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Study of Third-Order Microscopic Optical Nonlinearities in Sequentially Built and Systematically Derivatized Structures

Ming-Tang Zhao, Marek Samoc, Bhanu P. Singh, and Paras N. Prasad*

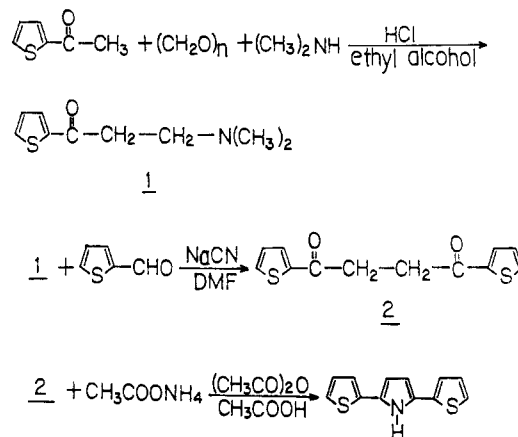
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With a goal of understanding the structure-property relationship for third-order microscopic optical nonlinearity, we have investigated the nonlinearities of a number of sequentially built and systematically derivatized π -conjugated structures by using degenerate four-wave mixing. To examine the nature of effective conjugation, we have measured the third-order microscopic nonlinearities, γ , for several para polyphenyls and compared the dependence on the number of repeat units with that observed in the α -thiophene oligomers. Our results show that while the limiting conjugation length in each conjugated series may be different, it becomes much shorter for polyphenyls than that for polythiophenes. Systematically derivatized α -terthiophene structures have also been investigated. The substitution of a pyrrole or a benzene unit in the place of the central thiophene ring in the α -terthiophene structure reduces the γ value. The substitution of polarizable iodine atoms at the end α positions of α -terthiophene increases the γ value. Even larger increases in the γ values are observed with the mononitro and dinitro substitutions at the α positions in the α -terthiophene structure. Possible theoretical reasons for such changes in the γ values for derivatized structures are discussed.

Introduction

Polymeric materials with extended π conjugation have been recognized as an important class of third-order nonlinear optical media with large nonresonant third-order optical susceptibility, $\chi^{(3)}$, and femtosecond response time derived from π -electron delocalization. The increased effective conjugation and hence large π -delocalization length have been recognized as a way of achieving large microscopic nonlinearity, γ , and consequently, large $\chi^{(3)}$.¹⁻³ Measurements of $\chi^{(3)}$ in various conjugated polymeric structures have yielded a nonresonant value of only less than 10^{-9} esu.³ The question may arise whether there is an intrinsic theoretical limit of $\chi^{(3)}$ reached by increasing effective conjugation length. Our theoretical understanding of microscopic third-order optical nonlinearity in organic structures is very limited in providing a clear answer to this question. The limited theoretical work on conjugated structures predicts leveling off of γ per repeat unit, and hence $\chi^{(3)}$, as the number of repeat units becomes very large.^{4,5} We have addressed this conjugation length dependence in a previous paper⁶ where we investigated the dependence of γ on the number of repeat units, N , in the thiophene oligomers with $N = 1-6$. In this system no saturation of γ was observed, indicating that the theoretical limit of effective conjugation was not reached for $N = 6$. The slope of the γ vs N curve indicated that the saturation of γ would be for $N > 6$. The question may arise: (i) How does conjugation manifest itself in various structures? (ii) Do we achieve the theoretical limit of conjugation in actual structures? In this paper we address these questions by comparing the third-order nonlinear optical behaviors of two sequentially built conjugated structures: (i) poly-*p*-phenyls and (ii) thiophene oligomers. Our results indicate that π conjugation alone cannot be relied upon to significantly enhance the optical nonlinearities. We must understand the conformational effects and the role of substituents so that our understanding of the molecular structure-property relation can be improved. For this purpose, we have studied the microscopic third-order nonlinearities of a series of

SCHEME I



systematically derivatized structures derived from α -terthiophene. The study of sequentially built and systematically derivatized structures can play a major role in identifying avenues other than π conjugation for enhancing optical nonlinearity.

In this work, we utilize the degenerate four-wave mixing technique to study benzene, *p*-biphenyl, *p*-terphenyl, and a derivatized *p*-pentaphenyl in tetrahydrofuran (THF) solutions. This technique yields both the magnitude and the sign of γ . We also study five different analogues and derivatives of α -terthiophene (α -terthienyl): (i) 1,4-dithienylbenzene in which the central thiophene unit of α -terthiophene is replaced by a benzene unit; (ii) 2,5-dithienylpyrrole in which the central thiophene unit of α -terthiophene is replaced by a pyrrole unit; (iii) α -diiodoterthiophene with both end α positions substituted by the iodine atoms; and (iv) α -mononitro- and α -dinitroterthiophenes with one and two end α positions replaced by the NO_2 groups. Again, their solutions in THF with various concentrations are used for the degenerate four-wave mixing experiment to obtain both the magnitude and the sign of γ .

Experimental Section

1. Syntheses of Various Compounds. The compounds (up to tetramer) in the poly-*p*-phenyl series were obtained from the Aldrich Chemical Co. and utilized without further purification. The alkoxy ($-\text{OC}_{10}\text{H}_{21}$) derivatized *p*-pentaphenyl was synthesized and kindly provided by Dr. B. Reinhardt of the Polymer Branch of the Air Force Wright Aeronautical Laboratory, Dayton, OH.

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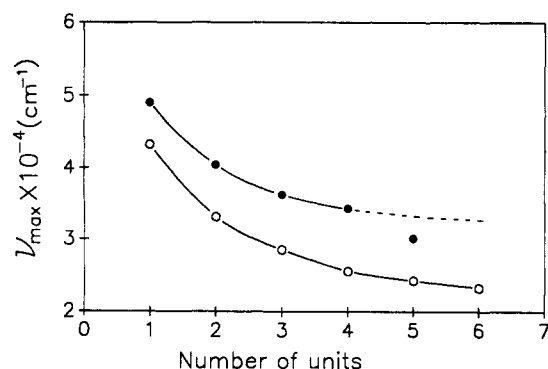
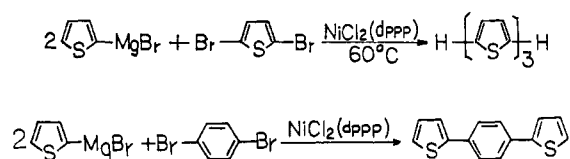


Figure 1. Band gap ν_{\max} is plotted as a function of the number of repeat units for the two series: poly-*p*-phenyls, ●, (the point that is off the curve at $N = 5$, corresponds to the alkoxy derivatized *p*-pentaphenyl); thiophene oligomers, ○.

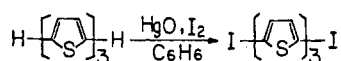
α -Terthiophene and 1,4-dithienylbenzene were synthesized according to the published synthetic schemes shown below.^{7,8}



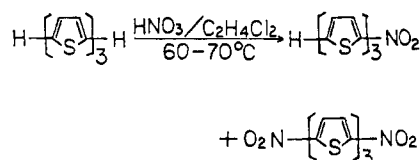
Both final products were recrystallized from methanol-toluene and further purified by gel permeation chromatography.

2,5-Dithienylpyrrole was prepared according to Scheme I.⁹ The product was purified by column chromatography (Al_2O_3). The pure 2,5-dithienylpyrrole, a pale yellow solid, was identical in all respects with that reported in the literature.⁹

α -Diiodoterthiophene was obtained¹⁰ by iodinating α -terthiophene with the use of HgO and I_2 in benzene. The reaction yielded a mixture of α -monoiodo and α -diiodo terthiophenes, which were separated by column chromatography.



The preparations of α -mononitro- and α -dinitroterthiophene were carried out according to the following scheme.



The two compounds formed were separated and purified by column chromatography.

The above compounds were characterized by their melting points, UV-visible spectra, NMR spectra, and mass spectrometry.

2. Measurement of Band Gap. In order to qualitatively relate the second hyperpolarizability with the band gap for a compound, the UV-visible absorbance spectra for poly-*p*-phenyls and the derivatized α -terthiophenes were obtained from their THF solutions. A Shimadzu spectrophotometer (Model UV-260) was used and a 1-cm quartz cuvette was used as a sample cell. Figure 1 shows the dependence of band gaps in poly-*p*-phenyls (with solid circles) and thiophene oligomers (with hollow circles) on the number of repeat units N . The data point that is away from the curve at $N = 5$ in poly-*p*-phenyls was obtained on alkoxy ($-\text{O}-\text{C}_{10}\text{H}_{21}$) derivatized *p*-pentaphenyl.

3. Measurement of Second Hyperpolarizability. The relationship between the orientationally averaged second hyperpo-

larizability, γ , of a molecule in an isotropic medium and its third-order bulk susceptibility, $\chi^{(3)}$, is given as

$$\langle \gamma \rangle = \chi^{(3)} / (L^4 N) \quad (1)$$

where N is the number of molecules per cubic centimeter and L is the local field factor, which in the Lorentz approximation^{11,12} is given by

$$L = \frac{1}{3}(n^2 + 2) \quad (2)$$

where n is the refractive index of the medium, which was measured with an Abbe refractometer at the sodium D line (589 nm). For a solution where solute and solvent do not interact, the effective $\chi^{(3)}$ is a coherent superposition of contributions by both the solute and the solvent

$$\chi_{\text{eff}}^{(3)} = L^4 (N_{\text{solute}} \gamma_{\text{solute}} + N_{\text{solvent}} \gamma_{\text{solvent}}) \quad (3)$$

Degenerate four-wave mixing (DFWM) in a backward wave pump geometry was used to measure $\chi^{(3)}$ for different THF solutions of the various compounds. The principle behind the DFWM process is that when two counterpropagating radiation fields $E_1(\omega, t)$ and $E_2(\omega, t)$ interact with a probe field $E_3(\omega, t)$ in a nonlinear medium, a conjugate wave $E_4(\omega, t)$ is produced due to an oscillating nonlinear polarization generated in the medium.

The intensity of the conjugate wave $E_4(\omega, t)$ can be described as¹¹

$$I_4(\omega, t) = [\omega / (2\epsilon_0 c n^2)]^2 (\chi^{(3)})^2 I_1(\omega) I_2(\omega) I_3(\omega) \quad (4)$$

where I_1 , I_2 , and I_3 are the intensities of counterpropagating radiation fields $E_1(\omega, t)$ and $E_2(\omega, t)$ and probe field $E_3(\omega, t)$, respectively. l is the interaction length. Therefore, a measurement of the DFWM signal intensity I_4 yields the value of the bulk susceptibility $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$.

The experimental arrangement used for degenerate four-wave mixing (DFWM) utilized a laser system in which the IR output of a mode-locked continuous wave (CW) Nd:YAG laser (Spectra-Physics, Model 3800) was first compressed in a grating-fiber compressor (Spectra-Physics, Model 3690) and then frequency-doubled to sync-pump a CW dye laser (Spectra-Physics, Model 375). The dye pulses were subsequently amplified in a three-stage amplifier (Spectra-Physics, Model PDA) pumped by frequency-doubled pulses from a 30-Hz Q-switched pulsed Nd:YAG laser (Spectra-Physics, Model DCR-2A) to generate around 400 fs nearly transform-limited pulses with the energy of 0.4 mJ at 602 nm (by appropriate choice of dyes). For our study a peak power density of around 400 MW/cm² was used. The beams in the backward wave geometry for DFWM were focused onto the sample cell containing the THF solution of the sample. The conjugate signal was detected by a photodiode and processed by a boxcar averager (EG&G Princeton Applied Research, Model 4200).

The bulk susceptibilities $\chi_{1111}^{(3)}$ (all beams vertically polarized) of the samples in the form of THF solutions of various compositions were measured with CS_2 used as a reference.¹³ The value for CS_2 was taken as 6.8×10^{-13} esu as reported by Xuan et al. who used picosecond pulses.¹⁴ In order to compare the γ values obtained with different references, we also used CCl_4 as a reference ($\gamma = 2.29 \times 10^{-36}$ esu¹⁵) and found that the experimental results based on these two references agreed well with each other within the uncertainty of our measurements (around 15%). For each compound, the THF solutions with different concentrations and the reference were measured under the same conditions to obtain DFWM signals. The $\chi_{\text{eff}}^{(3)}$ for the different concentrations was calculated from eq 4. With the use of eq 3, the γ value for the solute was obtained from a least-squares fit of the concentration

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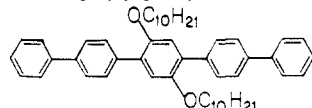
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TABLE I: Comparison of Values of λ_{\max} , ν_{\max} , and the Orientationally Averaged Second Hyperpolarizabilities for the Poly-*p*-phenyl and Thiophene Oligomer⁶ Series^a

		<i>N</i>				
		1	2	3	4	5
	λ_{\max} , nm	203.7	246.8	275.8	291.3	331.4 ^b
	$10^{-4}\nu_{\max}$, cm ⁻¹	4.909	4.052	3.626	3.433	3.018 ^b
	$\langle\gamma\rangle$, esu	6.4×10^{-36}	2.9×10^{-35}	8.5×10^{-35}		2.1×10^{-34} ^b
		$\pm 8.0 \times 10^{-37}$	$\pm 4.5 \times 10^{-36}$	$\pm 1.5 \times 10^{-35}$		$\pm 1.7 \times 10^{-35}$
	λ_{\max} , nm	231.0	301.8	350.2	390.6	412.0
	$10^{-4}\nu_{\max}$, cm ⁻¹	4.329	3.313	2.856	2.560	2.427
	$\langle\gamma\rangle$, esu	4.1×10^{-36}	2.3×10^{-35}	1.6×10^{-34}	8.0×10^{-34}	2.6×10^{-33}

^aThe errors for γ values in the poly-*p*-phenyl series are computed on the basis of the assumption of a 15% error in the intensity of the conjugate signals. ^b*p*-Pentaphenyl:



dependence. The needed local field factors L were approximated by using eq 2.

Results and Discussion

1. Poly-*p*-phenyls vs Thiophene Oligomers. For the DFWM measurements on poly-*p*-phenyls ($N = 1-5$), the following concentration ranges were used: (i) benzene, 1–11.2 M; (ii) *p*-biphenyl, 0.1–0.5 M; (iii) *p*-terphenyl, 0.05–0.2 M; (iv) alkoxy derivatized *p*-pentaphenyl: 0.01–0.1 M. The values of $\langle\gamma\rangle$ calculated by the least-squares fitting of our data are listed in the Table I. Unfortunately, due to the poor solubility of *p*-quaterphenyl we were not able to get any meaningful measurements on its solutions. Since the measurements were made at 602 nm, which is quite far from the one-photon electronic resonance of benzene or any of the poly-*p*-phenyls, these $\langle\gamma\rangle$ values are considered to be nonresonant values. The experimentally observed concentration dependence together with the determined positive sign for γ confirms that they are nonresonant values. In the presence of one- or two-photon resonance, γ would be complex, yielding a different concentration dependence and, frequently, a negative sign for γ as has been observed for soluble polydiacetylenes.^{16,17} Another indication that the DFWM signals measured by us are nonresonant is that we have not observed any delayed component in the temporal behavior of the signals obtained by scanning the delay of the probe beam. The presence of such a component would indicate the formation of excited-state gratings by either a one-photon or two-photon absorption process. The dependence of $\log \langle\gamma\rangle_N$ on the number of phenyl repeat units is exhibited in Figure 2 (with solid circles). In this figure, the curve with hollow circles shows the dependence of $\log \langle\gamma\rangle_N$ on the number of thiophene repeat units, which has been reported in a previous paper.⁶

In the case of the thiophene oligomers, a rapid increase in the γ value as a function of N is found. In contrast, for poly-*p*-phenyls, the γ values rise slower and tend to level off faster. This result can be explained by examining the band-gap dependence of these two series on the number of repeat units as shown in Figure 1. In the thiophene oligomers, the leveling off of the band gap appears to happen at least after $N = 6$. The band gap for poly-*p*-phenyls shows a slightly slower decrease than that for thiophene oligomers as the chain length increases. This result indicates a more effective π delocalization for the thiophene oligomers. In the previous paper,⁶ we have compared the experimentally observed dependence of γ on the number of repeat units with that predicted by various theoretical models. This comparison confirms that the effective conjugation length is indeed carried through the hexamer. A trans conformation linking each thiophene ring would not have any steric interaction of hydrogens at β, β' positions, which may make it possible to assume a coplanar structure in the thiophene oligomers.

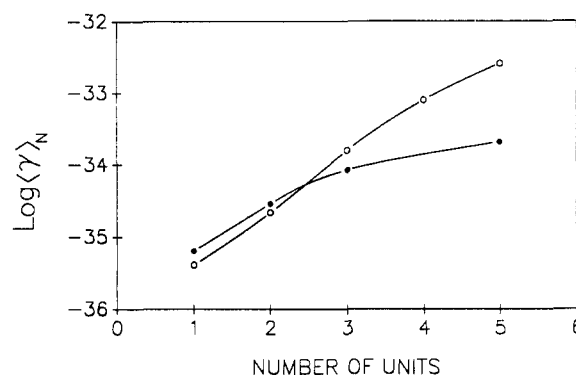


Figure 2. Values of γ_N are plotted on the log scale as a function of the number of repeat units for the two series: poly-*p*-phenyls, ●; thiophene oligomers, ○.

In the poly-*p*-phenyl series, on the other hand, the π -electron conjugation is hindered, presumably, because of the steric interaction of hydrogens at the 2,2' positions, which makes the neighboring benzene rings nonplanar. Even though the theoretical limit of effective conjugation may be $N > 20$, in an actual system such as the poly-*p*-phenyls, the effective conjugation length may be highly restricted because of rotation about the single bonds.

2. Comparison of α -Terthiophene with 1,4-Dithienylbenzene. As presented in section 1, we have observed that the γ values of thiophene oligomers increase relatively rapidly with the number of repeat units and that poly-*p*-phenyls do not show such a rapid increase. A probable explanation is the steric interaction between the β hydrogens at the neighboring benzene rings in poly-*p*-phenyls. The question may arise now whether it is possible to eliminate such steric interaction and thus increase the γ value if we make a thiophene–benzene alternating oligomer. This assumption seems to be reasonable because the thiophene oligomer is quite well conjugated and the benzene monomer has a larger γ value than the thiophene monomer. In order to test the assumption, we have compared the γ values of terthiophene and the simplest benzene–thiophene alternating oligomer 1,4-dithienylbenzene, in which the central unit of terthiophene is replaced by a benzene unit. Our experimental results show that α -terthiophene has a slightly larger γ value than does 1,4-dithienylbenzene and the former compound has a longer absorbance wavelength. From these experimental results, we can conclude that conjugation is also hindered in the benzene–thiophene alternating oligomer, simply because a steric interaction exists between the β hydrogens in thiophene and the hydrogens at position 2 in benzene.

3. Comparison of α -Terthiophene with 2,5-Dithienylpyrrole. Now we examine what happens when we replace the central thiophene unit with a pyrrole unit in a thiophene trimer. The comparison of the γ values (listed in Table II) for α -terthiophene and 2,5-dithienylpyrrole reveals that the former compound has a slightly larger γ value. This result is in general agreement with

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TABLE II: Values of λ_{\max} , ν_{\max} , the Orientationally Averaged Second Hyperpolarizabilities γ , and γ Extrapolated to Zero Frequency for 1,4-Dithienylbenzene, 2,5-Dithienylpyrrole, and a Series of Derivatized Terthiophenes^a

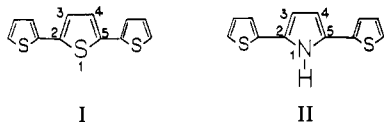
	λ_{\max} , nm	$10^4 \nu_{\max}$, cm ⁻¹	$\langle \gamma \rangle$, esu	$\gamma_{\omega=0}$, esu
	327.4	3.054	1.0×10^{-34} $\pm 1.8 \times 10^{-35}$	2.4×10^{-35}
	344.2	2.905	1.3×10^{-34} $\pm 1.9 \times 10^{-35}$	2.5×10^{-35}
	350.2	2.856	1.6×10^{-34} $\pm 2.0 \times 10^{-35}$	3.1×10^{-35}
	373.0	2.681	5.0×10^{-34} $\pm 9.0 \times 10^{-35}$	7.2×10^{-35}
	419.2	2.385	7.2×10^{-34} $\pm 1.2 \times 10^{-34}$	5.1×10^{-35}
	438.2	2.282	1.7×10^{-33} $\pm 3.2 \times 10^{-34}$	8.3×10^{-35}

^aThe errors for γ values in each compound are computed on the basis of the assumption of 15% error in the intensity of the conjugate signals.

the band gaps for these two compounds. The longer wavelength of maximum absorbance for α -terthiophene than that for 2,5-dithienylpyrrole qualitatively shows that α -terthiophene has a more effective conjugation. Therefore, alternate replacing of thiophene units in a thiophene oligomer with pyrrole units does not enhance the optical nonlinearities.

The small difference of γ values for these two compounds is probably because of the 3d orbital participation in the case of sulfur. Epiotis et al.¹⁸ have used a one-electron molecular orbital approach to explain the physical and chemical differences observed in five-membered ring heteroaromatic compounds. In this paper, we try to use this model to explain the different influences of the thiophene and pyrrole units on the γ values of the thiophene oligomer and the thiophene-pyrrole alternating oligomer. According to their model, thiophene or pyrrole molecular orbitals can be considered as a linear combination of the *cis*-butadiene fragment molecular orbitals and the sulfur or nitrogen atomic orbital. The butadiene fragment has four molecular orbitals with different energies. The highest occupied molecular orbital Φ_2 (HOMO) and the lowest unfilled molecular orbital Φ_3 (LUMO) are called frontier orbitals. In Φ_2 , C(2)–C(3) and C(4)–C(5) are bonding, but C(3)–C(4) is antibonding; in Φ_3 , C(3)–C(4) is bonding, but C(2)–C(3) and C(4)–C(5) are antibonding. According to frontier orbital theory, the interaction of the LUMO of the butadiene fragment and the occupied ϕ_z atomic orbital (AO) of a heteroatom results in a charge transfer into Φ_3 . As a result, in the process of forming a heteroatomic compound from the *cis*-butadiene fragment, the bond orders C(2)–C(3) and C(4)–C(5) decrease at the same time the C(3)–C(4) bond order increases.

The charge transfer from the ϕ_z orbital into Φ_3 is expected to occur for both I and II,



but an additional effect is expected to occur only in the thiophene oligomer (I), namely, a charge transfer from the HOMO, Φ_2 , into the empty 3d_{xy} orbital having the same symmetry as that of Φ_2 . This effect further decreases the bond orders in C(2)–C(3) and C(4)–C(5) and increases that in C(3)–C(4). In other words, these two charge-transfer processes work together, and both tend to equalize the bond orders of the carbon-carbon bonds in the central five-membered ring (see I). It is thought that this results in greater π -electron delocalization and greater hyperpolarizability. Our experiments are in agreement with this interpretation, but show

that the effect is not very big; i.e., $\langle \gamma \rangle$ for α -terthiophene (I) is about 30% greater than that for 2,5-dithienylpyrrole (II).

4. Effect of Iodine Substitution. In this section, we report on the influence of α -substituted iodine atoms on the hyperpolarizabilities of the thiophene oligomers. The γ values for α -terthiophene and α -diiodoterthiophene show that the latter has a larger γ value (see Table II). One simple explanation is that the high polarizability of the iodine atom gives rise to increased nonlinearity.

An alternative explanation is that the iodine atom, as an electron donor, will provide d electrons to interact with the empty π orbital of thiophene. As a result, the conjugated π -electron backbone is extended beyond the thiophene ring. In other words, the conjugation chain length for α -diiodoterthiophene can be expected to be longer than that for α -terthiophene. This hypothesis is also supported by a comparison of the band gaps for these two compounds. The absorption of α -diiodoterthiophene is at a longer wavelength than that of α -terthiophene. The conclusion can thus be derived that iodine substitution in a thiophene oligomer may enhance its optical nonlinearities.

5. Effect of Nitro Group Substitution. The substitution of a nitro group at the end α positions in the α -terthiophene molecule leads to a significant enhancement of γ (see Table II). The experimental result is in qualitative agreement with an ab initio calculation from this group that finds γ for nitroacetylene to be higher than that for acetylene itself.¹⁹ The increased γ values for mononitro- or dinitroterthiophene indicate that the electron-withdrawing group NO₂ extends the π -electron delocalization beyond the thiophene ring. Again the theoretical contour plots of the third derivative of electron density (related to γ) suggest this electron delocalization. Qualitatively, this delocalization can be described as follows. The π orbitals of the thiophene ring and the π orbitals of the NO₂ group interact and form a longer conjugated π -electron backbone, which increases the γ values. This is the so-called mesomeric effect. Mesomeric effects have been utilized to explain the effect of the substituents on unsaturated compounds. The mesomeric effect implies an extension of the π -electron system of the hydrocarbon over the substituent itself. The mathematical procedure is based on the assumption that the new wave function should involve a linear combination of both the hydrocarbon and substituent π orbitals. The reason why the γ values for dinitroterthiophene are larger than that for mononitroterthiophene is that the former has a longer conjugation length. Again the trend of band gap for these compounds is consistent with the delocalization effect. The substitution of a nitro group in a thiophene oligomer seems to be a very good way to increase its γ value, but the introduction of a nitro group also greatly causes the maximum absorbance wavelength to be red-shifted. Therefore, as nitro groups are introduced to higher thiophene oligomers, the γ values will tend to contain some resonant component instead of pure nonresonant value.

6. Dispersion Effect. The experimental values of γ quoted here were all measured at a single wavelength of 602 nm. While the comparisons between the various molecules are conveniently carried out in this way and the enhancement of the nonlinearity is observed, there may be a question concerning the relative importance of two factors that can influence the value of γ . One factor is the increase of the static hyperpolarizability caused by the extension of the π -electron system and, possibly, introducing a stronger anharmonicity in the π -electron system. The other factor is a simple dispersion effect. Since the increase of the number of repeat units in an oligomer or substitution with electrophilic and/or nucleophilic groups modifies the energies of the excited states, there is also a modification of the frequency dependence of the polarizabilities and the hyperpolarizabilities. Clearly, in all cases our working wavelength is well beyond the absorption threshold, and we did not observe any experimental indications of the presence of resonance effects in the four-wave mixing signal. However, the dispersion will certainly account for

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some enhancement of γ at 602 nm when the lowest lying excited state of a molecule ("band gap") is lowered by substitution toward the operating wavelength.

The experimental determination of the whole dispersion curve for γ for all the molecules studied by us is beyond the scope of this work because of experimental difficulties in obtaining tunable femtosecond pulses. One can, however, try to assess the possible effects of dispersion by assuming the major part of the nonlinearity of an extended π -electron system to come from the lowest excited state. In a simple two-state picture the third-order nonlinearity can be accounted for by considering an anharmonic oscillator equation^{11,20}

$$m\ddot{x} + \omega_0^2 x + \Gamma\dot{x} + bx^3 = eE(t) = eF(e^{i\omega t} + e^{-i\omega t}) \quad (5)$$

where m is the electron mass, e is the electron charge, F is the field amplitude, and ω its frequency. ω_0 stands here for the resonance frequency of the oscillator, Γ is the damping coefficient, and b is the anharmonic coefficient responsible for the third-order nonlinearity. Assuming that the induced dipole moment can be expressed in powers of the field as

$$\mu = ex = \alpha E + \gamma E^3 \quad (6)$$

one can derive the dispersion relation for the hyperpolarizability. For the hyperpolarizability component relating to degenerate four wave mixing, i.e. $\gamma(-\omega; \omega, -\omega, \omega)$, we obtain

$$\gamma(\omega) = \gamma(O) \frac{[(\omega_0^2 - \omega^2)^2 - \omega^2 \Gamma^2] \omega_0^8}{[(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2]^3} \quad (7)$$

Far from resonance the damping term becomes negligible, and one can write

$$\gamma(\omega) = \gamma(O) \frac{\omega_0^8}{(\omega_0^2 - \omega^2)^4} \quad (8)$$

This relation will certainly overestimate the dispersion effect

because of the omission of the damping term and because of the assumption that only one excited state contributes to the experimental γ . In comparison, a free electron model using the perturbative sum-over-state approach shows that $\chi^{(3)}$ depends inversely on the sixth power of the band gap.¹² We have used, however, eq 8 to extrapolate the experimental values to zero frequency. The results are collected for the derivatized α -terthiophene structures in Table II. It can be seen that, in this two-level anharmonic oscillator model, the influence of the shift of the "band gap" on the values of γ at 602 nm is substantial (although admittedly overestimated, as point out above). While for molecules that absorb in the UV the extrapolated values are not drastically different from those at 602 nm, the dispersion may account for a significant enhancement in some cases. It is, however, comforting to find that the qualitative trend of the substituent effect even with these zero frequency extrapolated values is the same.

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Registry No. PhH, 71-43-2; PhPh, 92-52-4; *p*-PhC₆H₄Ph, 92-94-4; Ph(*p*-C₆H₄)₂Ph, 135-70-6; 2'',5''-bis(decyloxy)-1,1':4',1'':4'',1''':4''',1''':4''''-quinquephenyl, 122964-95-8; thiophene, 110-02-1; α -bithiophene, 492-97-7; α -terthiophene, 1081-34-1; α -tetra-thiophene, 5632-29-1; α -pentathiophene, 5660-45-7; 1,4-bis(2-thienyl)-benzene, 23354-94-1; 2,5-bis(2-thienyl)pyrrole, 89814-62-0; 2,5-bis(5-iodo-2-thienyl)thiophene, 104499-99-2; 2-(2-thienyl)-5-(5-nitro-2-thienyl)thiophene, 122845-17-4; 2,5-bis(5-nitro-2-thienyl)thiophene, 122845-18-5.

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Vibrational Spectroscopic Studies of the Phase Transitions in Cyclohexane at High Pressure

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The vibrational spectra (infrared and Raman) of cyclohexane have been obtained as a function of pressure by use of diamond anvil cells. In cyclohexane two phase transitions were detected, at 5.1 and 9.6 kbar, from the splittings in the internal modes and from changes in the slopes on plots of ν versus pressure. The high-pressure phase, stable above 9.6 kbar, is identical with the phase obtained at low temperature. The vibrational spectra indicate that the unit cell symmetry changes from O_h to D_{2h} at the first transition and then to C_{2h} at the second transition. Values for the mode Grüneisen parameter, γ_i , range from 0.006 to 0.039 in phase I, from -0.01 to 0.1 in phase III, and from 0.006 to 0.16 in phase II.

Introduction

Cyclohexane is a well-known example of a compound that undergoes an order-disorder transition in the solid state. The transition occurs at 186.1 K,¹ and an X-ray crystallographic investigation² indicated that the low-temperature phase II has a monoclinic structure, space group $C2/c$ (C_{2h}^6), with four molecules

per unit cell, changing to a face-centered cubic structure, phase I, space group $Fm\bar{3}m$ (O_h^5), with four molecules per unit cell. The transition has been subject to numerous vibrational spectroscopic investigations.³⁻⁸ Most of these are consistent with the crys-

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