analysis of the results and the interpretation of the spectral features allow us to establish structure–property relationships. These relationships are particularly helpful in the understanding of the mechanisms which rule the nonlinear optical behavior of organic polyconjugated compounds and in view of the design of new and improved materials. Comparison with other techniques, when available, correlate nicely with the conclusions reached with the vibrational method. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1311–1320, 1998

Key words: vibrational spectroscopy; infrared and Raman intensities; nonlinear optical properties; polyene systems

INTRODUCTION

In the search for new efficient organic materials to be used in nonlinear optics for the development of molecular devices, polyenic molecules are of particular interest. Particularly appealing is the relative ease with which they can be chemically functionalized in order to optimize their performance with respect to a certain property. These kinds of molecules exhibit significant third-order polarizabilities¹ which increase superlinearly when the number n of conjugated double bonds increases. Recently, the highest γ values ever ob-

served have been reported for polyene systems with $n \cong 140$.²

Unsymmetrical substitution of the polyene chain with the introduction of a donor group (D) at one end of the chain and of an acceptor group (A) at the other end defines a class of push–pull polyenes. These molecules exhibit, in addition to their large second-order hyperpolarizability, also significant first-order hyperpolarizability β .³ These highly polarizable molecules provide very promising materials for nonlinear optics.

The molecular nonlinear optical (NLO) responses (both β and γ) can be optimized by a suitable choice of chain length (n) and donor–acceptor strength. This justifies the need for further investigations that should provide a deeper understanding of the way in which these molecular parameters affect the NLO behavior. In this article, we propose a new way to look at the structure/property relationships of interest in nonlin-

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Table I (A) Calculated Ab Initio β_μ (Electronic) and β_μ^r (Vibrational) Values; (B) Experimental β^r for Push-Pull Molecules (See Scheme)

	(A) Ab Initio, 3-21G			(B)
	Vibrational	\mathcal{Y} Vibrational ^a	Electronic	Experimental Vibrational
IIIa	1.07	1.04	1.88	3.01
IIIb	7.33	8.77	7.43	9.72
IIIc	19.57	23.70	16.54	19.67
IV $n = 1$	1.16	0.64	1.02	1.02
IV $n = 3$	3.47	3.91	3.21	3.46
Va	8.35	8.78	3.08	7.21
All- <i>trans</i> retinal	3.32	3.85	2.24	2.76
<i>p</i> -Nitroaniline	1.11	0.25	0.79	—
4-Amino-4'-nitro 1-1'-Biphenyl	2.83	1.27	2.87	—

Units are 10^{29} esu.

^a These values are obtained only from the contribution of the \mathcal{Y} oscillation (see text).

ear optics which is based on vibrational spectroscopy.

VIBRATIONAL METHOD

It has been recently shown⁴ that it is possible to obtain accurate estimates of the molecular NLO responses of organic polyconjugated systems by means of the vibrational spectra. This vibrational method has been tested on a large variety of molecules already known for their large first- and second-order hyperpolarizabilities (β and γ). For the evaluation of static hyperpolarizabilities, the vibrational method requires the knowledge only of vibrational observables, namely; vibrational frequencies and absolute infrared, Raman, and hyper-Raman intensities. The analytic expressions for vibrational hyperpolarizabilities are given by:⁵

$$\beta_{nmp}^r = \frac{1}{4\pi^2 c^2} \sum_k \left(\frac{1}{\nu_k^2} \right) \left[\left(\frac{\partial \mu_n}{\partial Q_k} \right) \left(\frac{\partial \alpha_{mp}}{\partial Q_k} \right) + \left(\frac{\partial \mu_m}{\partial Q_k} \right) \left(\frac{\partial \alpha_{np}}{\partial Q_k} \right) + \left(\frac{\partial \mu_p}{\partial Q_k} \right) \left(\frac{\partial \alpha_{nm}}{\partial Q_k} \right) \right] \quad (1)$$

$$\gamma_{nmps}^r = \frac{1}{4\pi^2 c^2} \sum_k \left(\frac{1}{\nu_k^2} \right) \left[\left(\frac{\partial \mu_n}{\partial Q_k} \right) \left(\frac{\partial \beta_{mps}}{\partial Q_k} \right) + \left(\frac{\partial \mu_m}{\partial Q_k} \right) \left(\frac{\partial \beta_{nps}}{\partial Q_k} \right) + \left(\frac{\partial \mu_p}{\partial Q_k} \right) \left(\frac{\partial \beta_{nms}}{\partial Q_k} \right) \right]$$

$$+ \left(\frac{\partial \mu_s}{\partial Q_k} \right) \left(\frac{\partial \beta_{nmp}}{\partial Q_k} \right) + \left(\frac{\partial \alpha_{nm}}{\partial Q_k} \right) \left(\frac{\partial \alpha_{ps}}{\partial Q_k} \right) + \left(\frac{\partial \alpha_{np}}{\partial Q_k} \right) \left(\frac{\partial \alpha_{ms}}{\partial Q_k} \right) + \left(\frac{\partial \alpha_{ns}}{\partial Q_k} \right) \left(\frac{\partial \alpha_{mp}}{\partial Q_k} \right) \quad (2)$$

The quantities $\partial \mu_n / \partial Q_k$, $\partial \alpha_{nm} / \partial Q_k$, $\partial \beta_{nms} / \partial Q_k$ (where n , m , and s indicate the Cartesian components) can be obtained from infrared intensities, Raman, and hyper-Raman cross sections, respectively. ν_k is the vibrational frequency of the k -th normal mode Q_k . Equations (1) and (2) are derived under the hypothesis of both mechanical and electrical harmonicity.

Using ab initio calculations, it is possible to evaluate all the quantities which appear in eqs. (1) and (2) in order to obtain β^r and γ^r . In the case of conjugated compounds, the comparison of these values with β and γ directly computed with ab initio derivative methods is very good, as can be seen in Table I for several push-pull polyenes. Moreover, the experimental β^r values are consistent with the β values determined with other experimental methods (e.g., electric field-induced second harmonic generation, hyper-Rayleigh scattering, third harmonic generation). It must be noted that a direct comparison between calculated and experimental β values is not always straightforward because of several problems, such as the extrapolation to static values (i.e., zero frequency), independent evaluation of the dipole moment in EFISH experiments, and dispersion effects (different exciting laser lines). For

these reasons, the most significant tests of the reliability of the vibrational approach can be obtained by the comparison of the trends of the NLO properties with the relevant structural parameters. On the contrary, an unambiguous comparison of absolute values can be obtained only theoretically (Table I).

The good agreement between β^r and γ^r and β and γ can be theoretically justified for the class of conjugated systems.⁶ The common and unique property of this class of compounds is the existence of a large electron/phonon coupling which forms the basis of many of their peculiar physical properties (e.g., conductivity in the doped and photoexcited state and NLO responses). Because of the existence of a large electron/phonon coupling, it is no longer possible to carry out an exact separation between nuclear motions (phonons) and electronic charge rearrangements. In this way, whenever deformations of the electronic cloud are excited, nuclear rearrangements are induced and, vice versa, nuclear oscillations along particular directions induce electronic-charge polarization. This concept allows the formulation of a simple “two-state two-form” model that has been used to study the electronic properties of push–pull polyenes.⁶ Within this model, it is possible to show that electronic and vibrational β (β and β^r) are strictly related, that is, they can be expressed in terms of the same electronic quantities.^{6d} In this work, we will use vibrational spectra to establish structure/NLO property relationships that can help in the understanding of some new physical properties.

EXPERIMENTAL

The vibrational method[†] is used here to study the molecular hyperpolarizabilities of different types of push–pull polyene molecules (see Scheme 1). Two series of push–pull diphenylpolyenes **I** and **II** were studied. Their quadratic NLO properties determined via EFISH experiments were already reported.^{3f} Two series of push–pull phenylpolyenes **III** and **IV** are also investigated. They possess the same weak acceptor at one end of the

polyenic chain and different donor substituents on the phenyl ring grafted at the opposite end. The quadratic hyperpolarizabilities of molecules of series **III** (derived from EFISH experiments, refs. 3a,c) as well as of polyenovanillins of series **IV** (from vibrational spectroscopy, ref. 4b) were previously reported. Finally, the behavior of push–pull diphenylpolyenes and phenylpolyenes is compared to that of push–pull polyenes **V**, **VI**, and **VII**, where donor and acceptor are directly grafted onto the polyenic chain.⁹

RESULTS AND DISCUSSION

The structural properties which account for the physical behavior of push–pull polyenes are the result of a subtle balance of different factors, among which of particular importance are the chain length and the donor and acceptor strength. For this reason, before undertaking a systematic study of the dependence of molecular hyperpolarizabilities from the molecular structure, it is necessary to consider separately the influence of the various parameters. Detailed studies exist in the literature^{3,10} on the characterization of molecular hyperpolarizabilities of push–pull polyenes based mainly on techniques such as EFISH (for β) and THG (for γ).

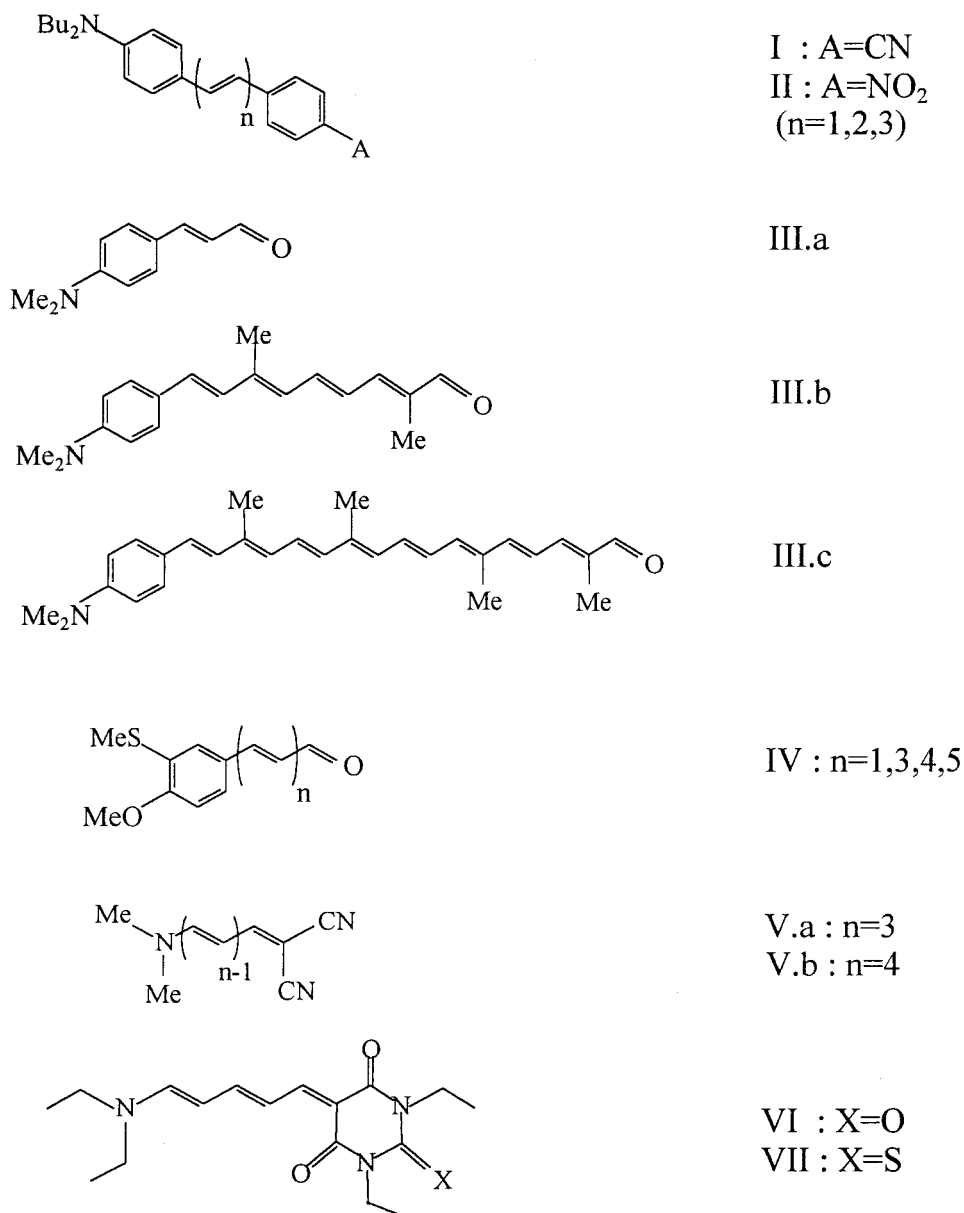
Here, we wish to use the vibrational method to determine β^r for different classes of polyene systems, as a function of the various structural parameters. In the following, we successively focus on the (i) chain length and (ii) acceptor and (iii) donor strength. Finally, we consider also the problem of how the molecular structure and NLO behavior are affected by the interaction with the surrounding medium. Particularly relevant is the study of solvent effects as a means for modulating the NLO responses of conjugated compounds. This problem was recently treated by several groups.^{7,11}

Chain Length

The usual way to study chain-length dependence of a certain property is by using power laws. In the case of molecular hyperpolarizabilities, several theoretical and experimental studies have been carried out aimed at the determination of the exponent α describing the growth rate [$\beta(\gamma) = kn^\alpha$].

We carried out such an analysis for two series of push–pull diphenylpolyenes (series **I** and **II**) to

[†] The detailed description of the procedure needed to obtain experimentally vibrational β was reported in ref. 7. It must be noted that the vibrational observables appearing in eq. (1) can be obtained as peak frequencies (ν_k) and from absolute infrared ($\partial\mu_n/\partial Q_k$) and Raman ($\partial\alpha_{nm}/\partial Q_k$) intensities. The measure of vibrational intensities is dealt with in standard spectroscopy texts (see, e.g., ref. 8).



Scheme 1

determine the exponent α . The results obtained (see Fig. 1) suggest that the relationship between (β^r) and (n) is linear. This finding is in good agreement with the results obtained with EFISH technique.^{3e} A substantially linear relationship between β^r and n ($\alpha \cong 1$) is found also in the case of the class of push-pull phenylpolyenes (**III** and **IV**, Fig. 2). As will be discussed later, to find a steeper dependence on the chain length, donor and acceptor directly grafted at the ends of the polyenic chain are needed (series **V**). In the case of second-order hyperpolarizabilities, a superlinear increase of γ^r was observed for polyenes and oligothiophenes.⁴

Acceptor Strength

In comparing the absolute β^r values obtained for series **I** and **II** (Fig. 1), we notice that the molecules with the stronger acceptor (series **II**) have higher β^r values for each chain length (n). The same kind of correlation holds for β as determined by EFISH experiments.^{3e}

Donor Strength

Results similar to (ii) can be obtained in the study of the dependence on the donor strength. For this purpose, we compared two series of push-pull

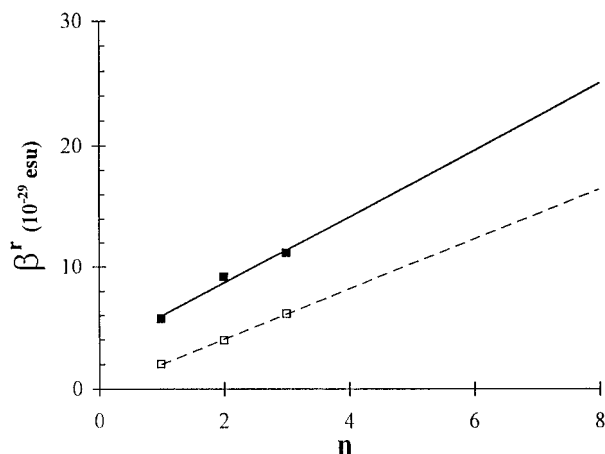


Figure 1 Plot of the experimental β^r values versus the number n of double bonds in the polyenic chain for the push–pull diphenylpolyenes series (□) **I** and (■) **II**. Logarithmic scales are shown. For all the data shown here, the estimated experimental error is about 15%.

phenylpolyenes (**III** and **IV**) (see Fig. 2). Again, the strongest donor substituent yields higher β^r values.

If we now compare these results with those reported in (ii) we observe that compounds of the type **III**, which have a donor group very similar to that of compounds of the type **I** and **II**, show an intermediate behavior, thus suggesting that the aldehyde group has an intermediate strength with respect to the cyanophenyl group and the nitrophenyl group. This observation brings in a new concept, which will be dealt with in greater detail later on, namely, that in designing new NLO chromophores the shielding effect induced by the terminal aromatic rings must be taken into account. It must also be noticed that the methyl side groups which occur in compounds **III.b** and **III.c** might affect the intramolecular charge-transfer efficiency.

ENVIRONMENTAL EFFECTS: STRUCTURE/PROPERTY RELATIONSHIPS FROM VIBRATIONAL SPECTRA

It has been recently shown by the groups of Marder and Brédas that the NLO response of push–pull polyenes can be modulated by using solvents of increasing polarity.¹¹ We showed that the same kind of evolution of first-order hyperpolarizability is predicted by the vibrational approach.⁷

The rationalization of this phenomenon is given if one considers push–pull polyenes as combination of neutral and charge-separated (zwitterionic) limiting-resonance forms. Qualitatively, a number of factors such as the donor/acceptor strength, the nature and size of the conjugated path, as well as external perturbations (e.g., dipolar interactions with the solvent) dictate the balance between the limiting-resonance forms. These factors will thus determine the structure of the molecule, in particular, the bond-length alternation (BLA), in the polyenic chain. For instance, for a given chain length, increasing the donor–acceptor strength will tend to stabilize charge separation. This results in a modulation of the bond-length or bond-order alternation which can be modulated from a polyenelike (alternated structure) through a cyaninelike (undimerized) chain to a zwitterionic structure where the bond alteration is completely reversed. It should be noticed that it is not possible to span the whole range covered by the structural parameter (from polyene to zwitterionic structure) with only one compound. Actually, to map different regions, it is necessary to change end groups. Since calculations have shown that the hyperpolarizabilities can be correlated to BLA, changes in NLO responses are expected by changing the BLA. In particular, calculations carried out on push–pull polyenes indicate that β is small for highly alternated structures and vanishes for equalized structures (i.e., cyaninelike) structures, whereas it peaks at intermediate BLA values.¹²

Changing the solvent polarity results in a modulation of BLA, which, in turn, affects the inten-

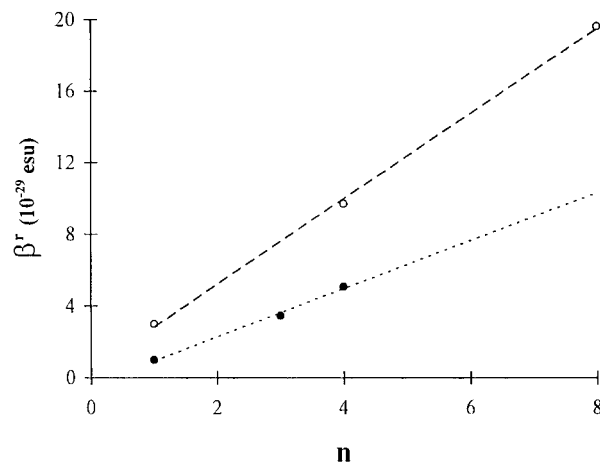


Figure 2 Linear chain-length dependence of the experimental β^r values for the series of push–pull phenylpolyenes (○) **III** and (●) **IV**.

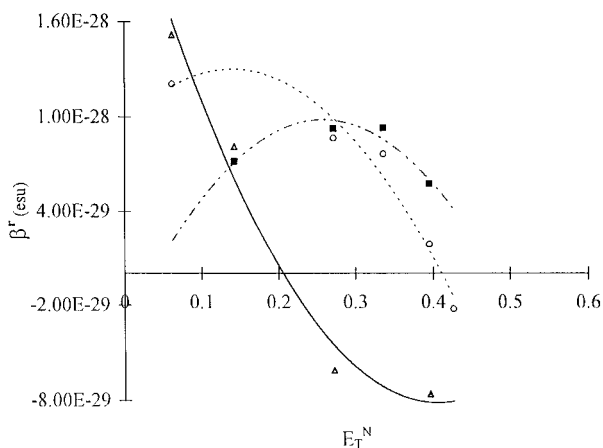


Figure 3 Experimental β^r values for molecules (■) **V.a**, (○) **VI**, and (△) **VII** in various solvents (CCl_4 , C_6H_6 , CHCl_3 , CH_2Cl_2 , CH_3CN , CH_3NO_2 in order of increasing polarity). Lines are only meant as guide to the eye. The scale on the abscissa corresponds to the empirical solvent polarity parameter E_T^N (ref. 9).

sity pattern of the vibrational spectra and, hence, the measured value of β^r . In Figure 3, we report the evolution of β^r for molecules **V.a**, **VI**, and **VII** as function of solvent polarity. Here, again, it should be stressed that the results obtained for β^r (including the sign inversion corresponding to going through the cyanine limit observed with molecule **VII**) parallels those obtained with the EFISH experiments.¹¹

As noted from Figure 3, molecules of the groups **V–VII**, where strong end groups are directly grafted on the ends of the polyenic chain, show a remarkable solvent effect. An idea of the efficiency of such end groups is given by the comparison of the results obtained for molecules **V.a** and **V.b**, where the number of double bonds n is increased by one (Fig. 4). In this case, we observe that the addition of only one double bond to the chain produces a very large increase in the absolute value of β^r (by about a factor of 4) opposite to what was observed previously in the case of push–pull diphenyl- and phenylpolyenes. This suggests that an analysis of chain-length dependence ($\beta^r = kn^a$) would lead to values of a larger than 1 (see Chain Length section). Such behavior has also been found with EFISH experiments on series **V** ($n = 2,4$) that yielded an a value of 4.7.¹³

As far as molecules **V.a** and **V.b** are concerned, it should be noted that the variation of β^r with solvent polarity is *similar* for both chain lengths. This similar solvent behavior indicates that, for this series of push–pull compounds with strong

end groups grafted on the polyenic chain and within the range of chain length considered here, the structural parameter (BLA) is not significantly affected.

In the case of push–pull phenylpolyenes with a rather weak acceptor end group (such as molecules of series **III**), it is still possible to obtain useful information from the solvent dependence of β^r , even if the modulation of the structural parameter by the polarity of the solvent is not as large (“stiffer” chains).

In this case, it can be seen from Figure 5 that molecules with increasing chain length show different behavior with solvent polarity. Only for the shortest molecule (**III.a**) does the trend of the experimental data seem to suggest that in correspondence of the most polar solvent employed (CH_3CN) β^r approaches its maximum value. On the other hand, the β^r values obtained for longer chains (**III.b** and **III.c**) seem to be far from a maximum. This observation can be rationalized by a “stiffening” of

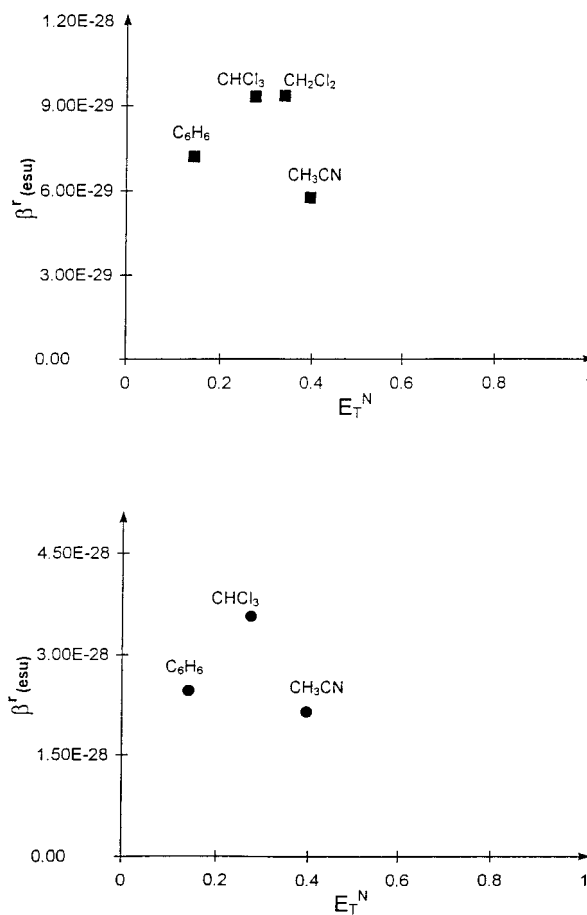


Figure 4 Experimental β^r values for molecules (top) **V.a** and (bottom) **V.b** obtained in different solutions.

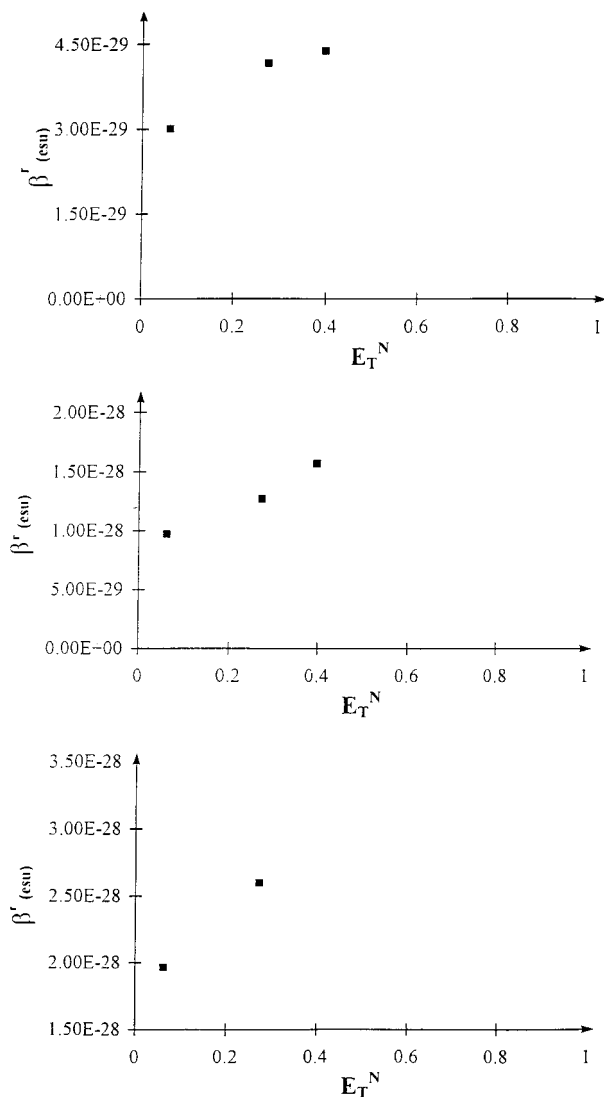


Figure 5 Evolution of experimental β^r with solvent polarity for molecules **IIIa**, **IIIb**, and **IIIc**, respectively, from top to bottom.

the chain structure or, in other words, by less effective donor–acceptor end groups with increasing chain length.¹⁴ Indeed, this is a reasonable behavior in view of the fact that the longer the chain the more closely the molecule resembles a centrosymmetric apolar polyene. Referring to the evolution of β with BLA reported in ref. 8, this implies that the structure of the longest molecules corresponds to a more alternated polyenic structure also in very polar solvents.

In conclusion, we find that in the case of push–pull phenylpolyenes with weak acceptor end groups (i.e., alternated polyenelike structures) the structural parameter is sensitive to chain

length already for small n values and the solvent behavior is chain length-dependent. On the contrary, when strong end groups are present (**V.a**, **V.b**), the chain structure is not so sensitive to the number of double bonds in the chain. In other words, in this second case, larger n values are needed to observe a remarkable chain-length dependence. In these cases, the structure is such that β is close to its maximum value and it is heavily affected by intermolecular interaction with the surrounding molecules (solvents of different polarities or similar molecules in the solid state).

From a spectroscopic point of view, these observations can be rationalized in the following way: If we compare the absolute infrared and Raman intensities of molecules of the series (**III**), on the one hand, and (**V**), on the other, we observe two different behaviors. For sake of simplicity, we focus only on the strongest band appearing in the spectra. This oversimplification is justified because this band gives the largest contribution to β^r (see Table I[‡]). This vibrational normal mode has been assigned to a collective vibration of the carbon backbone which is described by the in-phase stretching of C—C bonds and the shrinking of C=C. The relevance of this mode (usually defined as the \mathcal{R} mode) has been extensively discussed.¹⁵ The \mathcal{R} vibration corresponds to an oscillation of the chain dimerization, or BLA, that is, of the structural parameter involved in the modulation of the NLO response. The assignment explains why this vibration must provide the largest contribution to β^r . The absolute intensity values measured for this normal mode in the different molecules are reported in Table II.

We observed that in the series of push–pull phenyl polyenes chain lengthening induces a variation of the structural parameter (BLA), while in the case of molecules of series (**V**) the addition of one double bond significantly enhances the β^r values but does not modify the structural parameter. This observation can be rationalized when

[‡] The values reported in Table I show that approximate β^r values can be obtained by considering only the contribution to eq. (1) from the \mathcal{R} oscillation. The values computed according to

$$\beta_{ijk}^{\mathcal{R}} = (F^{-1})_{\mathcal{R}\mathcal{R}} \left(\frac{\partial \mu_i}{\partial \mathcal{R}} \frac{\partial \alpha_{jk}}{\partial \mathcal{R}} + \frac{\partial \mu_j}{\partial \mathcal{R}} \frac{\partial \alpha_{ik}}{\partial \mathcal{R}} + \frac{\partial \mu_k}{\partial \mathcal{R}} \frac{\partial \alpha_{ij}}{\partial \mathcal{R}} \right)$$

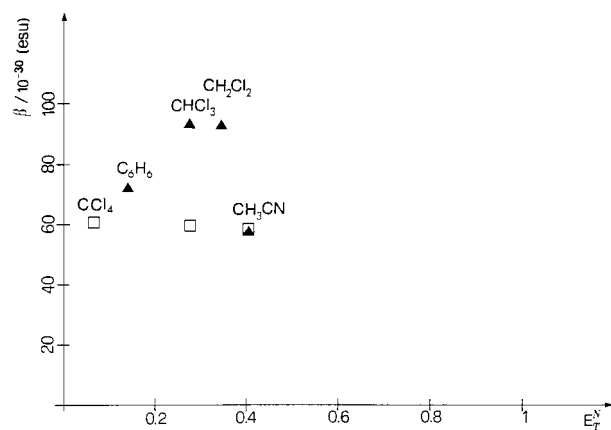
are very close to the values obtained by summing over all the normal modes. See also ref. 16.

Table II Intensity Evolution with Chain Length of the Most Relevant Infrared and Raman Band for Molecules III and V

Molecule	Double Bonds	ν_{M} (cm^{-1})	I_{IR} (km/mol)	I_{Raman} ($10^{-8} \text{ cm}^4 \text{ g}^{-1}$)
III.a	$n = 1$	1600	887	30
III.b	$n = 4$	1567	1081	407
III.c	$n = 8$	1521	878	1847
V.a	$n = 2$	1530	429	41
V.b	$n = 3$	1510	3297	269

the large enhancement of infrared intensities produced by the addition of just one double bond is considered (see Table II). This effect is the consequence of the presence of highly polar end groups which are able to efficiently polarize the whole chain, thus inducing extremely large intramolecular charge fluxes. On the contrary, in the case of more alternated polyenelike structures, the infrared spectra are practically unaffected by chain length. This can be rationalized if only the CC bonds close to the end groups are polarized. In this case, it is the Raman spectrum which mostly determines the β^r changes. Raman intensities are not very sensitive to polarization, but are mostly affected by the number of π electrons available. Indeed, the enhancement of the Raman intensities with increasing n is similar for both classes of compounds.

Finally, if we consider the diphenylpolyenes with the weakest acceptor end group among those available (series I), no solvent effect is observed at all. Indeed, comparing (Fig. 6) the solvent dependence of β^r for molecules I and V.a, we observe

**Figure 6** Comparison of β^r versus solvent polarity plots for molecules (▲) V.a and (□) I with the same number of double bonds in the chain.

two completely different behaviors: In one case, we observe the peaking of β^r , while in the other case, the molecule is not sensitive to the solvent polarity. The striking observation is that such a different behavior is the consequence just of the introduction in series V of a phenyl ring between the chain and the polar end groups. This suggests that the phenyl rings shield and weaken the effect of the polar groups on the chain structure. This shielding effect can be explained in terms of the “pinning” potential. The concept of the pinning of π electrons within aromatic and heteroaromatic rings was recently introduced¹⁷ to explain the Raman spectra of polyconjugated compounds. It represents an effect which competes the tendency of intramolecular delocalization of π electrons at large distances along the chain. This explains why the electronic mobility and the structural parameter along the chain is less affected by the solvent polarity. The aromaticity of the rings hinders the electrons to flow along the chain from the donor to the acceptor end group, resulting in the “pinning” of the charge distribution within the rings. We have thus seen that interactions with the surrounding media (solvents of various polarities) can modify the chain structure in such a way that the molecular hyperpolarizabilities are heavily affected.

Especially in view of possible device applications, an interesting question arises, namely: What kind of environment is experienced by a molecule in the solid state, that is, how the structure has evolved in the solid? It is not easy to answer this question because neither experimental nor theoretical tools are available. We can attempt, at least qualitatively, to give an answer to this question on the basis of the analysis of the vibrational spectra. The effect of the “environment” on the single molecule is a modulation of the BLA structural parameter (i.e., chain dimerization), which, in turn, produces a variation of

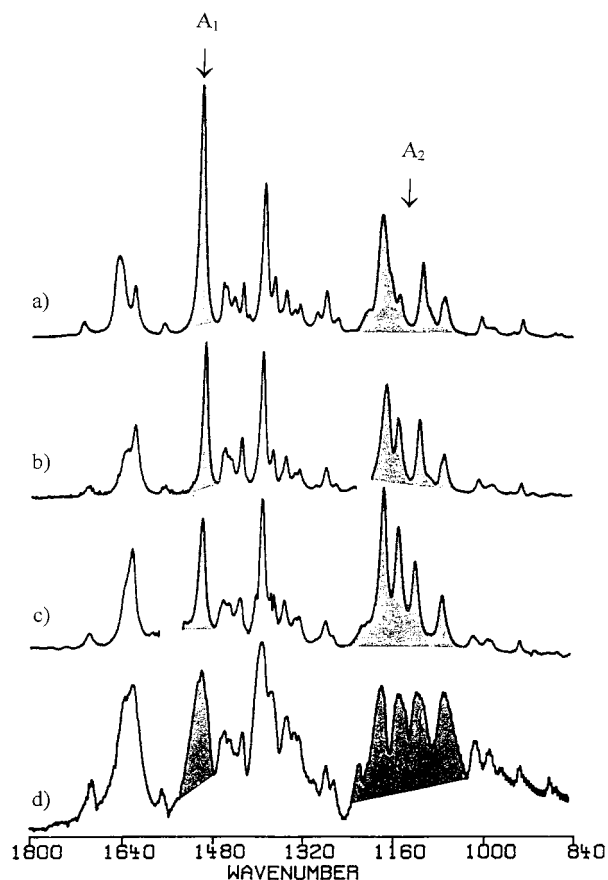


Figure 7 Infrared spectra of molecule **VI** dissolved in various solvents and in the solid state: (a) CCl_4 : $A_2/A_1 = 1.66$; (b) CHCl_3 : $A_2/A_1 = 3.04$; (c) CH_3NO_2 : $A_2/A_1 = 5.16$; (d) solid: $A_2/A_1 = 3.21$ (see text).

β' . Recalling eq. (1), this implies that the spectral intensity pattern must change accordingly. In Figure 7, we report the evolution of the infrared spectra of molecule **VI** when the polarity of the solvent increases (from a to c) with the corresponding decrease of the degree of bond alternation. The intensity pattern is seen to be heavily affected: In the high-frequency region of the spectra, the intensity pattern is reversed and, on the whole, the low-frequency region gains in relative importance. The spectrum of the solid shows some strong similarity with the spectrum of the most polar solvents. This means that in the solid the chain structure is not polyenelike. To be more quantitative, we can measure the intensity ratios of the two spectral regions. In this way, we obtain an indication of the kind of "effective" intermolecular interactions acting on the molecule and, hence, of its NLO response. From the data reported in Figure 7, we see that the situation for

the solid is very similar to that of the chloroform solution.

This idea can be generalized to the case of more complex environments. If we are able to relate some spectral feature to the structural parameter, we can obtain from the spectral evolution an estimate of the intermolecular interaction. This concept can be exploited, for example, in the case of biological systems where the NLO chromophore is grafted onto a protein molecule or is embedded in a membrane.¹⁸

CONCLUSIONS

In this work, we presented the experimental results obtained for different series of push-pull molecules. In all cases, we have found large β' values and we have been able to establish structure/property correlations. Our conclusions are similar to those found with other techniques. Moreover, the interpretation of the spectra yields a direct and easy way to estimate the structural parameter which characterizes π -electron delocalization. The key physical phenomenon which rationalizes this finding is the possibility of inducing a modulation of the electronic π polarizability with a suitable displacement of the nuclei as theoretically shown in ref. 6d.

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