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CNC₆H₄-*m*-NO₂, 619-24-9; CHOC₆H₄-*m*-NO₂, 99-61-6; (*E*)-MeOC₆H₄-*o*-CH=CHC₆H₄-*o*-NO₂, 55801-78-0; (*E*)-MeOC₆H₄-*m*-CH=CHC₆H₄-*o*-NO₂, 136827-60-6; (*E*)-MeOC₆H₄-*p*-CH=CHC₆H₄-*o*-NO₂, 112768-16-8; (*E*)-MeOC₆H₄-*o*-CH=CHC₆H₄-*m*-NO₂, 136827-61-7; (*E*)-MeOC₆H₄-*m*-CH=CHC₆H₄-*m*-NO₂, 14064-59-6; (*E*)-MeOC₆H₄-*p*-CH=CHC₆H₄-*m*-NO₂, 55532-22-4; (*E*)-MeOC₆H₄-*o*-CH=CHC₆H₄-*p*-NO₂, 28915-66-4; (*E*)-MeOC₆H₄-*m*-CH=CHC₆H₄-*p*-NO₂, 14064-58-5; (*E*)-MeOC₆H₄-*p*-CH=CHC₆H₄-*p*-NO₂, 4648-33-3; (*E*)-BrC₆H₄-*o*-CH=CHC₆H₄-*p*-NO₂, 136827-62-8; (*E*)-BrC₆H₄-*m*-CH=CHC₆H₄-*p*-NO₂, 7297-54-3; (*E*)-BrC₆H₄-*p*-CH=CHC₆H₄-*p*-NO₂, 24325-71-1; (*E*)-PhN=CHC₆H₄-*p*-NO₂, 1614-00-2; (*E*)-MeC₆H₄-*p*-N=CHC₆H₄-*p*-NO₂, 33442-37-4; (*E*)-MeOC₆H₄-*p*-N=CHC₆H₄-*p*-NO₂, 39963-93-4; (*E*)-MeOC₆H₄-*p*-CH=NC₆H₄-*p*-NO₂, 97221-15-3; (*E*)-NHC₆H₄-*p*-N=NC₆H₄-*p*-NO₂, 70734-98-4; (*E*)-N(Et)₂OHC₆H₄-*p*-N=NC₆H₄-*p*-NO₂, 136827-63-9; (*Z*)-MeOC₆H₄-*p*-CH=C(CN)C₆H₄-*p*-NO₂, 42172-62-3; (*Z*)-BrC₆H₄-*p*-CH=C(CN)C₆H₄-*p*-NO₂, 50632-41-2; (*Z*)-BrC₆H₄-*p*-N=C(CN)C₆H₄-*p*-NO₂, 136827-66-2; PhH, 71-43-2; PhMe, 108-88-3; PhOH,

108-95-2; PhSH, 108-98-5; PhOMe, 100-66-3; PhSMc, 100-68-5; PhNH₂, 62-53-3; PhNMe₂, 121-69-7; PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; PhSO₂Me, 3112-85-4; PhSO₂F, 368-43-4; PhCN, 100-47-0; PhCHO, 100-52-7; PhCOCF₃, 434-45-7; PhNO, 586-96-9; PhNO₂, 98-95-3; PhC₂H(CN)₂, 2700-22-3; (*E*)-PhCH=CHPh, 103-30-0; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-PhCH=CHNH₂, 4309-66-4; (*E*)-PhCH=CHNMe₂, 838-95-9; (*E*)-PhCH=CHNO₂, 1694-20-8; (*E*)-2-(4-julolidinephenyl)-1-cyanoethenenitrile, 126691-59-6; (*E*)-2-(4-julolidinephenyl)-1,2-dicyanoethenenitrile, 126691-60-9; (*E*)-1-(3-methyl-4-methoxyphenyl)-2-(4-nitrophenyl)ethene, 120191-48-2; (*E*)-1-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)ethene, 51042-54-7; (*E*)-1-(3-fluoro-4-methoxyphenyl)-2-(4-nitrophenyl)ethene, 136827-64-0; (*E*)-1-(2,4-dimethoxyphenyl)-2-(4-nitrophenyl)ethene, 136827-65-1; (*E*)-1-(2,4-dinitrophenyl)-2-(4-methoxyphenyl)ethene, 129540-40-5; 2-phenyl-1,4-dioxane, 827-53-2; 1,4-dimethoxy-2-phenylbenzene, 7372-85-2; (*E*)-2,3,6,7-tetrahydro[4-[2-(4-nitrophenyl)ethenyl]phenyl]-1*H*,5*H*-benzo[*i*]quinolizine, 136827-67-3; (*E*)-2,3,6,7-tetrahydrophenyl-1*H*,5*H*-benzo[*i*]quinolizine, 136827-68-4.

Experimental Investigations of Organic Molecular Nonlinear Optical Polarizabilities. 2. A Study of Conjugation Dependences

Lap-Tak Cheng,* Wilson Tam,

Central Research and Development Department, E. I. Du Pont de Nemours & Co. (Inc.), Experimental Station, P.O. Box 80356, Wilmington, Delaware 19880-0356

Seth R. Marder, Albert E. Stiegman,

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109

Geert Rikken,

Philips Research Laboratories, P.O. Box 80000, 5600JA, Eindhoven, The Netherlands

and Charles W. Spangler

Department of Chemistry, Northern Illinois University, Dekalb, Illinois 60115 (Received: May 13, 1991; In Final Form: August 5, 1991)

In the present contribution, we broaden our investigations to include the conjugation dependences of molecular optical hyperpolarizabilities. In addition to the benzene and stilbene derivatives reported earlier, dc electric field induced second-harmonic generation (EFISH) and third-harmonic generation (THG) measurement results on the hyperpolarizabilities of a wide range of donor-acceptor-substituted π systems are presented. These include results for styrene, biphenyl, fluorene, diphenylacetylene, various phenylvinyl heterocyclics, oligomeric polyphenyl, α,ω -diphenylpolyene, α -phenylpolyene, and α,ω -diphenylpolyene, as well as other extended phenylvinyl derivatives. Drawing from the experimental phenomenology illustrated by a large set of internally consistent data, issues concerning the efficacies of various conjugation units, conjugation planarity, aromaticity and bond alternation, and electron localization and delocalization effects, as well as the conjugation length and end-group dependences, are examined.

Introduction

In the preceding paper,¹ structure-property relations for donor-acceptor-substituted organics and their molecular nonlinear optical polarizabilities were examined with dc electric field induced second-harmonic generation (EFISH) and third-harmonic generation (THG) experiments. We detailed a novel experimental methodology which is relatively accurate and experimentally efficient. Using benzene and stilbene derivatives as model compounds, we focused our attention on the electronic biasing strengths, charge-transfer couplings, substitution patterns, and linear property trade-offs of various substituents. Although steady enhancement of hyperpolarizabilities were realized with increasing donor-acceptor strengths and appropriate substitution patterns,

the most significant enhancement of both β and γ resulted from the extension of conjugation with the stilbene derivatives. This is a well-known result since the early work of Oudar and others.² Further investigations with computations predicted strong enhancements of hyperpolarizabilities through conjugation extension in polyene systems,³ and such enhancement was subsequently confirmed in α,ω -diphenylpolyene,⁴ α -phenylpolyene,⁵ and polyene⁵ derivatives by experiments.

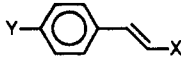
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TABLE I: Results on 4- and β -Substituted Styrenes (Units in esu)


X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^\circ \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
CN	OMe	CHCl ₃	(304)	4.2	2.3	7.0	11 \pm 5
CN	NMe ₂	CHCl ₃	(364)	6.0	2.8	23	29
CHO	Br	CHCl ₃	(298)	2.0	2.3	6.5	36
CHO	OMe	CHCl ₃	(318)	4.2	2.5	11	28
CHO	NMe ₂	CHCl ₃	(384)	5.6	2.6	30	63 \pm 5
COMe	OMe	CHCl ₃	(316)	4.0	2.7	8.9	29
NO ₂	H	CHCl ₃	(312)	3.8	2.0	8.0	29
NO ₂	OH	CHCl ₃	(352)	5.1	2.4	18	52 \pm 10
NO ₂	OMe	CHCl ₃	(352)	4.6	2.6	17	35 \pm 10
NO ₂	NMe ₂	CHCl ₃	(438)	6.5	3.2	50	
NMe ₂	NO ₂	CHCl ₃	(438)	5.9	2.6	35	

While the expectation of enhanced hyperpolarizabilities for extended π systems is quite reasonable considering the increased numbers of polarizable and hyperpolarizable electrons and the reduced energy gaps of the charge-transfer (CT) states in such structures, subtleties concerning the structural features of a π system, such as bond alternation and aromaticity, are also expected to play important roles. Such structure-property relationships have thus far received only peripheral attention. In the present study, we broaden our investigations to include the detailed conjugation dependences of hyperpolarizabilities. In addition to the benzene and stilbene derivatives reported earlier, measurement results on the hyperpolarizabilities of a wide range of donor-acceptor-substituted π systems are presented. These include results for styrene, biphenyl, fluorene, diphenylacetylene, various phenylvinyl heterocyclics, oligomeric polyphenyl, α,ω -diphenylpolyene, α -phenylpolyene, and α,ω -diphenylpolyene, as well as other extended phenylvinyl derivatives. Emphasis is placed on the detailed dependences between molecular quadratic hyperpolarizability and conjugation characteristics. In the remainder of this paper, the nonlinear optical experiments and data analysis scheme will be summarized. Measurement results on various classes of materials will be presented in a manner which facilitates discussions. Systematics in the measurement results as they relate to the planarity, aromaticity, bond alternation, and length of various π systems will be discussed.

Experimental Section

To obtain various relevant molecular parameters, a lengthy set of physical and optical measurements are needed. These include, on a series of solutions with graded concentrations, measurements of density, refractive index at several wavelengths, solution dielectric constant, THG, and EFISH amplitudes as well as their coherence lengths for harmonic generations. These measurements respectively determine the specific volume of a solute molecule in solution, solution dispersion, dielectric properties, and the THG and EFISH nonlinear susceptibilities for each solution. The details of our experimental methodology were given in the preceding paper¹ and are summarized below.

The experimental setup for EFISH and THG consists of a 20-Hz Nd:YAG laser with 10-ns pulses of 0.4 J in energy. The 1.06- μ m output pumps a hydrogen Raman shifter, providing up to 120 mW of Stokes-shifted radiation at 1.91 μ m. This radiation serves as the fundamental for both the EFISH and THG experiments. The output harmonic wavelengths are at 954 and 636 nm, respectively. For most lightly colored compounds with absorption edge at wavelengths below 500 nm, the measurement can be considered as minimally influenced by dispersive enhancement. THG and EFISH experiments are carried out with an unconventional technique in which the harmonic amplitudes and coherence lengths are measured separately. For the determination of harmonic amplitudes, we adopted a tight-focusing geometry in which the focal region of the laser beam is placed at the window-liquid interface of a "single interface" sample cell. The sample cell is equipped with a thick (2 cm) front optical window and two adjacent liquid chambers (3 cm path length) holding a reference liquid and a sample solution for comparative mea-

surement. Electrodes are fabricated at the front window-liquid interface so that both THG and EFISH measurements can be carried out concurrently. The coherence lengths for the harmonic generations are determined with a wedged liquid cell consisting of two crystalline quartz windows, which generate sufficient second- and third-harmonic radiations for easy measurement.

With the known THG and EFISH nonlinearities and coherence lengths of the window material and the reference liquid at 1.91 μ m (BK7-grade A glass: $\chi^{(3)}_{\text{THG}} = 4.7 \times 10^{-14}$ esu, $I_{\text{THG}} = 16.7$ μ m, $\chi^{(3)}_{\text{EFISH}} = 3.5 \times 10^{-14}$ esu, and $I_{\text{EFISH}} = 38.8$ μ m; toluene: $\chi^{(3)}_{\text{THG}} = 9.9 \times 10^{-14}$ esu, $I_{\text{THG}} = 18.3$ μ m, $\chi^{(3)}_{\text{EFISH}} = 9.1 \times 10^{-14}$ esu, and $I_{\text{EFISH}} = 73.5$ μ m), as well as the coherence lengths of the sample solution, the solution nonlinear susceptibilities can be computed from the ratios of the harmonic intensities measured at the sample and reference liquid chambers. From the measured solution properties, following a full Onsager local field treatment for both static and optical fields and taking the infinite dilution limits for all concentration-dependent quantities, the relevant molecular properties including the dipole moment, μ ; the static linear polarizability, α° ; the vectorial projection of the quadratic hyperpolarizability tensor along μ , β ; and the scalar part of the cubic hyperpolarizability, γ , are calculated.

Results and Discussion

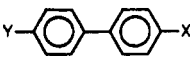

1. Styrene Derivatives: The Efficacy of Vinyl Extension. We first extend our investigations to the styrene derivatives. The relevant molecular parameters (μ , α° , β , and γ) have been determined for 10 4-donor, β -acceptor substituted and one 4-acceptor, β -donor substituted styrene derivatives at infinite dilution in chloroform solutions. Combinations of donors and acceptors with varying strengths are used to obtain a wide range of β values. Results are tabulated in Table I (see ref 1 for details concerning experimental conditions and uncertainties).

The extent of charge transfer and thus the β values are expected to be sensitive to the molecular geometry of the styrene derivatives. While the geometry is not known for the asymmetrically substituted charge-transfer (CT) derivatives, all available experimental and theoretical evidence indicates that the parent unsubstituted styrene has a planar geometry.⁶ Since the CT interaction is favored by a planar geometry, CT derivatives are expected to have planar structures. In addition, since all carbon atoms in styrene are sp^2 hybridized, there is little variation in the π -electron distribution among the ring and vinyl carbons, giving an essentially zero dipole moment (<0.3 D⁷). Any polarization of the structure can be largely attributed to interactions between styrene and substituents. Therefore, results obtained for CT styrene derivatives can be reasonably compared to those for the benzene and stilbene derivatives studied earlier.¹

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TABLE II: Results on 4,4'-Disubstituted Biphenyls and Fluorenes (Units in esu)

X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^o \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
							
H	H	<i>p</i> -dioxane	252	0.0	2.2	0.0	10
CN	H	<i>p</i> -dioxane	272	4.0	2.4	1.9	17
COCH ₃	H	<i>p</i> -dioxane	280	3.1	2.7	2.0	8
NO ₂	H	<i>p</i> -dioxane	304	3.8	2.5	4.1	15
SO ₂ C ₆ H ₁₂ OH	NMe ₂	CHCl ₃	340	6.0	4.6	13	38
CN	OH	<i>p</i> -dioxane	292	4.8	2.5	6.3	10
COCH ₃	OMe	<i>p</i> -dioxane	304	3.4	2.9	4.9	23
NO ₂	Br	<i>p</i> -dioxane	306	2.7	2.9	4.4	32
NO ₂	OH	<i>p</i> -dioxane	334	4.9	2.6	7.7	37
NO ₂	OMe	<i>p</i> -dioxane	332	4.5	2.8	9.2	39
NO ₂	NH ₂	CHCl ₃	372	5.0	2.8	24	70
		NMP		7.8	2.6	24	96
NO ₂	NMe ₂	CHCl ₃	390	5.5	3.4	50	130
							
H	H	<i>p</i> -dioxane	262	0.0		0.0	
CN	H	<i>p</i> -dioxane	284	3.9	2.6	3.0	8
NO ₂	H	<i>p</i> -dioxane	328	4.1	2.6	5.1	29
NO ₂	Br	<i>p</i> -dioxane	330	2.8	2.6	6.0	30
NO ₂	OMe	<i>p</i> -dioxane	356	4.7	2.7	11	28
NO ₂	NMe ₂	<i>p</i> -dioxane	410	5.6	3.6	40	95
		CHCl ₃	417	6.0	3.6	55	

Since styrene has a conjugation length intermediate to those of benzene and stilbene, the β values of its derivatives are expected to fall between those of benzene and stilbene derivatives. Comparison of entries in Table I and those of Tables II and III of ref 1 confirms this expectation for all donor-acceptor pairs. For the case of NMe₂ and NO₂ substituents, the β values are 12×10^{-30} , 50×10^{-30} , and 73×10^{-30} esu for benzene, styrene, and stilbene derivatives, respectively. Clearly, β increases nonlinearly with conjugation length. The vinyl addition going from the benzene to the styrene structures appears to have a much greater enhancement on β than the phenyl addition going from the styrene to the stilbene structures. This observation has been noted before.^{2a,8} Comparison with properties of the planar fluorene derivatives (see Table II) discussed below also leads to such a conclusion. We will return to the detailed conjugative length dependence of hyperpolarizability in a later section where derivatives with extended conjugations are examined. However, the efficacy of the vinyl unit over that of the phenyl unit is noteworthy since it offers greater efficiency per unit molecular volume. It is also interesting to note that the superior accepting strengths of the dicyanovinyl and tricyanovinyl groups⁹ arise largely from the vinyl extension of conjugation length. This can be seen by comparing the β values of 5.0×10^{-30} , 23×10^{-30} , 32×10^{-30} , and 50×10^{-30} esu for 1-(*N,N*-dimethylamino)-4-X-benzene where X = CN, CHCHCN, CHC(CN)₂, and CCNC(CN)₂, respectively. Accounting for dispersive enhancement according to a two-state approximation,¹⁰ $\beta(\omega=0)$ are 4.4×10^{-30} , 19×10^{-30} , 24×10^{-30} and 33×10^{-30} esu. Clearly the vinyl extension results in more than a factor of 4 enhancement while each additional cyano group leads to about a 30% increase only.

When the donor and acceptor positions are interchanged as illustrated with derivatives of NMe₂ and NO₂, significant differences are found in their properties. While the CT band position and bandwidth are very similar, the oscillator strength of 4-(*N,N*-dimethylamino)phenyl- β -nitrostyrene is found to be 1.6 times higher than that of 4-nitrophenyl- β -(*N,N*-dimethylamino)styrene. This is consistent, within the two-state approximation, with the lower β value found for the later derivative, which also has a lower

dipole moment. Since the styrene parent compound possesses a small dipole moment with excess charge on the vinyl fragment, the dipole moment and β value of the former derivatives, where the substituent-induced electronic asymmetry is in the same direction as that of the conjugation, are expected to be higher than those found for the later. Therefore, it is generally advantageous to have the acceptor substituted at the vinyl position when $\mu\beta$ is to be optimized.

2. Biphenyl, Fluorene, and Oligophenylene Derivatives: Conjugation Planarity. An interesting structure-property relationship concerns the dependence of the hyperpolarizability on conjugation planarity. Clearly, such a dependence is expected because of the diminution of π -electron overlap in a nonplanar geometry, which will certainly hamper donor-acceptor interactions and reduce quadratic nonlinearities. An estimate of the torsional effect on optical nonlinearity can be obtained from spectroscopic evidences. It is well-known that a nonzero torsional angle, θ , between two π systems will lead to an increase of the transition energy and a reduction of the extinction coefficient of the π - π^* transition.¹¹ For small θ , the former effect is relatively minor, while the extinction coefficient $\epsilon(\theta)$ is found to decrease as $\cos^2(\theta)$.¹² Within the two-state approximation, in which the long axis hyperpolarizability β_{xxx} is proportional to ϵ , the torsional effect on β is expected to be weak since $\cos^2(\theta)$ is a slowly varying function for small θ . Theoretical studies of the torsional effect between donor orbital and the π system in CT phenyl derivatives have led to similar conclusions.¹³ In addition, for donor- and acceptor-substituted derivatives, one may expect the torsion itself to be dependent on the charge-transfer strength of the substituents. To further explore these topics, we have investigated the linear and nonlinear optical properties of 4-donor,4'-acceptor-substituted biphenyls with nonzero torsions and the corresponding fluorene derivatives with planar structures. Measurement results are given in Table II.¹⁴

The torsional angle in biphenyl is well-known and the gas-phase and solution-phase values are at about $\theta_m = 40^\circ$ and 30° , respectively.^{15,16} These values are determined by potential barriers

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TABLE III: End-Group-Dependent Torsional Angle As Deduced from Spectroscopic and Hyperpolarizability Data

D, A	R_λ	θ_λ , deg	R_β	θ_β , deg
H, NO ₂	0.78	28	0.80	27
Br, NO ₂	0.79	27	0.73	31
OMe, NO ₂	0.85	23	0.83	24
NMe ₂ , NO ₂	0.89	19	0.91	18

arising from the steric hindrance of the ortho hydrogens near $\theta = 0^\circ$ and the loss of resonance energy near $\theta = 90^\circ$. From perturbative arguments, the decrease of resonance energy is well approximated by $\cos^2(\theta)$.¹⁷ For CT derivatives, it is reasonable to expect lower θ values since CT interaction should introduce additional resonance energy and certain double bond character to the biphenyl linkage according to familiar arguments based on resonance structures. For fluorene, the two phenyl fragments are near planar due to the *o,o'*-methylene bridge. Assuming minimum perturbation of the π system as a result of the strained five-member ring (which is a reasonable assumption considering the similarity of their spectra), CT fluorene derivatives can be taken as planar analogues to biphenyl derivatives in our study of the torsional effects on hyperpolarizability.

Measurement results on biphenyl and fluorene derivatives are characterized by their similarities and can be summarized as follow. The low-energy feature in the absorption spectrum of unsubstituted fluorene is found to be 10 nm red-shifted from that of biphenyl. For both donor-acceptor-substituted biphenyl and fluorene derivatives, this low-energy band acquires CT character and its λ_{\max} shifts to higher value (up to 155 nm) with increasing electronic biasing strength of the substituents. For a given donor-nitro pair, fluorene derivatives consistently show similar μ , higher λ_{\max} , and higher β values in comparison with biphenyls. Denoted as $\Delta\lambda_{CT}^F = \lambda_{\max}(\text{CT fluorene derivatives}) - \lambda_{\max}(\text{fluorene})$ and $\Delta\lambda_{CT}^B = \lambda_{\max}(\text{CT biphenyl derivatives}) - \lambda_{\max}(\text{biphenyl})$, these spectral shifts are good indicators of the charge-transfer nature of the excitations and the ratio $R_\lambda = \Delta\lambda_{CT}^B/\Delta\lambda_{CT}^F$ reflects the influence of torsion on CT. Although the β values of the fluorene derivatives are higher than those of the biphenyl analogues, the differences are small and the ratio $R_\beta = \beta^B/\beta^F$ approaches unity with increasing donor-acceptor strength.

Qualitatively, if one assumes that the observed differences in spectroscopic and nonlinear optical data between fluorene and biphenyl derivatives are due to torsional hindrance of the CT interaction, the torsion angle of biphenyl derivatives can be crudely estimated according to the expected $\cos^2(\theta)$ dependences of resonance stabilization and hyperpolarizability discussed earlier. Using $\theta_\lambda = \arccos(R_\lambda)^{1/2}$ and $\theta_\beta = \arccos(R_\beta)^{1/2}$, the deduced θ values from spectroscopic and nonlinear optical measurements are in good agreement (see Table III). While the θ values fall within the expected range of 20° – 30° , the torsional angle shows a decreasing trend with increasing donor-acceptor strength. X-ray data²³ on single crystal of *p*-amino-*p*-nitrobiphenyl revealed a near-planar geometry with a torsion about the phenyl-phenyl bond of about 3° . This geometry is probably quite different from the solution geometry since crystal-packing effects are known to strongly influence torsion (biphenyl has a planar geometry in its crystalline state). However, X-ray data also show that the phenyl-phenyl distance in *p*-amino-*p*-nitrobiphenyl gives no evidence of quinonoid character, suggesting that CT is limited in the ground state and the polarization is confined to region immediately connected to the donor and acceptor. This may help explain the similar dipole moments of fluorene and biphenyl derivatives and their relatively low values when compared to phenyl derivatives.

Although the torsional dependence of hyperpolarizability appears to be weak for small torsional angle, this effect is expected to be cumulative and become quite important for conjugated

structures with two or more torsional angles. The arguments used in the biphenyl case can be extended to that of the ter- and quaterphenyl derivatives by associating a $\cos^2(\theta)$ factor with each torsional angle, such that $\beta(\theta_1, \theta_2, \theta_3) \propto \cos^2(\theta_1) \cos^2(\theta_2) \cos^2(\theta_3)$. For small θ 's, the torsional effect leads to an asymptotic reduction of β . A competing effect is the general enhancement of β due to the extension of conjugation. To further explore the balance of these two effects in oligomeric polyphenyl derivatives, we compare the experimental results on 4'-amino- and 4'-methoxy-4-nitropolyphenyl derivatives up to four phenyl units with the computational results on the β values of polyphenyls with planar geometries published by Morley et al.³ Measurement results are given in Table IV.

For the 4'-(*N,N*-dimethylamino)-4-nitropolyphenyls, Morley's calculation revealed an unexpected rapid saturation of the hyperpolarizability with the conjugation length even for planar geometries, predicting an increasing β up to a saturating value at six phenyl units, and a volume-normalized hyperpolarizability, ρ_β , peaking at the terphenyl derivatives. Contrary to this prediction, measurement results in Table IV show a maximum β for the biphenyl derivative for the amino series and a virtual equality between bi- and terphenyl derivatives for the methoxy series. Clearly, ρ_β maximizes at the biphenyl derivatives for both series. The experimental trend in β is also found to correlate with trends in λ_{\max} , which shifts to higher values with increasing β . Since the donor group of the phenylene series studied by Morley differs from those we have measured, a direct comparison of the β values cannot be made. However, the ratio of β_n/β_{n+1} , where n is the number of phenyl units, can be compared to reveal the effects of nonplanar geometries.

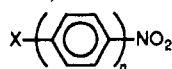
The theoretical $\beta_n(\omega=0)$ for $n = 1$ –4 phenyl units are 12.3×10^{-30} , 31.4×10^{-30} , 42.2×10^{-30} , and 47.7×10^{-30} esu, with ratios of $\beta_n/\beta_{n+1} = 0.39, 0.74$, and 0.89 for $n = 1, 2$, and 3 , respectively. For the 4'-amino series, the experimental $\beta_n(\omega=0)$ values, deduced from $1.91\text{-}\mu\text{m}$ measurements according to the two-state model, are 8×10^{-30} , 19×10^{-30} , 13×10^{-30} , and 9×10^{-30} esu with $\beta_n/\beta_{n+1} = 0.4, 1.5$, and 1.4 , where $n = 1, 2$, and 3 , respectively. To see if this difference between experimental and theoretical results can be accounted for by the torsional effect, the theoretical β_n values are corrected according to the $[\cos^2(\theta)]^n$ dependence discussed previously. Using a θ value of 30° , such an exercise yields corrected β_n/β_{n+1} ratios of $0.52, 1.0$, and 1.2 for $n = 1, 2$, and 3 , respectively. This is in reasonable agreement with the experimental results, and the down turn of β values at $n = 3$ can readily be accounted for with reasonable θ values and the $[\cos^2(\theta)]^n$ dependence.

Our findings on the oligophenylene derivatives can be summarized as follow: (1) Donor-acceptor biphenyls have lower β values relative their fluorene analogous due to torsion along the phenyl-phenyl bond. (2) The differences in β are, however, small presumably due to a weak dependence on torsion for small angles. (3) As the donor and acceptor strength increases, the β values for the biphenyl and the fluorene derivatives converge. (4) This appears to be a result of an end group effect on the torsional angle resulting in more planar biphenyl derivatives with strong donor-acceptor substituents. (5) The β values maximize at biphenyl for the oligophenylene series. (6) The rapid saturation and decrease of β with length can be explained by the combined effect of the intrinsic ineffectiveness of the phenyl extension which leads to rapid saturation of β and the geometric constraints on π overlap due to the torsional angles between phenyl units.

3. Diphenylacetylene and Oligomeric α,ω -Diphenylpolyene Derivatives: Extreme Bond Alternation. In order to study the effect of orbital hybridization and bond alternation on hyperpolarizability, we have examined a series of α,ω -diphenylpolyene CT derivatives containing up to three triple bonds. Theoretical investigations of the longitudinal polarizabilities, α_{zz} , and the second hyperpolarizabilities, γ_{zzzz} of $(-C\equiv C)_n$ and $(-C\equiv C)_n$ have been reported. For $n = 1$ –3, an ab initio study¹⁸ found lower α_{zz} while

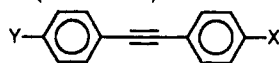
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TABLE IV: Results on 4,4'-Nitropolyphenyl Oligomers (Units in esu)

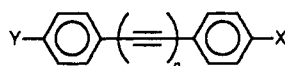


<i>n</i>	X	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^o \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
1	NH ₂	NMP	370 (384)	7.8	1.6	10	21
2	NH ₂	NMP	372 (386)	7.8	2.6	24	96
3	NH ₂	NMP	360 (388)	7.6	3.5	16	124
4	NH ₂	NMP	344 (354)	10	3.3	11	133
1	OMe	<i>p</i> -dioxane	302	4.6	1.5	5.1	10
2	OMe	<i>p</i> -dioxane	332	4.5	2.8	9.2	39
3	OMe	<i>p</i> -dioxane	340	5.0	3.8	11	

TABLE V: Results on 4,4'-Disubstituted Diphenylacetylenes (Units in esu)



X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^o \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
SO ₂ Me	NH ₂	CHCl ₃	(338)	6.5	3.4	13	59
CO ₂ Me	SMe	CHCl ₃	(328)	2.9	3.5	8	14
CO ₂ Me	NH ₂	CHCl ₃	(332)	3.8	3.7	15	62
COMe	SMe	CHCl ₃	(336)	3.7	3.6	9.8 ± 2	19 ± 10
COMe	NH ₂	CHCl ₃	(334)	3.3	3.2	12	29
COPh	NH ₂	CHCl ₃	(352)	3.7	3.7	19	57
CN	SMe	CHCl ₃	(333)	4.0	3.5	15	35
CN	NH ₂	CHCl ₃	(342)	5.2	3.2	20	55
CN	NHMe	CHCl ₃	(358)	5.7	3.4	27	90
CN	NMe ₂	CHCl ₃	(372)	6.1	3.7	29	99
NO ₂	Br	CHCl ₃	(335)	3.0	3.5	10	50
NO ₂	OMe	<i>p</i> -dioxane	(356)	4.4	3.9	14	52
NO ₂	SMe	CHCl ₃	(362)	4.0	3.8	20	95
NO ₂	NH ₂	CHCl ₃	(380)	5.5	3.2	24	120
NO ₂	NH ₂	NMP	(410)	5.5	3.6	40	140
NO ₂	NHMe	CHCl ₃	(400)	5.7	4.0	46	130
NO ₂	NMe ₂	CHCl ₃	(415)	6.1	4.1	46	151

TABLE VI: Results on 4,4'-Disubstituted α,ω -Diphenylpolyene Oligomers (Units in esu)

<i>n</i>	X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^o \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
1	CN	SMe	CHCl ₃	(333)	4.0	3.5	15	35
2	CN	SMe	CHCl ₃	(330 ± 40)	3.7	3.8	17 ± 2	42 ± 10
1	CN	NH ₂	CHCl ₃	(342)	5.2	3.2	20	55
2	CN	NH ₂	NMP	(388)	$\alpha = 3.4, \mu\beta = 11 \times 10^{-47}$ esu			
1	NO ₂	SMe	CHCl ₃	(362)	4.0	3.8	20	95
2	NO ₂	SMe	CHCl ₃	(338 ± 40)	3.9	4.0	17 ± 2	61 ± 10
1	NO ₂	NH ₂	NMP	(410)	$\alpha = 3.6, \mu\beta = 22 \times 10^{-47}$ esu			140
2	NO ₂	NH ₂	CHCl ₃	(334 ± 50)	6.3	4.4	28 ± 2	81 ± 10
			NMP	(416)	$\alpha = 4.0, \mu\beta = 24 \times 10^{-47}$ esu			
3	NO ₂	NH ₂	NMP	(440 shoulder)		$\alpha = 4.0, \mu\beta = 41 \times 10^{-47}$ esu		

a tight-binding calculation¹⁹ using Hückel wave functions reported higher γ_{zzzz} for the acetylenic structures. Both studies found rapid increases in their respective properties with *n*. However, the experimental γ^{THG} for α,ω -diphenylpolyene with one and two triple bonds were found to be significantly lower than that of α,ω -diphenylpolyene analogues.²⁰ Therefore, from a perturbative picture in which β arises from the polarization of γ by an internal field created by donor-acceptor substituents,²¹ the acetylenic linkages are anticipated to be less effective than the ethylenic ones for asymmetric polarizability. This conjecture is borne out by experiments. Measurement results on 17 4-donor,4'-acceptor-disubstituted diphenylacetylenes are given in Table V.

Despite the extended and planar structure of diphenylacetylene in comparison to that of biphenyl, only moderate increases of β values are observed. The disparity between diphenylacetylene and *trans*-stilbene derivatives (see Table III of ref 1) is even more

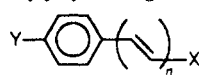
striking considering the similarity of the two structures. For all combinations of donor and acceptor groups examined, the diphenylacetylenic derivatives are found to be much less nonlinear, with β values about 50% lower than that of the *trans*-stilbene analogues. Since β is a measure of the asymmetric long axis polarizability between the two ends of these elongated molecules, it is unlikely that the difference in axial symmetry is responsible for the lower values. The difference in orbital hybridizations between the acetylenic and ethylenic linkages is, however, more significant. Although the π orbitals of both linkages are coplanar with the phenyl rings, the p orbitals of the sp-hybridized acetylenic carbons, which are electron rich due to the low energy of the σ orbitals, may lead to less effective π delocalization due to the orbital energy mismatch with the p orbitals of the sp²-hybridized phenyl carbons. In addition, due to the short triple bond length, p-orbital overlap is maximized in the acetylenic resonance structure. These factors are likely to result in a localization of electron density at the phenyl rings. Such a difference of course does not exist in the *trans*-stilbene structure where all carbons are sp² hybridized, allowing effective delocalization of all the π electrons.

The consequences of extreme bond alternation are further illustrated with additional acetylenic units in the π system.

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TABLE VII: Results on 4-Donor, β -Acceptor-Substituted α -Phenylpolyene Oligomers (Units in esu)


n	X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^\circ \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
0	CHO	MeO	neat	280	3.5	1.7	2.2	8
1	CHO	MeO	CHCl ₃	(318)	4.0	2.5	12	28
2	CHO	MeO	CHCl ₃	(350)	4.3	3.0	28	43
3	CHO	MeO	CHCl ₃	(376)	4.6	3.5	42	120
0	CHO	NMe ₂	<i>p</i> -dioxane	326	5.1	2.0	6.3	17
1	CHO	NMe ₂	CHCl ₃	(384)	5.6	2.6	30	63
2	CHO	NMe ₂	CHCl ₃	(412)	6.0	3.3	52	140
3	CHO	NMe ₂	CHCl ₃	(434)	6.3	4.0	88	257
0	CHC(CN) ₂	MeO	CHCl ₃	(350)	5.5	1.7	9.8	25
1	CHC(CN) ₂	MeO	CHCl ₃	(392)	5.8	2.5	32	83
0	CHC(CN) ₂	NMe ₂	CHCl ₃	(420)	7.8	2.8	32	72
1	CHC(CN) ₂	NMe ₂	CHCl ₃	(486)	8.4	3.2	82	
2	CHC(CN) ₂	NMe ₂	CHCl ₃	(520)	9.0	3.6	163	

Measurement results of several α,ω -diphenyldiyne and one α,ω -diphenyltriyne derivatives are given in Table VI. The absorption spectra of the 4'-amino,4-nitro series have been reported before.²² Strong intramolecular CT bands are observed together with low energy $\pi-\pi^*$ transitions which show considerable vibronic structures for the extended derivatives. To the extent that λ_{\max} for the CT band can be determined, no clear red shift of λ_{\max} and increase of ϵ are found when the acetylenic bridge is extended from one to three triple bonds. Furthermore, structural analysis²³ of the series have shown that quinoidal character is present only in the phenyl fragments and the acetylenic linkages remain largely unchanged in the ground state. A high degree of invariance of the quinoidal distortions across the series was also noted.

On the basis of the spectral and structural behaviors, it can be concluded that the π system is poorly delocalized in the ground state and the extent of charge transfer in the ground and excited states is relatively independent of the length of the acetylenic linkage. The acetylene linkage acts as a rather passive conduit to transfer charge into what are ultimately highly localized orbitals at the nitrophenyl and aniline fragments. Considerations based on resonance structures can be invoked to rationalize these observations. Delocalization of charge along the π system must be considered as effective mixing of not only the neutral acetylenic and the fully charge separated cumulenonic resonance structures, but also the mixing of intermediate structures in which charges are localized at other positions along the carbon backbone. Due to the large difference in the single and triple bond lengths, all structures containing allene fragments are high in energy because of reduced p overlap, and their mixings are therefore energetically disfavored in the ground state. Therefore, charge is not effectively delocalized into the acetylenic linkage. Such conclusions are supported by the current molecular studies. The $\mu\beta$ values for all combinations of donor and acceptor groups are found to be essentially the same for the mono- and diyne derivatives, while moderate enhancement is realized for the triyne derivatives. Thus charge localization as a result of extreme bond alternation is seen to strongly constrain the hyperpolarizability. In particular, the strong length dependence is severely curtailed. This behavior is quite different from that of the α,ω -diphenylpolyene series.

4. Oligomeric α -Phenylpolyene and α,ω -Diphenylpolyene Derivatives: Conjugation Extension. While it is generally perceived that extension of the π system between donor and acceptor groups is an effective route to enhance hyperpolarizability, experimental confirmations^{2b,4,5} have been reported only for polyene derivatives most of which contain phenyl end groups. Data presented above on oligomeric polyphenyl and α,ω -diphenylpolyene derivatives clearly show that conjugation extension does not in general lead to higher hyperpolarizability. In this section, the structural details

which influence the efficacy of a conjugated system will be explored from a chemical view point. Measurement results for α -phenylpolyene and α,ω -diphenylpolyene derivatives are presented. The power law dependence of β on conjugation length and the end-group effects on the exponent are discussed.

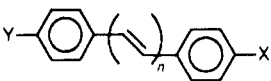
Morley's computation results predicted dramatically different length dependences for the planar polyphenyl and the polyenic derivatives.³ The former is found to saturate rapidly at very modest value while the latter series of comparable length affords values up to 50 times higher without saturation. Polarization of the phenyl unit, whose aromatic character advocates an equal distribution of the π electrons among the carbon π orbitals, into a quinoidal form is energetically costly, and this energetic consideration may account for its relative ineffectiveness. In particular, for extended phenylenic or phenylvinyl conjugations, the charge separation resulting from donor-acceptor interactions may tend to localize at the end groups to allow the unpolarized central region to preserve aromatic stabilization. Therefore, the aromatic centroid represents a potential barrier of lower orbital energy and leads to poor delocalization of the π systems. In the α,ω -diphenyltriyne derivatives considered earlier, the extreme bond alternation of the acetylenic linkage, whose cumulenonic charge-separated forms are energetically disfavored, clearly leads to charge localization at the phenyl end units. For polyene derivatives, since the neutral and other charge-separated states formally consist of similar π system of alternating single and double bonds and are equally favored based on energy considerations, effective delocalization is realized for derivatives with length up to the saturation limit, which is in turn determined by bond alternation. Due to their reduced aromaticity and polyene-like structures, similar arguments suggest auspicious predictions for the hyperpolarizabilities of oligomeric polyquinoid, polythiophene, and other heteropentacyclic derivatives.

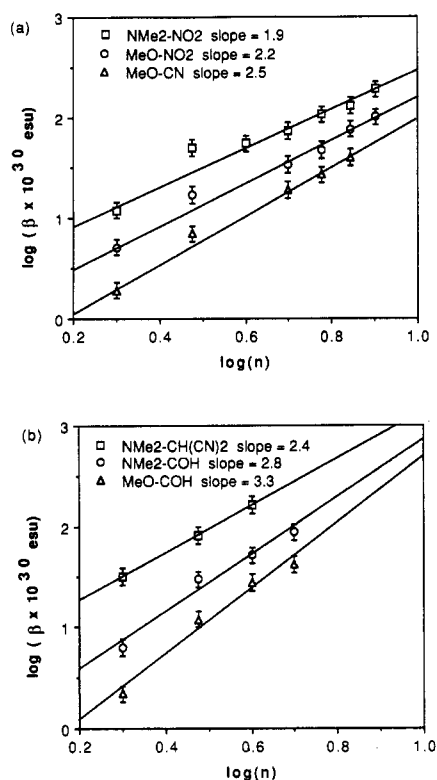
The conjugation length dependence of β is investigated with oligomeric α -phenylpolyene and α,ω -diphenylpolyene derivatives with a range of donor and acceptor groups. Measurement results are given in Table VII and VIII. Together with results obtained for benzene, styrene, fluorene, and stilbene derivatives, the length dependence of planar structures consisting of ethylenic units with phenyl end caps from $n = 2$ up to 8 double bonds can be studied (if each phenyl unit is considered as contributing two double bonds). Structures capped at both ends by phenyl groups behave quite differently from those capped at just the donor end. Results for the two series are therefore presented and analyzed separately. Benzene derivatives are used as the short conjugation length limit for both series to insure consistency in our observations. Logarithmic plots of β vs n for the two series are given in Figure 1. Power law dependences with conjugation lengths are also found for the λ_{\max} of CT bands and they are plotted in Figure 2. Except for the benzene derivatives, all results are obtained in chloroform solutions. The solvent dependence of the benzene results is not expected to be very large ($\approx 10\%$) and should not lead to significantly different exponents. Least-squares fits give reasonably good linear fits for all data sets. Systematic deviations in both

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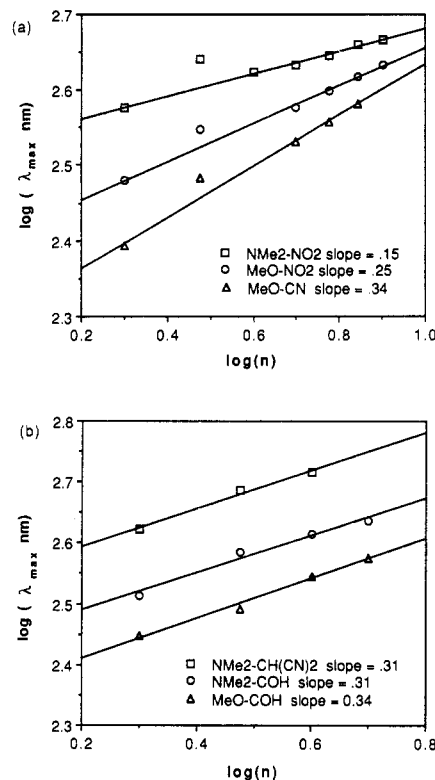
TABLE VIII: Results on Disubstituted α,ω -Diphenylpolyene Oligomers (Units in esu)

									
n	X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^\circ \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$	
1	CN	OMe	CHCl ₃	(340)	3.8	3.4	19	54	
2	CN	OMe	CHCl ₃	(360)	4.5	3.8	27	122	
3	CN	OMe	CHCl ₃	(380)	4.4	4.4	40	234	
1	NO ₂	Br	CHCl ₃	(356)	3.4	3.2	18	45	
2	NO ₂	Br	CHCl ₃	(378)	3.5	3.9	21	146	
3	NO ₂	Br	CHCl ₃	(400)	3.8	4.4	35	224	
1	NO ₂	MeO	CHCl ₃	(376)	4.5	3.4	34	93	
2	NO ₂	MeO	CHCl ₃	(397)	4.8	4.0	47	130	
3	NO ₂	MeO	CHCl ₃	(414)	5.1	4.2	76	230	
4	NO ₂	MeO	CHCl ₃	(430)	5.8	4.8	101		
1	NO ₂	MeS	CHCl ₃	(380)	4.3		34		
2	NO ₂	MeS	CHCl ₃	(398)	4.5	4.2	55	206	
1	NO ₂	NMe ₂	CHCl ₃	(430)	6.6	3.4	73	225	
2	NO ₂	NMe ₂	CHCl ₃	(442)	7.6	4.0	107		
3	NO ₂	NMe ₂	CHCl ₃	(458)	8.2	4.2	131		
4	NO ₂	NMe ₂	CHCl ₃	(464)	9 \pm 1		190 \pm 50		

Figure 1. Conjugation length dependences, where $n = 2$, for each phenyl unit, for (a) α,ω -diphenylpolyene and (b) α -phenylpolyene CT oligomers.

β and λ_{\max} of the styrene derivatives if included in the α,ω -diphenylpolyene series, as in previous works,^{2b,4} are, however, noted (see Figures 1a and 2a). Since the experimental accuracy in λ_{\max} determinations are high (± 2 nm) and the deviations for all donor-acceptor pairs are toward the long-wavelength side of the trend corroborating with the higher β values, the styrene structure is viewed as incompatible with the diphenyl capped series and results for styryl derivatives are not used to determine exponents.

Clearly, the magnitude of the exponent η which describes the power law dependence of $\beta \propto L^\eta$, where L is a length scale, depends strongly on the counting scheme used to determine L for a series of chemical structures studied. If η is to be compared with a physical model, such as results obtained from a free electron theory²⁴ and an effective internal field model,²¹ L , which is the delocalization length in the theories just mentioned, must be

Figure 2. λ_{\max} length dependences, where $n = 2$, for each phenyl unit, for (a) α,ω -diphenylpolyene and (b) α -phenylpolyene CT oligomers.

accurately determined. This is particularly important for the short-length structures in determining the power dependence. However, it is difficult to rigorously account for the extent of delocalization into the acceptor and/or donor orbitals. For substituents such as amino, carbonyl, nitro, and di- and tricyanovinyl groups, conjugation extension is extensive due to the strong participation of their orbitals in the ground state. When such orbitals are accounted for, results on η can readily be increased by 1 or higher. These considerations have largely been ignored in the past.

A second consideration concerns the dispersive enhancement associated with measurement results obtained for the extended structures which have relatively low-lying CT transitions. Even with the longest convenient optical frequency such as 1.91 μm , dispersive enhancement is significant and is progressively more so as the CT transitions bathochromically shift with conjugation length. Corrections are often attempted by reporting β_0 values⁹ which are deduced from the dispersion expression for the two-state model. As the π system is extended, the number of states con-

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TABLE IX: Exponents Determined from Data in Literature and Those Obtained in the Current Study for the Conjugation Length (n As Defined in Text) Dependence of Phenyl-Capped Oligomeric Polyene Derivatives

source (ω)	structure	length (n)	η for			
			$\beta(\omega)$	β_0	$\mu\beta(\omega)$	$\mu\beta_0$
ref 2b (1.9 μm)	$\text{Me}_2\text{N-Ph-(=)}_x\text{-Ph-CN}$	2, 5, 6			2.6	
ref 4 (1.06 μm)	$\text{MeO-Ph-(=)}_x\text{-Ph-NO}_2$	2, 3, 5, 6, 7, 8	3.1	2.6	3.3	2.8
ref 5 (1.34 μm)	$\text{Me}_2\text{N-Ph-(=)}_x\text{-COH}$	3, 6, 8, ^a 10			2.7	2.4
ref 5 (1.34 μm)	$\text{C}_6\text{H}_4\text{S}_2\text{(=)}_x\text{-COH}$	1, 4, 6, ^a 8			2.6	2.3
ref 3 ^b	$\text{Me}_2\text{N-(=)}_x\text{-NO}_2$	2, 4, 6, 8, 10	2.5 ^c			
ref 3 ^b	$\text{Me}_2\text{N-(=)}_x\text{-COH}$	2, 3, 4, 5, 6	2.7 ^c			
this work (1.9 μm)	$\text{Me}_2\text{N-Ph-(=)}_x\text{-Ph-NO}_2$	2, 3, 5, 6, 7, 8	1.9	1.9	2.2	2.1
this work (1.9 μm)	$\text{MeO-Ph-(=)}_x\text{-Ph-NO}_2$	2, 3, 5, 6, 7, 8	2.2	2.0	2.3	2.2
this work (1.9 μm)	$\text{MeO-Ph-(=)}_x\text{-Ph-CN}$	2, 3, 5, 6, 7, 8	2.5	2.3	2.4	2.3
this work (1.9 μm)	$\text{Me}_2\text{N-Ph-(=)}_x\text{-CH(CN)}_2$	2, 3, 5, 6, 7, 8	2.4	2.1	2.6	2.3
this work (1.9 μm)	$\text{Me}_2\text{N-Ph-(=)}_x\text{-COH}$	2, 3, 5, 6, 7, 8	2.8	2.7	3.1	2.9
this work (1.9 μm)	$\text{MeO-Ph-(=)}_x\text{-COH}$	2, 3, 5, 6, 7, 8	3.3	3.2	3.6	3.5

^a Contains one acetylenic unit. ^b Computational results. ^c Calculated at $\omega = 0$.

tributing significantly to the hyperpolarizability increases rapidly.²⁵ Therefore, it is doubtful that such β_0 values are free from systematic errors. When short-wavelength lasers are used for the measurements, this problem is exacerbated. In addition, due to the low solubilities of the extended derivatives, their fractional experimental uncertainties are generally significantly larger than those of the shorter members of the series.⁴ Since data are compressed at large n for a power law dependence, and the relatively high uncertainties for the extended derivatives procures lower statistical weights, the values of the exponents are often determined primarily by derivatives of short and moderate lengths. Therefore, experiments involving longer derivatives do not necessarily yield more reliable results.

A third critical issue concerns the deformational contribution, which is dominated by the electronic cubic polarizability, γ , to the EFISH signal.²⁶ As γ increases with both the conjugation length and β , this contribution becomes more significant for extended structures and must be taken into account prior to the determination of $\mu\beta$. Failure to do so will lead to overestimated exponents. Due to the presence of solvent cascading²⁷ and dispersive enhancement in THG, our procedure of making such a correction by relying on THG results is by no means rigorous.¹ However, it is probably better than ignoring such an effect. Again this uncertainty is less severe for the shorter derivatives.

Because of the reservations just discussed, we refrain from attaching great physical significance to the magnitude of the exponents. We have chosen a simple counting scheme in which donor and acceptor groups are excluded from the molecular length, and the length parameter n represents the number of double bonds with a count of 2 for each phenyl ring present in the conjugation. In order to make a numerical comparison with previous results, data given in refs 2b, 4, and 5 as well as computational results from ref 3 are analyzed according to the current scheme and the exponents, together with those obtained from our measurements, are tabulated in Table IX. All exponents fall within a range of about 2–3. Differences with previous results can be readily attributed to the differences in methodologies, counting schemes for L , as well as uncertainties discussed earlier, and will not be pursued further. We instead focus on the variations found within the current study. Two key features of the current findings are as follows: (1) the α -phenylpolyene and α,ω -diphenylpolyene series do not have the same exponents and the difference is about 0.6 with higher values for the former series; and (2) within each series, the exponents are end-group dependent and their values appear to be inversely related to the combined donor–acceptor strength or the magnitude of the hyperpolarizability.

The different exponents between the two series clearly point to the more efficient nature of the α -phenylpolyene series since,

for a given extension from the benzene derivatives, significantly higher β value is realized. The only structural difference between the two series is the presence of one additional phenyl ring. Morley's calculation³ and our discussions on styrene, fluorene, and stilbene derivatives suggest that the phenyl unit is much less effective than the olefinic unit for hyperpolarizability. A different counting scheme for L which better reflects this difference may eliminate the difference in the power law behaviors. By assigning one unit length for each phenyl unit, the difference between the two series as well as the deviation observed for the styryl derivatives is largely eliminated. All the exponents decrease from 1.9–3.3 to 1.5–2.2. Therefore, we can conclude that there is indeed a difference in effectiveness per unit physical length for the two series and the difference may be seen as further evidence that the olefinic unit is superior to the phenyl unit in engineering hyperpolarizability. This difference may be a result of the aromatic stabilization of the phenyl π system as discussed before. The two-dimensional nature of the phenyl ring should also be considered.²⁸ The magnitude of the new exponents are, however, considerably lower than those calculated by Morley for polyene systems with similar end groups (see Table IX).

The observed end-group dependence that gives lower exponents for the strong end groups may be partly rationalized by the extension of electron delocalization into the substituent orbitals, since it is reasonable to expect that stronger substituents will result in a longer delocalization length, which in turn results in a correction toward higher exponents. An alternative speculation may attribute the end-group dependence to bond alternation effects that are well-known for polyene systems. From simple valence bond considerations, the degree of bond alternation in CT polyene derivatives should be somewhat relieved as a result of the donor–acceptor stabilization of charge-separated resonance structures. However, such an effect appears to be insignificant judging from the moderate rate with which the CT bands bathochromically shift as a function of increasing chain length. As can be seen in Figure 2, the CT bands for both series red shift with n , but the exponents for λ_{max} are much less than unity, which is the familiar result from Hückel theory for systems free from bond alternation.²⁹ In any case, a reduction of bond alternation by strong donor–acceptor substituents will logically lead to a lower band gap and higher nonlinearity at saturation, which likely requires higher exponents for the length dependence. This is opposite to the observed end-group effects.

The most probable explanation for the end-group dependence is the recognition that the hyperpolarizabilities of extended CT structures are dominated by the participation of the π systems which become increasingly more polarizable. The end groups which dominate the asymmetric polarizability of the short structures play a reduced role in extended structures, resulting in a diminishing differential in properties of the extended structures

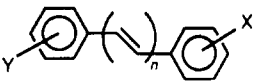
(25) (a) Docherty, V. J.; Pugh, D.; Morley, J. O. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1179–1192. (b) Li, D.-Q.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707–1715. (c) Ulman, A. *J. Phys. Chem.* **1988**, *92*, 2385–2390.

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TABLE X: Results on 2'-Acceptor,2- or 4-Donor-Substituted α,ω -Diphenylpolyene Oligomers (Units in esu)


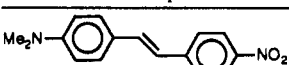
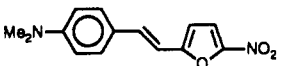
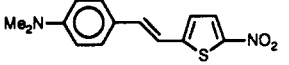
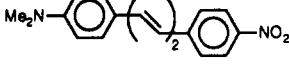
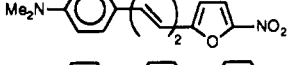

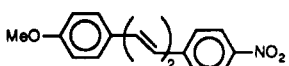
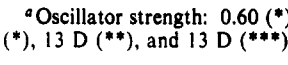
n	X	Y	solvent	λ_{\max} , nm	$\mu \times 10^{-18}$	$\alpha^o \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
2	2'-CN	2-OMe	CHCl ₃	(354)	3.8	3.7	4.5	60
3	2'-CN	2-OMe	CHCl ₃	(376)	3.8	4.4	7.1	147
2	2'-CN	4-OMe	CHCl ₃	(356)	3.9	3.7	2.6	88
3	2'-CN	4-OMe	CHCl ₃	(378)	3.9	4.3	4.3	165
2	4'-CN	2-OMe	CHCl ₃	(358)	4.9	3.8	16	90
1	2'-NO ₂	2-OMe	CHCl ₃	360s	3.8	3.3	4.4	29
2	2'-NO ₂	2-OMe	CHCl ₃	(376s)	3.7	3.8	6.4	51
3	2'-NO ₂	2-OMe	CHCl ₃	(392s)	4.1	4.4	11	131
1	2'-NO ₂	4-OMe	CHCl ₃	390s	3.5	3.3	3.8	35
2	2'-NO ₂	4-OMe	CHCl ₃	(370s)	3.8	3.8	4.9	75
3	2'-NO ₂	4-OMe	CHCl ₃	(392s)	3.8	4.3	11	123
1	4'-NO ₂	2-OMe	CHCl ₃	362	5.0	3.3	22	61
2	4'-NO ₂	2-OMe	CHCl ₃	(380)	4.3	3.7	17	55
3	4'-NO ₂	2-OMe	CHCl ₃	(412)	4.8	4.5	56	149

with different substituents. Since the hyperpolarizability is expected to saturate at some length due to the presence of bond alternation and other localization effects, and it is likely that saturation occurs prior to the unphysical crossing of the lines for different end groups in Figure 1, a high saturation limit of about 35 double bonds can be deduced. This is not in disagreement with the computation results of Morley that predicted an onset of saturation at $n \approx 20$ for the α,ω -(*N,N*-dimethylamino)nitropolyenes.³

The properties of extended α,ω -diphenylpolyene derivatives with 2'- or 4'-acceptor, 2- or 4-donor substitution patterns are also examined. Measurement results are presented in Table X. The β values for these compounds are always considerably lower than the 4'-acceptor,4-donor-substituted derivatives despite comparable CT band positions. The lower values can be attributed to two reasons. Firstly, the effective length of the conjugation is reduced. Secondly, for compounds with 2'-acceptor substitution, the very low values are the result of an experimental artifact of the EFISH measurement, which projects only the vectorial component of the hyperpolarizability tensor onto the molecular dipole. Since the dipole moment direction is dominated by the large group dipole moment of the highly polar nitro and cyano groups, it deviates significantly from the long molecular axis along which β is expected to be the highest. Along that axis, considerably higher β components are expected. It is interesting to note that, in spite of a shorter effective conjugation length, the 2'-acceptor,2-donor derivatives are found to have consistently higher values than the 2'-acceptor,4-donor analogues. These geometric factors are not as important for 4'-acceptor,2-donor-substituted derivatives since the group dipole moments of the donors are much weaker. The relative importance of through-resonance structures and geometric considerations in the interpretation of EFISH results was discussed in more detail in ref 1 where different substitution patterns on stilbenes were considered. The β values of all substitution patterns are found to increase with the extension of conjugation and the fractional increases appear to be quite comparable to the 4'-4-substituted derivatives.

5. Heteropentacyclic Derivatives: Minimization of Aromaticity. The observations presented above suggest that the hyperpolarizabilities of conjugated structures containing phenyl units can be enhanced by replacing phenyl groups with groups that have reduced aromatic stabilization and more polyene-like structures. To explore this hypothesis further, we have investigated CT structures in which phenyl units in conventional arene derivatives such as stilbene, diphenylbutadiene, and terphenyl are replaced with five-member heterocyclics such as furan and thiophene functionalities with reduced aromatic characters. Measurement results of these compounds together with results from their arene analogues are given in Table XI. In each case, the CT band occurred at longer wavelength and the β value was significantly higher for the heteropentacyclic derivative. Spectroscopic and solvatochromic measurements were made for the stilbene ana-

TABLE XI: Results on Heteropentacyclic and Related Arene Derivatives

compd	λ_{\max} , ^a nm	$\mu \times 10^{-18}$, esu	$\beta \times 10^{-30}$, esu
	430*	6.6	73
	478**	6.9	83
	492***	7.4	98
	442	7.6	107
	488	7.2	113
	340	5.0	11
	400	5.2	40
	397	4.8	47

^a Oscillator strength: 0.60 (*), 0.45 (**), and 0.42 (***). $\Delta\mu$: 13 D (*), 13 D (**), and 13 D (***).

logues. $\Delta\mu = \mu_e - \mu_g$ is extracted from solvatochromic shifts ($\Delta\nu$) of absorption spectra in solvents with closely matching refractive indexes but quite different dielectric constants (D) according to the following equation³⁰

$$hc(\Delta\nu) = \frac{2\mu_g(\mu_g - \mu_e)}{a^3} \Delta\left(\frac{D-1}{D+2}\right)$$

where h and c are Planck's constant and the speed of light, respectively. The Onsager radius, a , is taken to be 7 Å. No significant differences in oscillator strength and $\Delta\mu$ are found. This suggests that the higher nonlinearity originates largely from the reduction in CT transition energy which is believed to be a result of the destabilization of the ground state through partial elimination of aromatic energy. The strong correlation and trade-off between β and the λ_{\max} of the CT band is an recurring theme observed throughout our studies of the generic donor-conjugation-acceptor structures.^{1,31} This property places a practical limit

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on the available nonlinearities of organic materials for harmonic generation applications in the blue and green region.

6. Cubic Hyperpolarizability. As in ref 1, the salient features of our THG measurement results on molecular cubic hyperpolarizability, γ , are a general dependence on conjugation length and a strong correlation with β . In addition, there are clear differences among the different conjugated structures. For the polyphenyls and α,ω -diphenylpolyynes, conjugation extensions lead to much weaker increase of γ in comparison with that of the α -phenylpolyenes and α,ω -diphenylpolyenes (see Table IV, VI, VII, and VIII). Much of the same structural considerations, such as torsional effect, bond alternation, and aromatic stabilizations, used for the discussion of β can be used to rationalize these differences in γ .

Conclusion

We have systematically investigated the conjugation dependences of the quadratic optical hyperpolarizability of organic molecules with EFISH and THG measurements. Over 100 compounds covering a wide range of structures have been studied in order to demonstrate the existence of systematic trends and illustrate the importances of different characteristics of the π system. Issues concerning the efficacies of various conjugation units, conjugation planarity, aromaticity and bond alternation, and electron localization and delocalization effects, as well as the conjugation length and end group dependences, were addressed.

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Registry No. *p*-MeOC₆H₄CH=CHCN, 14482-11-2; *p*-Me₂NC₆H₄CH=CHCN, 4854-85-7; *p*-BrC₆H₄CH=CHCHO, 49678-04-8; *p*-MeOC₆H₄CH=CHCHO, 24680-50-0; *p*-Me₂NC₆H₄CH=CHCHO, 20432-35-3; *p*-MeOC₆H₄CH=CHCOCH₃, 3815-30-3; PhCH=CHNO₂, 5153-67-3; *p*-OHC₆H₄CH=CHNO₂, 22568-49-6; *p*-MeOC₆H₄CH=CHNO₂, 5576-97-6; *p*-Me₂NC₆H₄CH=CHNO₂, 22568-06-5; *p*-NO₂C₆H₄CH=CHNMe₂, 136795-65-8; *p*-PhC₆H₄CN, 2920-38-9; *p*-PhC₆H₄COCH₃, 92-91-1; *p*-PhC₆H₄NO₂, 92-93-3; *p*-Me₂NC₆H₄C₆H₄-*p*-SO₂(CH₂)₆OH, 134249-49-3; *p*-OHC₆H₄C₆H₄-*p*-CN, 19812-93-2; *p*-MeOC₆H₄C₆H₄-*p*-COCH₃, 13021-18-6; *p*-BrC₆H₄C₆H₄-*p*-NO₂, 6242-98-4; *p*-OHC₆H₄C₆H₄-*p*-NO₂, 3916-44-7; *p*-MeOC₆H₄C₆H₄-*p*-NO₂, 2143-90-0; *p*-NH₂C₆H₄C₆H₄-*p*-NO₂, 1211-40-1; *p*-Me₂NC₆H₄C₆H₄-*p*-NO₂, 2143-87-5; *p*-NH₂C₆H₄NO₂, 100-01-6; *p*-NH₂C₆H₄C₆H₄-*p*-C₆H₄-*p*-NO₂, 38190-45-3; *p*-NH₂C₆H₄C₆H₄-*p*-C₆H₄-*p*-C₆H₄-*p*-NO₂, 118837-15-3; *p*-MeOC₆H₄NO₂, 100-17-4; *p*-

MeOC₆H₄C₆H₄-*p*-C₆H₄-*p*-NO₂, 114253-99-5; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-SO₂Me, 135043-09-3; *p*-MeSC₆H₄C≡CC₆H₄-*p*-CO₂Me, 135043-10-6; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-CO₂Me, 119984-87-1; *p*-MeSC₆H₄C≡CC₆H₄-*p*-COCH₃, 135043-11-7; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-COCH₃, 123770-68-3; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-COPh, 135043-13-9; *p*-MeSC₆H₄C≡CC₆H₄-*p*-CN, 125138-98-9; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-CN, 119984-85-9; *p*-MeNHC₆H₄C≡CC₆H₄-*p*-CN, 135043-12-8; *p*-Me₂NC₆H₄C≡CC₆H₄-*p*-CN, 54273-31-3; *p*-BrC₆H₄C≡CC₆H₄-*p*-NO₂, 15795-01-4; *p*-MeOC₆H₄C≡CC₆H₄-*p*-NO₂, 39082-40-1; *p*-MeSC₆H₄C≡CC₆H₄-*p*-NO₂, 119984-89-3; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-NO₂, 7431-22-3; *p*-MeNHC₆H₄C≡CC₆H₄-*p*-NO₂, 101456-22-8; *p*-Me₂NC₆H₄C≡CC₆H₄-*p*-NO₂, 62197-66-4; *p*-MeSC₆H₄C≡CC₆H₄-*p*-CN, 119984-91-7; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-CN, 119984-86-0; *p*-MeSC₆H₄C≡CC₆H₄-*p*-NO₂, 119984-90-6; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-NO₂, 110175-15-0; *p*-NH₂C₆H₄C≡CC₆H₄-*p*-NO₂, 110175-16-1; *p*-MeOC₆H₄CHO, 123-11-5; *p*-MeOC₆H₄CH=CHCH=CHCHO, 49678-07-1; *p*-MeOC₆H₄CH=CHCH=CHCH=CHCHO, 72232-59-8; *p*-Me₂NC₆H₄CHO, 100-10-7; *p*-Me₂NC₆H₄CH=CHCH=CHCHO, 20432-36-4; *p*-Me₂NC₆H₄CH=CHCH=CHCH=CHCHO, 55298-77-6; *p*-MeOC₆H₄CHC(CN)₂, 2826-26-8; *p*-MeOC₆H₄CH=CHCHC(CN)₂, 136795-66-9; *p*-Me₂NC₆H₄CHC(CN)₂, 2826-28-0; *p*-Me₂NC₆H₄CH=CHCHC(CN)₂, 129179-87-9; *p*-Me₂NC₆H₄CH=CHCH=CHCHC(CN)₂, 136822-54-3; *p*-MeOC₆H₄CH=CHC₆H₄-*p*-CN, 57193-97-2; *p*-MeOC₆H₄CH=CHCH=CHC₆H₄-*p*-CN, 136795-67-0; *p*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*p*-CN, 136795-68-1; *p*-BrC₆H₄CH=CHC₆H₄-*p*-NO₂, 24325-71-1; *p*-BrC₆H₄CH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-69-2; *p*-BrC₆H₄CH=CHCH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-70-5; *p*-MeOC₆H₄CH=CHC₆H₄-*p*-NO₂, 4648-33-3; *p*-MeOC₆H₄CH=CHCH=CHC₆H₄-*p*-NO₂, 136795-71-6; *p*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-72-7; *p*-MeOC₆H₄CH=CHCH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-73-8; *p*-MeSC₆H₄CH=CHC₆H₄-*p*-NO₂, 20101-50-2; *p*-MeSC₆H₄CH=CHCH=CHC₆H₄-*p*-NO₂, 136795-74-9; *p*-Me₂NC₆H₄CH=CHC₆H₄-*p*-NO₂, 2844-15-7; *p*-Me₂NC₆H₄CH=CHCH=CHC₆H₄-*p*-NO₂, 67309-70-0; *p*-Me₂NC₆H₄CH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-75-0; *p*-Me₂NC₆H₄CH=CHCH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-76-1; *o*-MeOC₆H₄CH=CHCH=CHC₆H₄-*o*-CN, 136795-77-2; *o*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*o*-CN, 136795-78-3; *p*-MeOC₆H₄CH=CHCH=CHC₆H₄-*o*-CN, 136795-79-4; *p*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*o*-CN, 136795-80-7; *o*-MeOC₆H₄CH=CHCH=CHC₆H₄-*p*-CN, 136795-81-8; *o*-MeOC₆H₄CH=CHC₆H₄-*o*-NO₂, 55801-78-0; *o*-MeOC₆H₄CH=CHCH=CHC₆H₄-*o*-NO₂, 136795-82-9; *o*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*o*-NO₂, 136795-83-0; *p*-MeOC₆H₄CH=CHC₆H₄-*o*-NO₂, 112768-16-8; *p*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*o*-NO₂, 136795-84-1; *p*-MeOC₆H₄CH=CHCH=CHCH=CHCH=CHC₆H₄-*o*-NO₂, 136795-85-2; *o*-MeOC₆H₄CH=CHC₆H₄-*p*-NO₂, 28915-66-4; *o*-MeOC₆H₄CH=CHCH=CHC₆H₄-*p*-NO₂, 136795-86-3; *o*-MeOC₆H₄CH=CHCH=CHCH=CHC₆H₄-*p*-NO₂, 136795-87-4; styrene, 100-42-5; biphenyl, 92-52-4; fluorene, 86-73-7; diphenylacetylene, 501-65-5; 2-cyanofluorene, 2523-48-0; 2-nitrofluorene, 607-57-8; 2-bromo-7-nitrofluorene, 6638-61-5; 2-methoxy-7-nitrofluorene, 54961-21-6; 2-dimethylamino-7-nitrofluorene, 19221-04-6; 1-(4-dimethylaminophenyl)-2-(5-nitrofuranyl)ethene, 136795-62-5; 1-(4-dimethylaminophenyl)-2-(5-nitrothienyl)ethene, 136795-63-6; 1-(4-dimethylaminophenyl)-3-(5-nitrofuranyl)-1,3-butadiene, 136795-64-7; 2-(4-methoxyphenyl)-5-(4-nitrophenyl)furan, 126739-60-4.