J. Phys. Chem. 1993, 97, 9385-9391

Chain-Length Dependence of the Third-Order Polarizability of Disubstituted Polyenes. Effects of End Groups and Conjugation Length

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Received: January 5, 1993; In Final Form: June 22, 1993[●]

Various α,ω-disubstituted polyenes of increasing length and bearing various donor and acceptor end groups have been synthesized in order to investigate the chain-length dependence of their second-order hyperpolarizability γ. Both symmetric polyenes bearing electron-withdrawing or electron-donating end groups and asymmetric donor–acceptor (push–pull) polyenes have been studied for the same donor/acceptor couple. Values of γ have been obtained through the electric field induced second-harmonic generation (EFISH) and the third-harmonic generation (THG) experimental techniques. In each series of homologous compounds, the lengthening of the polyenic conjugated path results in a sharp increase in γ values. This behavior can be modeled by $\gamma = kn^a$ relationships with respect to the number of n of conjugated double bonds of the polyenic chain. The exponent value (a) depends on the substitution pattern. The steepest increase of γ is obtained when both end groups are electron donors. Very large values of γ are found for the longest symmetric polyenes bearing strong electron donors. No saturation effect has been noticed within the molecule size range investigated (up to 40 Å).

Introduction

The search for new efficient organic materials to be used in nonlinear optics has considerably extended over the past two decades. Organic derivatives received much attention in view of their efficiencies, the versality of their chemical structure, and their various ordering strategies at the supramolecular level.[1,2] They provide several possible organization schemes ranging from single crystals to functionalized polymers going through host–guest inclusion or Langmuir–Blodgett films.

Within this domain of investigation, polyenic oligomers are of particular interest as model systems of one-dimensional conjugated chromophores.[3,4] This family of molecules presents, in addition to their large first-order hyperpolarizability β in the case of donor–acceptor compounds,[5–7] significant second-order hyperpolarizabilities.[8–13] This property may lead to applications in the realm of all-optical signal processing.

It is generally accepted that extended conjugation systems, in particular polymers, lead to large values of γ. In the case of linear polyenes, the longitudinal component of γ is the dominant component of the third-order polarizability as a result of the quasi-one-dimensional nature of the π-electron network. Furthermore, enhancement of γ has often been predicted when increasing the number n of conjugated double bonds of the polyenic chain, leading to $\gamma = kn^a$ relationships. However, discrepancies remain for the exponent a depending on the method of calculation and on the size range.[3,14–23] Exponent values are expected to taper off at large chain lengths, suggesting that γ/n approaches an asymptotic value for infinite chains.[18,24]

Therefore, a systematic experimental investigation of the variation of γ for polyenes of increasing length is of particular interest. Additionally, it would be relevant to explore the possible occurrence of saturation of γ/n at long chain length. An onset of saturation has been predicted around $n = 9$ for the linear polarizability α of polyenes[17,25] and around $n = 15$–20 for their third-order polarizability γ.[19,24]

Another relevant point examined in this paper is the influence of electroactive end groups grafted onto the polyenic chain. It has been suggested that polar substituents would enhance γ[17] and that donor–acceptor substitution on polyenic chains should increase the nonlinear properties of linear conjugated chains through a breaking of the centrosymmetry.[19] It has also been shown that electron-donating substituents could significantly enhance the cubic hyperpolarizability of polarizable systems through increase of the electron density in the π-conjugation.[26]

In this paper, we report the results of third-order polarizability measurements performed on synthetic α,ω-disubstituted polyenes of increasing length and bearing various electroactive end groups. We investigated the dependence of γ on the conjugation length for two series of symmetric polyenes (Schemes I and II), bearing either acceptor end groups (series I where the electron-withdrawing substituents are formyl moieties) or donor end groups (series II where the electron-donating substituents are dimethylaniline moieties). Additionally, we examined the length dependence of γ for the series of donor–acceptor ("push–pull") polyenes having the same donor and acceptor end groups (series III) mentioned above (Scheme III). The results are discussed in terms of conjugation length as well as substitution pattern.

For the sake of comparison at the same conjugation path length, two additional symmetric polyenes, exhibiting stronger donor and acceptor end groups, have been characterized (Scheme IV). Compound **IV** presents the efficient electron-withdrawing p-nitrophenyl end group. In compound **V**, julolidine moieties—an even stronger electron-donating group than the dimethylanilino one[27,28]—are grafted at both ends of the polyenic chain.

Experimental Section

1. Synthesis. Compounds of series I are gifts from Hoffmann-Laroche AG (Basel). Regarding molecules of series II, the shortest compound ($n = 3$) has been synthesized by means of a reaction similar to that already described,[29] although using a slightly different procedure.[30–32] For the longest molecules, the synthetic approach was to functionalize the symmetric conjugated dialdehydes of series I. These molecules have been used in the synthesis of natural carotenoids,[33] and this strategy led to compounds exhibiting the conjugated polyenic skeleton of the carotenoids. The presence of the characteristic methyl side groups on the carotenoid backbone confers both better solubility and stability to the polyenic chain, as compared to one which is unsubstituted. Symmetrical double condensations using the

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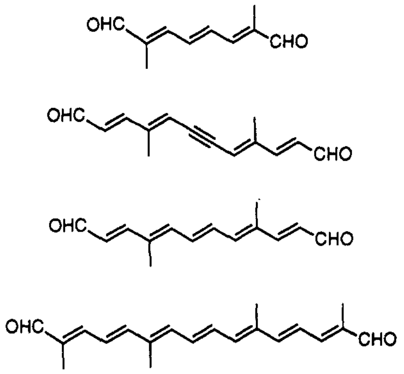
[●] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

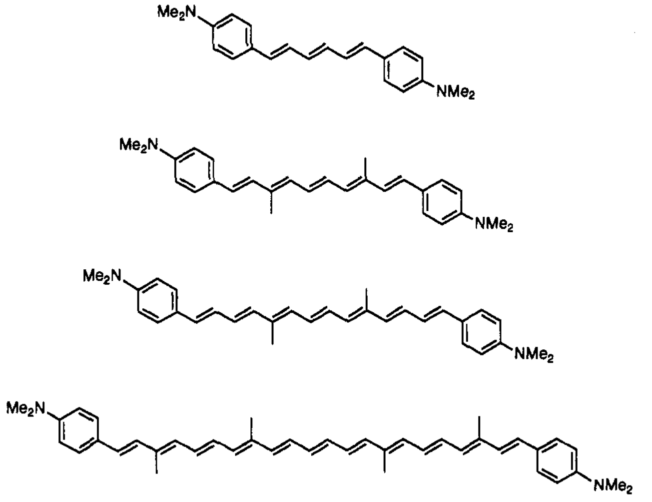
0022-3654/93/2097-9385$04.00/0

SCHEME I



Series I

SCHEME II



Series II

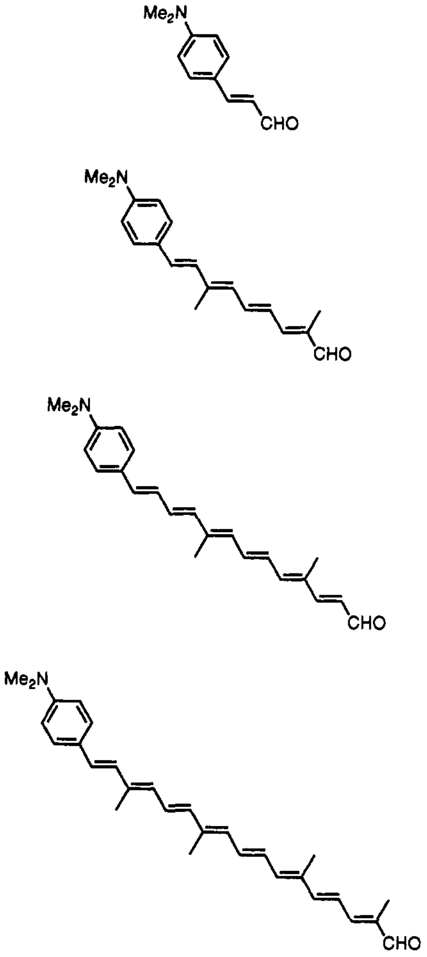
Wittig reaction in liquid–liquid phase-transfer conditions[32,34] at room temperature yielded molecules **II**, $n = 5$, and **II**, $n = 7$ (Scheme V). To obtain the longest compound **II**, $n = 11$, a different synthetic pathway proved requisite (Scheme V).[35] It is based upon asymmetrical monocondensation followed by symmetrical coupling using Horner–Emmons–Wittig condensation in solid–liquid phase-transfer conditions at room temperature.[30-32] The products were purified by flash chromatography on silica gel and isolated in respectively 14%, 65%, and 45% yields.

The same strategy and similar procedures and purification steps afforded compounds **IV**, $n = 7$, and **V**, $n = 7$, starting from molecule **I**, $n = 5$. A Horner–Emmons–Wittig reaction in solid–liquid phase-transfer conditions at room temperature yielded molecule **IV**, $n = 7$, in 73% yield. Molecule **V**, $n = 7$, was obtained by Wittig condensation in solid–liquid phase-transfer conditions at room temperature[36] in 40% yield (Scheme VI). The phosphonium derivative of julolidine used in the Wittig condensation (Scheme VI) was prepared, in one step, by reacting julolidine with equivalent amounts of formaldehyde, potassium iodide, and triphenylphosphine in a mixture of refluxing toluene and acetic acid for 8 h. The pure phosphonium salt was obtained in 92% yield as an orange solid after crystallization in diethyl ether.

The synthesis of push–pull polyenes of series **III** has been reported previously.[5,37,38]

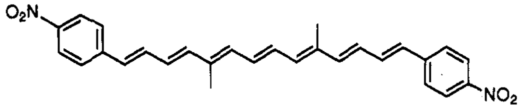
All the chemicals and the solvents used were of the highest purity commercially available. Purifications by column chromatography were performed on silica gel 60 (Merck, 230–400 mesh), using dichloromethane as the eluant, in dim light and under nitrogen.

SCHEME III

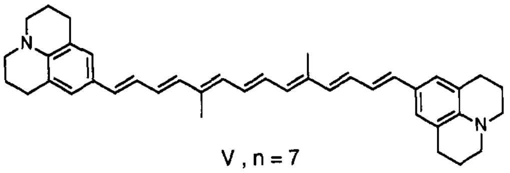


Series III

SCHEME IV



IV , n = 7



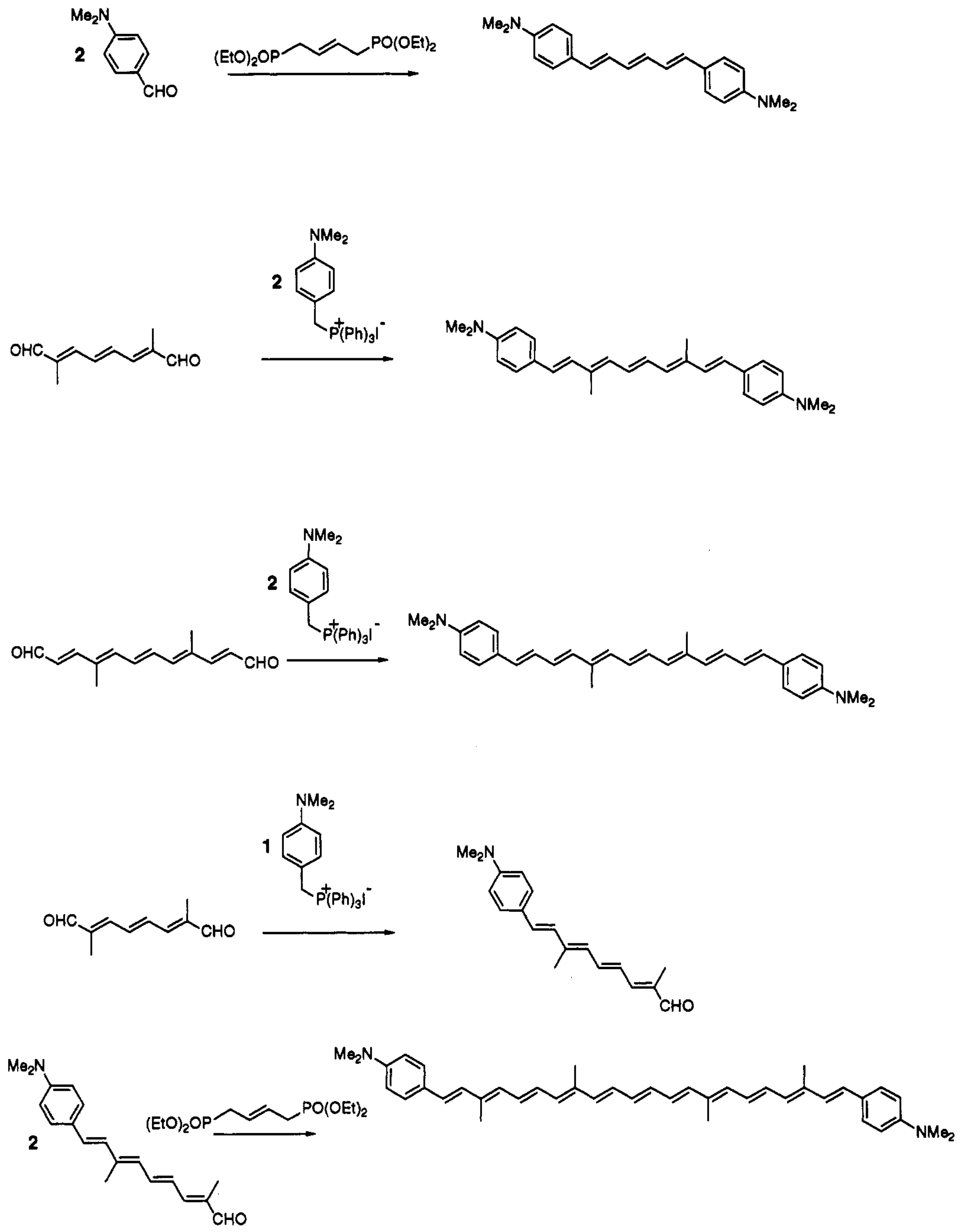
V , n = 7

All new compounds were characterized by IR, NMR, and mass spectroscopy. In particular, the ^1H NMR spectra are in agreement with *all-trans* structures.

2. Absorption Spectra. Electronic absorption spectra have been performed in spectroscopic grade solvents by using a Perkin-Elmer Model 554 spectrophotometer.

3. EFISH and THG Measurements. Nonlinear measurements have been performed by use of three different sources: a Q-switched Nd^{3+}:YAG laser emitting pulses of about 10-ns duration at 1.064 μm; a Q-switched and mode-locked Nd^{3+}:YAG laser emitting pulse trains of about 90-ns envelope duration (individual pulses of 160-ps duration) at 1.34 μm; and the first Stokes radiation, at 1.907 μm, of the YAG emission at 1.064 μm generated in an hydrogen Raman cell at 60 bar. All third-order polarizabilities are determined from solution measurements in acetone at different mass concentrations.

SCHEME V



In the case of symmetric molecules, second-harmonic radiation in the presence of a static electric field (electric field induced second-harmonic generation, or EFISH, technique) is generated via a purely electronic mechanism, with no additional orientational second-order nonlinear contribution (β). The signal at the double frequency is spatially and spectrally filtered by a spectrophotometer and detected by a photomultiplier. In order to filter off the instabilities due to the laser source, the signal is divided by a reference signal generated in a highly efficient organic powder. The solutions are placed in a wedge-shaped cell, and a high-voltage pulse is switched on in synchronism with the incoming laser pulse. Translating the prismatic cell transversely to the beam direction modulates the harmonic signal (Maker fringes) with a coherence length l_c related to the dephasing between bound and free waves in the solution:[39]

$$lc = \lambda/4(n^{2\omega} - n^{\omega})$$

where n^{ω} (respectively $n^{2\omega}$) is the refractive index of the solution at the fundamental (respectively harmonic) frequency and λ is the fundamental wavelength.

The amplitude of these fringes can be related to the susceptibility of the liquid, Γ. By performing measurements relative to the pure solvent, one can evaluate the contribution of the solute molecule and its nonlinear polarizability assuming independent molecules with an adequate local field correction.

The susceptibility of the solution, $\Gamma(x)$, depends on the mass concentration x according to the following relationship:

$$\Gamma(x) = \frac{1}{(1 + x)}(\gamma(fM\rho x/N_a) + \Gamma(0))$$

where M is the molar mass and γ the hyperpolarizability of the nonlinear molecule. $\Gamma(0)$ is the susceptibility of the pure solvent, ρ the density of the solvent, N_a the Avogadro number, and f the local field factor.

In the case of asymmetric polar molecules, the third-harmonic generation (or THG) must be used. The EFISH technique leads

SCHEME VI

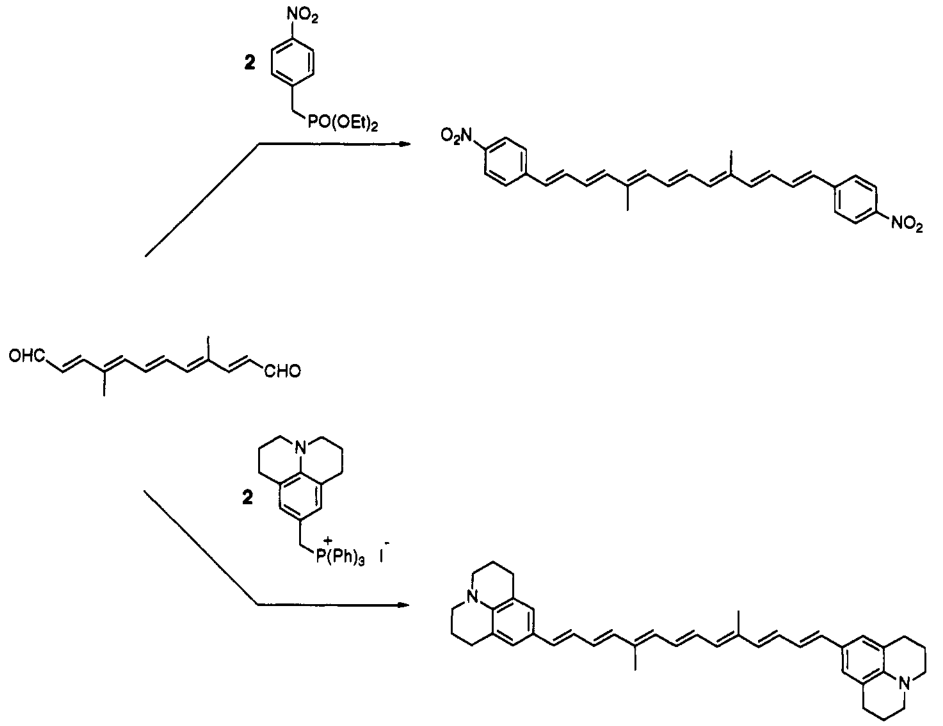


TABLE I: Characteristics of the Maximal Absorption Peak and Second-Order Hyperpolarizability Values for Compounds of Series I

n	λ_{max} [log ϵ_{max}] (nm)	$\gamma_{1.34}^{SHG}$ (10^{-36} esu)	N[a]
3	328 [4.78]	170 ± 20	3
5	392 [4.83]	500 ± 100	5
5′	370 [4.40]	290 ± 30	5′
7	446 [5.03]	1200 ± 150	7

[a] Number of equivalent double bonds (with respect to the total length). The analogous compound of molecule I, $n = 5$, where the central double bond has been replaced by a triple one is indicated by $n = 5'$.

TABLE II: Characteristics of the Maximal Absorption Peak and Second-Order Hyperpolarizability Values for Compounds of Series II

n	λ_{max} [log ϵ_{max}] (nm)	$\gamma_{1.34}^{SHG}$ (10^{-36} esu)	N[a]
3	408 [4.85]	900 ± 150	6
5	448 [4.90]	2700 ± 300	8
7	476 [5.04]	12000 ± 1200	10
11	516 [5.18]	41300 ± 8000	14

[a] Number of equivalent double bonds (with respect to the total length).

TABLE III: Characteristics of the Maximal Absorption Peak and Second-Order Hyperpolarizability Values for Compounds of Series III

n	λ_{max} [log ϵ_{max}] (nm)	$\gamma_{1.06}^{THG}$ (10^{-36} esu)	$\gamma_{1.34}^{THG}$ (10^{-36} esu)	$\gamma_{1.91}^{THG}$ (10^{-36} esu)	N[a]
1	384 [4.53]	–	700 ± 120	200 ± 50	2.5
4	444 [4.67]	-3600 ± 500	–	1200 ± 120	5.5
6	472 [4.83]			4000 ± 200	7.5
8	498 [4.96]	-9000 ± 1200	–	7600 ± 600	9.5

[a] Number of equivalent double bonds (with respect to the total length).

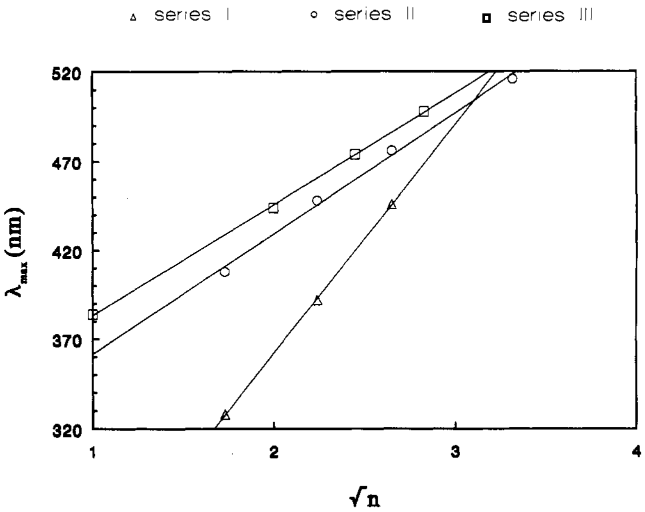


Figure 1. Plot of the maximal absorption wavelengths versus the square root of the number n of carbon–carbon double bonds of the polyenic chain for series I–III.

to combined β and γ contributions that cannot be sorted out without additional THG experiments.[13,40] The apparatus and data acquisition setup are the same as those for the EFISH experiment. The coherence length is now given by:

$$l_c = \lambda/6(n^{3\omega} - n^{\omega})$$

Results and Discussion

All the experimental results are collected in Tables I–V. For each molecule, the maximum absorption wavelength and the corresponding molar extinction coefficient (in M^{-1} cm^{-1}) were measured in dichloromethane.

1. Effect of the Length of the Conjugation Path on the Three Polyenic Series. In each series of homologous compounds (series I–III), the lengthening of the polyenic chain induces hyperchromic and bathochromic shifts (Tables I–III). This is shown in Figure 1, where the values of the maximum absorption wavelength, λ_{max}, have been plotted as a function of the square root of n, the number of conjugated carbon–carbon double bonds of the polyenic chain. Each series displays a behavior in agreement with a linear dependence of λ_{max} with the square root of n, as already reported for polyenes.[41,42]

In the present study, the harmonic wavelength (either the second harmonic of 1.34 μm for EFISH or the third harmonic of 1.91 μm for THG) is located within the transparency range of the molecules. Nevertheless, the resonance enhancement due to the

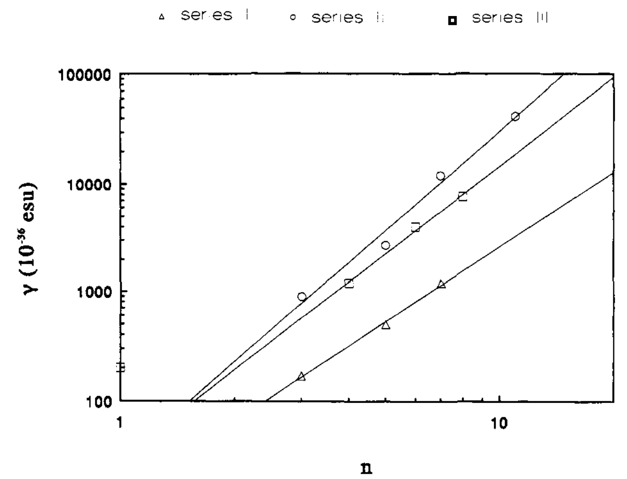


Figure 2. Plot of the γ^{SHG} values (measured at 1.34 μm) for the two series of symmetric polyenes I (bis-acceptor compounds) and II (bis-donor compounds) and of the γ^{THG} values (measured at 1.91 μm) for the series of asymmetric polyenes III (push-pull compounds) as a function of the number n of carbon-carbon double bonds of the polyenic chain, using logarithmic scales.

proximity of the first absorption band is probably large (by a factor of several units, as evidenced in ref 13) but comparable to that of other similar experiments performed on polyenic compounds.[12,13] The enhancement factor is more pronounced for the longest molecules as a result of the bathochromic effect of increasing chain length.

In each series of homologous compounds, the lengthening of the polyenic conjugation path results in a sharp increase in γ values (Tables I–III).

For the two series of symmetrically disubstituted polyenes (series I and II), the logarithmic plots of the γ^{SHG} values versus n evidence a linear dependence of $\log(\gamma)$ versus $\log(n)$ leading to $\gamma = kn^a$ relationships (Figure 2). The lower exponent value corresponds to the bis-acceptor series (series I) and the higher one to the bis-donor family (series II). The respective a values are 2.3 and 3.0. This behavior leads to very large values of γ for the longest bis-donor polyenes, while no saturation effect is observed for the size range investigated (up to 40 Å).

In addition, it should be noted that the donor end groups include a phenyl ring. Actually, this moiety is part of the conjugated path. Therefore, it is relevant to study the variation of γ as a function of N, where N includes an equivalent contribution of the phenyl rings to the conjugated electronic system. Since one phenyl ring can be considered as equivalent to one and a half double bonds, in terms of effective conjugation length,[23] this leads to $N = n$, $n + 3$, and $n + 1.5$ for series I, II, and III, respectively. The logarithmic plots of the γ values versus N again show a linear dependence of $\log(\gamma)$ on $\log(N)$, yielding $\gamma = kN^a$ relationships (Figure 3). Exponent values of 2.3 and 4.65 are thus obtained for the bis-acceptor (series I) and bis-donor (series II) compounds, respectively. An intermediary experimental value of 3.6 has been reported for symmetric model polyenes (or so-called neutral compounds).[43] These results suggest a much steeper increase of γ with length for bis-substituted polyenes bearing donor end groups. However, one must keep in mind that these exponent values, although derived from the same methodology (i.e., EFISH experiments performed at 1.34 μm), are calculated on resonance-enhanced γ^{SHG} values. The enhancement factors are related to electronic absorption features. As a result of the increase of the enhancement factor with increasing chain length, the exponents inferred from experimental γ^{SHG} values are magnified with respect to those corresponding to static $\gamma(0)$ values, and this effect depends on the molecular structure.

It should be mentioned that recent calculations conducted on disubstituted polyenes indicated a steeper increase of the static $\gamma(0)$ values for bis-donor with respect to bis-acceptor or donor-acceptor substitution.[23]

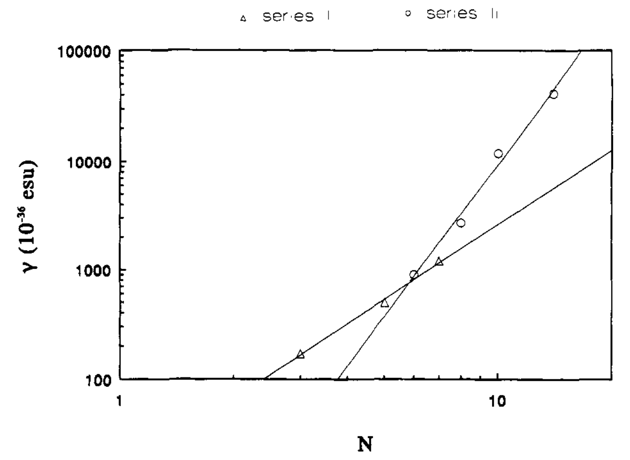


Figure 3. Plot of the γ^{SHG} values for the two series of symmetric polyenes I and II (measured at 1.34 μm) as a function of the equivalent number of carbon-carbon double bonds N ($N = n$ for series I and $N = n + 3$ for series II), using logarithmic scales.

In the case of the asymmetric push-pull polyenes (series III), THG experiments have been performed to measure the cubic hyperpolarizabilities in order to avoid any second-order contribution. Since the validity of the two-level model[39] is highly questionable to account for the frequency dispersion of γ values, it is not possible to perform a quantitative comparison of these hyperpolarizabilities with those of the symmetric bis-substituted polyenes. A reliable $\gamma(0)$ determination would necessitate THG measurements at several different wavelengths, in order to deduce with a sufficient accuracy the various parameters (μ_{01}, μ_{12}, $\Delta\mu$) contributing to the $\gamma(0)$ value.[13]

For the push-pull molecules of series III, the logarithmic plot of the γ^{THG} values versus n also shows a linear dependence of $\log(\gamma)$ on $\log(n)$, although the value for molecule **III**, $n = 1$, falls our of line (Figure 2). The nonalignment of this first point with the other ones has already been noticed in refs 5 and 6 for the β values of the same series. The comparatively high γ (and β) value obtained for the generic compound of series III (i.e., III, $n = 1$) may be accounted for by large interactions between the donor and acceptor groups. The electrons of the unique carbon-carbon double bond are strongly associated to the end groups whereas the electronic structures of the longer analogs are closer to that of one-dimensional polyenes. Therefore, if one excludes the point corresponding to $n = 1$, the $\gamma \propto n^{2.7}$ relationship may be established for series III. In terms of variation of γ^{THG} as a function of the conjugated path length (i.e., $N = n + 1.5$), this leads to the $\gamma \propto N^{3.4}$ relationship (Figure 4). This latter exponent value is close to the one measured in the same conditions on the series of push-pull polyenes bearing a benzodithia moiety instead of the dimethylanilino one as the donor group.[13]

2. Effect of the Triple Bond. Comparison of the λ_{max}, ϵ_{max}, and γ values obtained for the symmetric dialdehyde of series I presenting five double bonds and its analog where the central double bond has been replaced by a triple bond (indicated in Table I by $n = 5'$) points to the detrimental effect on the polarizability brought about by the triple bond. As displayed in Table I, the presence of the triple bond results in lower values. The hypochromic and hypsochromic effects of the replacement, in a conjugated polyenic chain, of a double bond by a triple one have already been reported in carotenoids. Moreover, this phenomenon is more pronounced when it affects the central double bond.[33] The triple bond creates a potential barrier in the conjugated polyenic backbone, hindering the π-electron displacements and resulting in a drop of the polarizability. However, it should be stressed that γ^{SHG} is less resonance enhanced in the case of the acetylenic analog, as a result of the hypsochromic

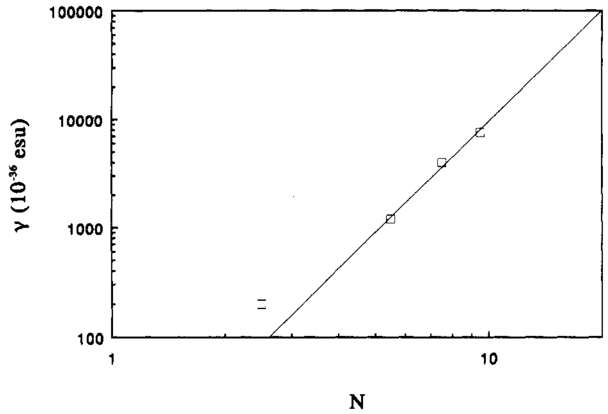


Figure 4. Plot of the γ^{THG} values for the series of asymmetric polyenes III (measured at 1.91 μm) as a function of the equivalent number of carbon–carbon double bonds N ($N = n + 1.5$), using logarithmic scales.

TABLE IV: Characteristics of the Maximal Absorption Peak and Second-Order Hyperpolarizability Values for Compounds of Series IV and V (n = 7)

series (n = 7)	λ_{max} [log ϵ_{max}] (nm)	$\gamma_{1.34}^{SHG}$ (10^{-36} esu)	$\gamma_{1.34}^{THG}$ (10^{-36} esu)	N^a
IV (n = 7)	490 [4.93]	3800 ± 600	−7000 ± 1000	10
V (n = 7)	494 [4.95]		−40000 ± 6000	10

[a] Number of equivalent double bonds (with respect to the total length).

TABLE V: Values of Absorption Wavelengths and Second-Order Hyperpolarizabilities of Symmetric Bis-Substituted Polyenes as a Function of Different Electroactive End Groups

series	$n(N)$	"end groups"	λ_{max} (nm)	$\gamma_{1.34}^{SHG}$ (10^{-36} esu)	$\gamma_{1.34}^{THG}$ (10^{-36} esu)
I	7(7)	formyl	446	1200 ± 150	
II	5(8)	dimethylanilino	448	2700 ± 300	
II	7(10)	dimethylanilino	476	12000 ± 1200	
IV	7(10)	nitrophenyl	490	3800 ± 600	−7000 ± 1000
V	7(10)	julolidino	494		−40000 ± 6000

effect of the triple bond. Therefore, only reliable determination of frequency-independent γ values would allow one to derive final conclusions.

3. Effect of the End Groups. As previously seen for the chain-length dependence of γ, the substituents grafted onto the ends of the conjugated chain significantly influence γ. Since the γ^{THG} values measured for push–pull polyenes cannot be directly compared with the γ^{SHG} determined for symmetric bis-substituted polyenes, we will focus here on the comparison of the γ values of symmetric polyenes bearing end groups of various electron-donating or electron-withdrawing strengths.

This comparison should preferably be made between molecules having comparable N values rather than between compounds with identical n values but with different numbers of phenyl rings. Results on various bis-donor and bis-acceptor polyenes of similar conjugation length (N = 7–8 or N = 10) are collected in Table V.

Comparison of the γ^{SHG} values of compounds **II** and **IV**, n = 7 (both N = 10 and displaying identical conjugation path), clearly shows the superiority of the donor group, relative to the acceptor one, in terms of the hyperpolarizability γ (Table V). The enhancement factor between the nitro and dimethylamino derivatives **IV** and **II**, n = 7, is 3.1. The exaltation effect of the donor group as compared to the acceptor one is probably even stronger than indicated by the direct comparison of γ values, since compound **IV**, which exhibits a larger λ_{max} value, provides a more resonant nonlinear response than compound **II**. Therefore, the increase of γ(0) when going from the nitro to the dimethylamino molecule could be still stronger than that of the measured γ^{SHG} values.

The effect of electron-donating substituents seems to be confirmed when one compares the γ^{THG} values of compounds **IV** and **V**, n = 7 (identical conjugation path), measured at 1.34 μm. These molecules have similar λ_{max} values, and therefore the experimental hyperpolarizabilities correspond to similar resonance enhancements, but the hyperpolarizability is 5.7 times higher for the julolidino than for the nitro derivative (Tables IV and V). It should be mentioned that, in this case, the comparison is done on γ^{THG} instead of γ^{SHG} values since only THG measurements at 1.34 μm lead to a THG signal distinct from that of the pure solvent. Owing to the low solubility of the molecule, EFISH experiments at 1.34 μm as well as THG experiments at 1.91 μm do not provide a detectable nonlinear response of the solution in such nonresonant configurations. In this particular case, THG experiments at 1.34 μm result in a large increase of γ related to resonance effect, and the modulus of γ probably contains a significant imaginary contribution.

Examination of compounds **I**, n = 7, and **II**, n = 5, corresponding to approximately equal N values (7 and 8, respectively) but to different numbers of carbon–carbon double bonds (and different numbers of phenyl rings), confirms the superiority of donor groups relative to acceptor ones in terms of cubic nonlinear response (Table V).

However, it must be pointed out that such comparisons hold only for a given domain of conjugation length. Figure 3 suggests that, if one extrapolates the behavior of γ toward small N values, a reversal of the tendency is expected, the nonlinearity of bis-acceptor compounds becoming similar, or even higher, than that of the corresponding bis-donor molecules. This trend seems to be confirmed by examination of the experimental γ^{THG} values reported in the literature for the short bis-donor and bis-acceptor polyenes **II**, n = 3, and **IV**, n = 3.[12] As opposed to the case of the longer analogs discussed in this work (**II**, n = 7, and **IV**, n = 7), the bis-acceptor substitution led to a higher γ value. Such inverse behavior has also been predicted for series of bis-amino and bis-formyl polyenes, the crossing point being located around n = 5.[23] However, such comparisons between similar—but not identical—theoretical or experimental studies can only be qualitative. Actually, the γ values reported in ref 23 are static ones, while comparison between our results measured by EFISH at 1.34 μm and those of ref 12 measured by THG at 1.907 μm is also questionable, the frequency dispersion factors being quite different. A more complete explanation of our experimental results in terms of the relative magnitudes of γ and exponent values for various pairs of end groups would require extended quantum chemical calculations.

Conclusion

Polyenic molecules represent an important class of compounds exhibiting high third-order polarizabilities. Results from the present study indicate that electron-donating substituents have a favorable influence on the γ hyperpolarizabilities, both in terms of their absolute values (for a large enough number of double bonds) and in terms of their variation with respect to the number of conjugated π electrons. However, a reliable determination of frequency-independent γ values, which requires further frequency-dispersed nonlinear spectroscopic measurements, is needed to identify the different parameters underlying the mechanisms of third-order polarizabilities.

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