

AD-A235 622



WL-TR-91-4015



**THE SYNTHESIS AND EVALUATION OF THIRD-ORDER
OPTICAL NONLINEARITIES OF MODEL COMPOUNDS
CONTAINING BENZOTHAZOLE, BENZIMIDAZOLE AND
BENZOXAZOLE MOIETIES**

Bruce A. Reinhardt, Marilyn R. Unroe, Mark Prazak, and Robert C. Evers
Polymer Branch
Nonmetallic Materials Division

James J. Kane, Chetan Jariwala and Mark Sinsky
Department of Chemistry
Wright State University
Dayton, OH 45435

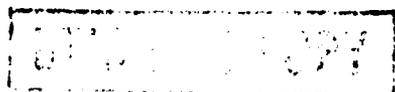
Mingtang Zhao, Marek Samoc and Paras N. Prasad
Photonics Research Laboratory, Department of Chemistry
State University of New York at Buffalo
Buffalo, NY 14214

February 1991

Final Report for Period February 1988 to July 1990

Approved for public release; distribution unlimited.

**MATERIALS DIRECTORATE
WRIGHT LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AFB, OH 45433-6533**



91 5 08 017

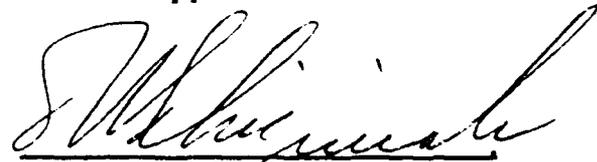
NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligation whatsoever. The fact that the Government may have formulated or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication, or otherwise in any manner construed, as licensing the holder, or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public including foreign nations.

This technical report has been reviewed and is approved for publication.


ROBERT C. EVERS, Project Scientist
Polymer Branch
Nonmetallic Materials Division


T. E. HELMINIAK, Chief
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER


 **MERRILL L. MINGES, Director**
Nonmetallic Materials Division

If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization, please notify WL/MLBP, Wright-Patterson AFB, OH 45433-6533, to help us maintain a current mailing list.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b RESTRICTIVE MARKINGS			
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.			
2b DECLASSIFICATION / DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) WL-TR-91-4015		5 MONITORING ORGANIZATION REPORT NUMBER(S)			
6a NAME OF PERFORMING ORGANIZATION Materials Directorate, Wright Laboratory		6b OFFICE SYMBOL (If applicable) WL/MLBP	7a NAME OF MONITORING ORGANIZATION		
6c ADDRESS (City, State, and ZIP Code) Wright-Patterson Air Force Base, Ohio 45433-6533		7b ADDRESS (City, State, and ZIP Code)			
8a NAME OF FUNDING / SPONSORING ORGANIZATION Air Force Systems Command		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c ADDRESS (City, State, and ZIP Code) Wright-Patterson Air Force Base, Ohio 45433-6533		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. Q3	WORK UNIT ACCESSION NO. 07
11 TITLE (Include Security Classification) The Synthesis and Evaluation of Third-Order Optical Nonlinearities of Model Compounds Containing Benzothiazole, Benzimidazole, and Benzoxazole Moieties					
12 PERSONAL AUTHOR(S) Bruce A. Reinhardt, Marilyn R. Unroe, Mark Prazak, and Robert C. Evers; James J. Kane, Chetan Jariwala,					
13a TYPE OF REPORT Final		13b TIME COVERED FROM Feb 88 TO Jul 90		14. DATE OF REPORT (Year, Month, Day) February 1991	15 PAGE COUNT 39
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
07	03		nonlinear optical properties		
20	05		degenerate four-wave mixing		
			third order hyperpolarizability		
			benzothiazole		
			benzimidazole		
			benzoxazole		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>A series of model compounds containing benzothiazole, benzimidazole and benzoxazole moieties were prepared and evaluated by femtosecond degenerate four-wave mixing techniques. Model compounds were evaluated as either solutions of various concentrations in tetrahydrofuran or as vacuum deposited films. In general, the trend toward nonlinearity was directly related to structural variations since no one- or two-photon resonances were observed in the models despite the consideration of time-response behavior and concentration dependence. The following generalizations are afforded: (i) microscopic third-order nonlinearity rapidly increases with an increase in the effective conjugation length for a quasi-one-dimensional molecule; (ii) incorporation of a sulfur containing heteroaromatic fused ring in the conjugated structure enhances nonlinearity; (iii) imidazole N-linkages enhance third-order optical nonlinearity by virtue of the transition from a quasi-one-dimensional to a two-dimensional delocalization of the π-electrons without sacrifice of optical transparency and solubility. Qualitative trends in nonlinearity within a series of models is compared with the predicted values from a recent semiempirical calculation.</p>					
20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL Marilyn R. Unroe			22b TELEPHONE (Include Area Code) (513) 255-9145	22c OFFICE SYMBOL WL/MLBP	

Block 12. (continued): and Mark Sinsky; Mingtang Zhao, Marek Samoc and Paras N. Prasad

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Directorate, Wright Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. Robert C. Evers as the Materials Laboratory Project Scientist. The coauthors of this report were Bruce A. Reinhardt, Marilyn R. Unroe, Mark Prazak, and Robert C. Evers, Materials Directorate (WL/MLBP). This report covers research conducted from February 1988 to July 1990. The government coauthors wish to thank personnel of the Materials Integrity Branch, WL/MLSA, Systems Support Division, Materials Directorate, for mass spectrum and elemental analysis determinations, the coauthors at SUNY, Buffalo, who were supported by the Air Force Office of Scientific Research, Directorate of Chemical and Atmospheric Sciences and WL/MLBP under AFOSR contract F49620-90-C-0021 for their evaluations of the materials and technical contributions to this report, and the coauthors of the Department of Chemistry, Wright State University, Dayton, OH, who were supported by the Air Force Office of Scientific Research, Directorate of Chemical and Atmospheric Sciences and WL/MLBP under AFOSR contract F49620-89-C-0027 for their synthetic contributions.



APPROVED FOR
NTIS GRA&I
DTIC TAB
UNANNOUNCED
JUSTIFICATION FOR
BY _____
DISTRIBUTION STATEMENT _____
A-1

TABLE OF CONTENTS

SECTION		PAGE
1.	INTRODUCTION	1
2.	RESULTS AND DISCUSSION	3
2.1.	Synthesis	
2.1.1.	Benzoxazole and Benzothiazole Model Compounds	3
2.1.2.	N-Phenylbenzimidazole Model Compounds	5
2.2.	Measurements of Third-Order Hyperpolarizabilities	8
2.2.1.	Benzothiazole, Benzimidazole and Benzoxazole	11
2.2.2.	Molecules With Two Aromatic Units	14
2.2.3.	More Complicated Combinations of Heterocyclic Molecules	16
2.2.4.	Conclusion	18
3.	EXPERIMENTAL	23
3.1.	Preparation of Model Compounds <u>1-5</u> , <u>7-10</u>	23
3.2.	Preparation of Model Compounds <u>6</u> , <u>11</u> , <u>12</u>	26
3.3.	Preparation of Thin Films	30
4.	REFERENCES	32

LIST OF ILLUSTRATIONS

FIGURE	PAGE
1 Time-resolved Degenerate Four-wave Mixing (DFWM) Signal for a 0.5M Solution of Benzoxazole in THF.	11
2 Concentration Dependence of Effective $\chi^{(3)}$ of Benzoxazole Solutions in THF.	12

LIST OF TABLES

TABLE	PAGE
1 Properties of Benzoxazole, Benzothiazole and Benzimidazole Compounds	7
2 Maximum UV-VIS Absorption Peaks (λ_{\max}) and Second-Order Hyperpolarizability Values (γ) for Benzothiazole, Benzimidazole and Benzoxazole	13
3 Maximum UV-VIS Absorption Peaks (λ_{\max}) and Second-Order Hyperpolarizability Values (γ) for Molecules With Two Connecting Units	15
4 Maximum UV-VIS Absorption Peaks (λ_{\max}) and Second-Order Hyperpolarizability Values (γ) for Molecules With Three or More Connecting Units	17
5 Experimentally Determined and Theoretically Calculated Second-Order Hyperpolarizabilities (γ) for Some Representative Benzothiazole Model Compounds	19

SECTION 1. INTRODUCTION

The search for nonlinear optical materials with very large values of the third-order susceptibility $\chi^{(3)}$ has attracted much interest from both the experimental and the theoretical points of view (References 1-2). Until recently most interest has focused on nonlinear materials belonging to the group of π -conjugated polymers. The properties of these polymers present a challenge to theoreticians and experimentalists because of both a variety of new properties brought about by their quasi-one-dimensional structure and the complications that are due to intermolecular interactions when in the solid state (ordering of chains, inter-chain charge or energy transfer, local field effects, etc.). However, at least part of the necessary knowledge of properties of an organic solid is gained by studying the properties of the molecules building a phase or by studying properties of model compounds resembling sections of a polymer backbone. With this intent, a systematic course of investigations was undertaken in which model molecules were synthesized and their third order hyperpolarizabilities (γ) were determined. The correlation with theoretical calculations performed using the *ab initio* and semiempirical quantum chemistry methods provided feedback necessary for rationalizing the obtained results and acquiring a predictive capability for more complicated systems (References 3-7).

Previous studies have shown how the third-order hyperpolarizability increases as a function of the chain length in oligomers of thiophene (Reference 3), benzene (Reference 4) and pyridine (Reference 5). The rapid increase of the γ values as subsequent units are added to the oligomer chain did not persist for long, but a saturation value of γ/N (where N is the number of repeat units in an oligomer chain) was reached. This limiting value was more rapidly attained in the benzene oligomer series than it was in the corresponding thiophene series. This experimental observation was postulated to be due to the more severe steric interactions of the hydrogen atoms in adjacent benzene rings in comparison to steric interactions of hydrogen atoms in adjacent thiophenes. Such steric interactions destroy planarity of the π -conjugated polymer chain and therefore reduce π -orbital overlap.

Within the simple coupled oscillator model of oligomeric chains (Reference 8), this reduction corresponded to a lower coupling constant for a system with stronger steric hindrances.

In some cases oligomeric or polymeric molecules made of heterocyclic structures may provide higher γ values not only because of a reduction in steric hindrances but also because of the participation of atomic orbitals of the heteroatoms in the molecular orbitals. The latter possibility may lead to a higher γ value by virtue of either a stronger overlap between the units or simply by a higher hyperpolarizability of a monomer molecule. In terms of a coupled anharmonic oscillator model considered in Reference 8, it means either a higher coupling constant or a larger local anharmonicity of the molecular oscillator.

This report presents a study of molecular second-order hyperpolarizabilities for a series of systematically modified molecules whose parent structures are benzothiazole, benzoxazole and benzimidazole. The structural choices for study were prompted by the importance of heteroaromatic structures in rod-like polymeric chains, such as the polybenzobisazoles (PBZ's), which possess interesting mechanical and optical properties. Besides the issue of the optimization of the structure to obtain the highest value of γ , the processibility of the materials was also of interest. Molecules with proper pendant groups that improve the solubility of oligomers and polymers in organic solvents and/or facilitate processing by spin coating or by Langmuir-Blodgett deposition were synthesized.

The modification of molecules by attaching pendant groups leads to variation of the hyperpolarizability by at least two opposing factors. First, pendant groups may improve the hyperpolarizability by either electron contribution of the pendant to the conjugated π -electron system of the backbone or by induced changes to the electron system by the pendant's inherent polar character. In contrast, the second and opposing factor is the pendant group alteration of the π -electron overlap by steric hindrance.

SECTION 2. RESULTS AND DISCUSSION

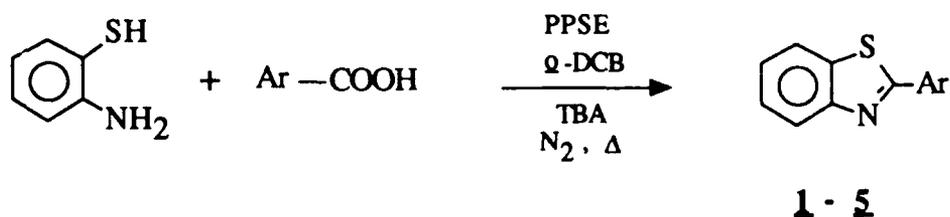
2.1. Synthesis

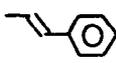
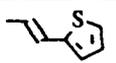
2.1.1. Benzoxazole and Benzothiazole Model Compounds

Various preparatory methods were initially considered for the synthesis of both the benzoxazole and benzothiazole model compounds. The standard method of condensation using polyphosphoric acid generally gave lower yields and produced a larger number of by-products especially with model compounds containing thiophene rings and/or long alkyl ether pendants. It was therefore necessary to develop a new method which could be used as a general method for all the compounds of interest. The method chosen was a modification of a method previously used for simple benzoxazoles (Reference 9) and benzothiazoles (Reference 10). This method involved the direct condensation of aromatic carboxylic acids with the appropriate aminophenol, aminothiophenol or their corresponding hydrochloride salts. The reagent chosen to catalyze the condensation/dehydration was trimethylsilylpolysphosphate (PPSE) (Reference 10). In all cases this procedure was found to give moderate to high yields of the model compounds while requiring a minimum amount of effort for purification.

The syntheses of benzothiazole model compounds **1-5** were carried out according to Scheme 1 (Procedure A). The yields of the model compounds in this series ranged between 50 and 90%.

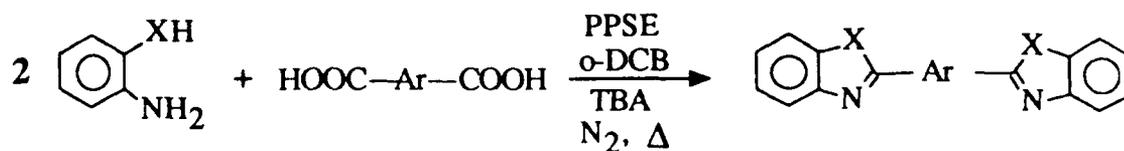
Scheme 1



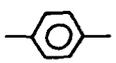
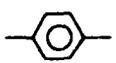
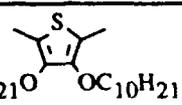
Ar	
	1
	2
	3
	4
	5

Bisbenzoxazole and bisbenzothiazole model compounds **7**, **8** and **10** were synthesized by the pathway described in Scheme 2 (Procedures B or D) in purified yields of 54-83%. The bisbenzothiazole model compound **9** was synthesized in 47% yield by a procedure found in the literature for similar materials (Reference 11) (Procedure C).

Scheme 2

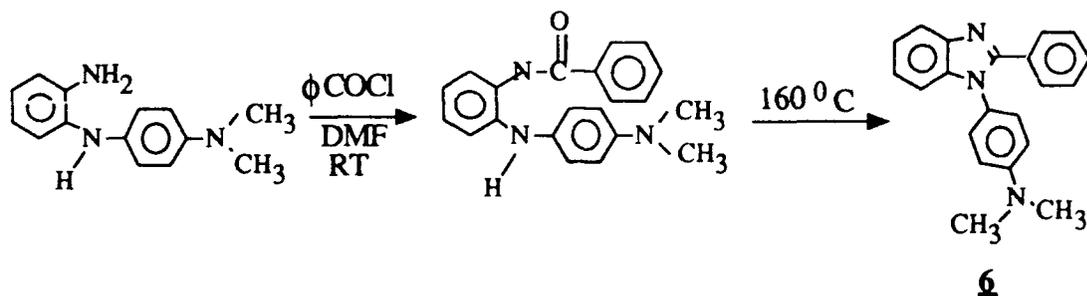


7 - 10

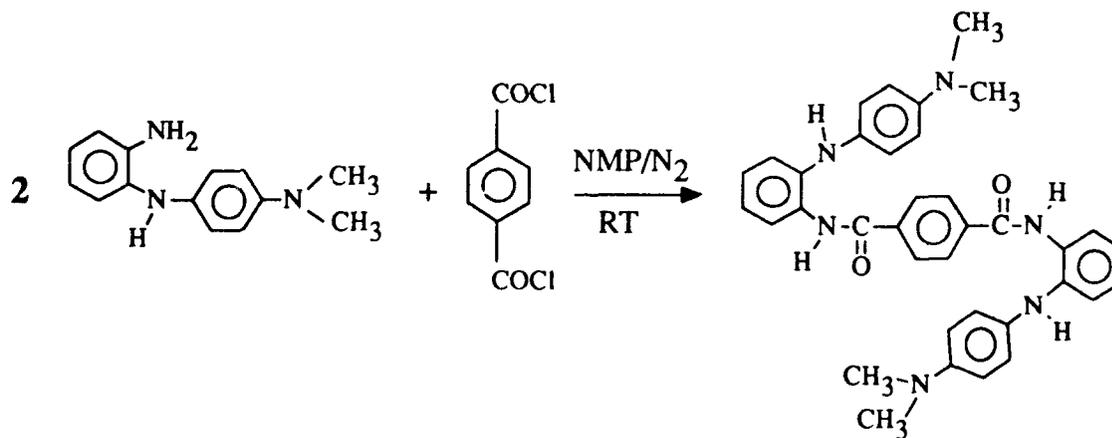
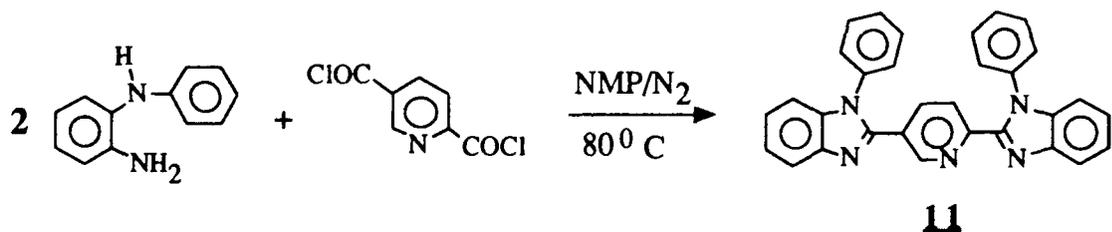
X	Ar	
O		7
S		8
S		9
S		10

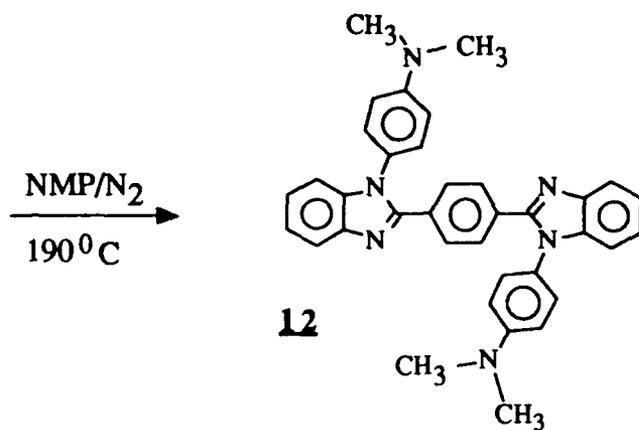
2.1.2. N-Phenylbenzimidazole Model Compounds

N-Phenylbenzimidazole compound **6** was prepared in moderate yield from the thermal ring closure of neat N-(4-dimethylaminophenyl)-N'-benzoyl-1,2-phenylenediamine (Procedure E).



N-Phenyl substituted bisbenzimidazoles **11** and **12** were prepared in fair to good yields by the ring closure in aprotic solution of either the *in situ* generated bisamide (Procedure F) or the isolated terephthalamide (Procedure G).





The characterization of all model compounds used in the study are located in Table 1.

Table 1. Properties of Benzoxazole, Benzothiazole and Benzimidazole Compounds

Compound Number	Synthetic Procedure	mp (solvent) yield (%)	Lit mp (solvent) <i>Lit Ref.</i>	Elemental Analysis Calculated (Found) or CARN ^a	IR Spectra ν (cm ⁻¹)
<u>1</u>	A	115.5-116.5° (ethanol) 90%	115-116° (ethanol) 12	known compound 883-93-2	1480,1440,1320, 11230, 1075,965, 770,735,690
<u>2</u>	A	135-136° (MeOH/H ₂ O) 73%	133-135° (ethanol) 13	known compound 716-80-3	1583,1456,1316, 982,978,727
<u>3</u>	A	101-103° (MeOH/H ₂ O) 78%	98-100° (EtOH/H ₂ O) 14	known compound 34243-38-4	1545, 1420, 920 760, 710, 700
<u>4</u>	A	112-114° (hexane) 81%	115° (ethanol) 15	known compound 104505-71-7	1628, 1500,1480
<u>5</u>	A	118-119° (hexane) 60%	117° (EtOH/H ₂ O) 16	known compound 5132-04-7	1622, 1480, 1175, 950, 760, 690
<u>6</u>	E	256-257° DMF/acetone 66%	-----	%C 80.48 (80.67) %H 6.11 (6.05) %N 13.41 (13.38)	2895, 1608,1525, 1474
<u>7</u>	B	356-357° (xylene) 85%	355-356° (pyridine) 17	known compound 904-39-2	1548,1452,1413, 1245,1059,850 760,745
<u>8</u>	B	263-265° (xylene) 83%	257-258° (benzene) 11	known compound 5153-65-1	1480,1433,1312 965,763
<u>9</u>	C	241-242° (toluene) 47%	232-233° (DMF) 18	known compound 18013-43-9	1547,1507,1462, 1430,1263,920, 756,697
<u>10</u>	D	92-93° (abs ethanol) 54%	-----	%C 68.83 (68.93) %H 7.60 (7.36) %N 4.23 (4.00)	2925,2850,1515, 1320,1050,755, 725
<u>11</u>	F	238-240° (EtOH/H ₂ O) 45%	-----	%C 80.33 (80.52) %H 4.57 (4.69) %N 15.11 (15.06)	3054, 1595,1499
<u>12</u>	G	> 320° 73%	-----	%C 78.81 (79.15) %H 5.88 (5.80) %N 15.32 (15.30)	2889, 1606, 1526, 1454

^a Chemical Abstracts Service registry number.

2.2. Measurements of Third-Order Hyperpolarizabilities

Degenerate four-wave mixing (DFWM) is a phenomenon in which the presence of three optical fields of the same frequency ω produce a nonlinear polarization at the same frequency which in turn becomes the source of the fourth beam. The direction of this beam is given by the phase-matching condition, i.e., the condition of conservation of the wave vector k . An equivalent description of the DFWM phenomenon is in terms of transient gratings formed by interaction of pairs of beams and the Bragg diffraction of the remaining beam from the phase and/or amplitude grating (References 19-21).

DFWM measurements were performed in a backward beam geometry (Reference 3) or in BOXCARS geometry (forward four-wave mixing). The laser system was described in previous publications (Reference 3). It delivered amplified, nearly transform limited 400 femtosecond pulses at 602 nm with the repetition frequency of 30 Hz and a maximum energy of approximately 0.4 mJ per pulse. An appropriate set of beam splitters was used to form three beams which could be synchronized with delay lines to arrive at the sample at the same time. The delay of one of the beams (the backward beam in the backward beam geometry or the out-of-plane beam in the BOXCARS geometry) could then be varied to record the temporal profile of the DFWM signal. The signal was observed as the phase conjugate to one of the forward beams in the backward beam geometry and in the position given by the appropriate phase-matching condition in the BOXCARS case. The signal was monitored with a photodiode and processed with a boxcar averager (EG&G Princeton Applied Research, Model 4200).

The intensity of the DFWM signal for liquid or solid samples, corresponding to the maximum of the profiles obtained by scanning the delay, was compared to the signal obtained for a reference sample under the same light intensity conditions. The bulk third-order susceptibility of the sample was then calculated from this comparison using

$$\chi^{(3)} = \sqrt{\frac{I}{I_s}} \left[\frac{n}{n_s} \right]^2 \frac{L_s}{L} \chi_s^{(3)} F \quad (1)$$

where I stands for the DFWM signal intensity, n is the refractive index of the medium, L is the interaction length, the subscript s refers to a reference sample, and F is the correcting factor taking into account the sample absorption. For those measurements which were performed on materials in the form of solid films, the obtained $\chi^{(3)}$ refers in a straightforward way to the microscopic hyperpolarizability of the investigated molecules. For measurements in solution, however, the contribution of the solvent nonlinearity must be taken into account. Therefore, the macroscopic third order susceptibility is then taken as

$$\chi^{(3)} = f^4 \left[N_s \gamma_s + N_x \gamma_x \right] \quad (2)$$

where γ_s and γ_x stand for the hyperpolarizabilities of the solvent and the solute respectively, N_s and N_x denote the respective number densities of the molecules and f is the local field factor approximated in this paper by the Lorentz expression, i.e.,

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

where n is the refractive index of the a solution at the frequency of the measurements (602 nm). These values were approximated using Abbe refractometer measurements at the sodium line (589 nm). Equation (2) was used to obtain least-squares fitted values of γ_s and γ_x for each series of concentration dependences of $\chi^{(3)}$. Errors in the determination of γ were calculated taking into account the uncertainties of the measurements of the DFWM intensities for individual points. These uncertainties may originate both in systematic errors and in random deviations because of laser beam instabilities. Intensity errors of 15% were estimated so that the resulting uncertainty of the values were then dependent upon experimental factors such as the concentration range used for the measurements, the number of data points and the ratio of the solute and solvent hyperpolarizabilities. Since in most cases dilute solutions were used for which the

refractive index was only slightly different from that of the solvent, this experimental error was minimized. In contrast, larger errors were encountered on the measurements of film specimens since the refractive index was assessed on potentially nonuniform films. The values of γ from solid film measurements bore a total error limit of 20%.

Since the hyperpolarizabilities entering Equation (2) are orientational averages of the respective fourth rank tensors of γ_{ijkl} and the measurements are performed on neat solid films, Equation (2) simplifies because there is no solvent contribution. However, there may be other complications due to imperfect orientational averaging in thin films and, possibly, inadequacy of the assumption of the isotropic Lorentz local field factor. For the lack of better knowledge, the average γ values for thin films were calculated using the assumption of an isotropic medium.

The values of γ obtained from DFWM measurements for all molecules investigated in this study are listed in Tables 2, 3, and 4. The positions of UV-VIS absorption maxima for solutions of these molecules in tetrahydrofuran (THF) are also listed. The model compounds investigated were divided into various groups according to structural similarity in order to facilitate comparisons and explanations.

Simple qualitative concepts were used to discuss the dependence of the γ values on the structure of molecules. The molecules investigated were considered as one-dimensional systems. In such systems the dominant contribution to the orientationally averaged γ is expected along the molecule backbone (z axis). Therefore, $\chi^{(3)}_{zzzz}$, is given as follows:

$$\chi^{(3)}_{zzzz} \propto \frac{e^{10}}{\sigma} \left[\frac{a_0}{d} \right]^3 \frac{1}{E_g^6} \quad (4)$$

where a_0 is the Bohr's radius, d is the average distance between neighboring carbon atoms, σ is the cross-sectional area per chain and E_g is the energy gap of the molecule. As a result, a molecule having a smaller band gap will have a larger $\chi^{(3)}$ and γ . The band gap, in turn, should depend on the degree to which the π -electrons are delocalized along the

molecular backbone. In a simple one-dimensional picture an effective "conjugation length" may be considered. As the conjugation length increases, the band gap decreases and the hyperpolarizability increases. In the following sections the nonlinearity of specific molecules as well as the changes in their absorption spectra with increasing chain length are discussed.

2.2.1. Benzothiazole, Benzimidazole, and Benzoxazole

The three heterocyclic molecules were studied in THF solutions. The concentration ranges were as follows: benzothiazole, 0.25 - 4.0 M; benzimidazole, 0.2 - 0.8 M; benzoxazole, 0.5 - 3.0 M. For each molecule, several THF solutions with different concentrations were studied and the corresponding DFWM signals were obtained. The temporal behavior of the DFWM signal for a benzoxazole solution is shown in Figure 1.

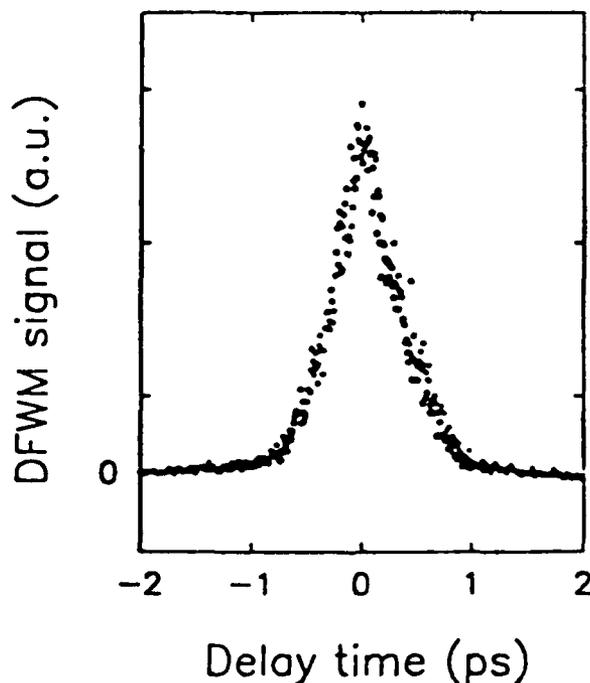


Figure 1. Time-resolved Degenerate Four-Wave Mixing (DFWM) signal for a 0.5 M Solution of Benzoxazole in THF.

The symmetric curve indicates that there is no one-photon or two-photon absorption involved in the DFWM process for this molecule at the measured wavelength of 602 nm.

The presence of any population grating induced by one-photon or two-photon absorption will result in an asymmetrically temporal DFWM signal. The temporal studies of the DFWM signal for benzothiazole and benzimidazole also did not show any asymmetry. It is therefore confirmed that the γ values for the three molecules at 602 nm are nonresonant values. This inference is also supported by the concentration dependence study of $\chi^{(3)}$ which yields a positive real value of γ for each compound. In the case of a one-photon or two-photon resonance, the γ value is not necessarily positive and it is always a complex quantity.

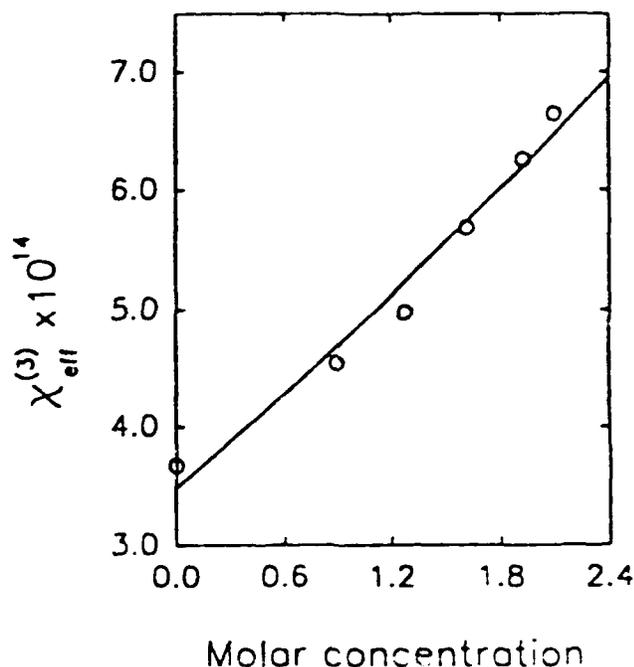
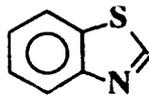
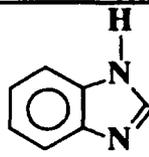
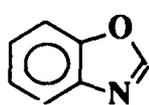


Figure 2. Concentration Dependence of Effective $\chi^{(3)}$ of Benzoxazole Solutions in THF. The Hollow Circles Are the Data Points and the Solid Curve is the Fit By Using Eq. (2).

Figure 2 shows the concentration dependence of effective $\chi^{(3)}$ for the benzoxazole molecule whose γ value can be obtained by fitting the concentration dependence. The γ values for the other two molecules can be obtained in the same way and are summarized in Table 2.

Table 2. Maximum UV-VIS Absorption Peaks (λ_{\max}) and Second-Order Hyperpolarizability Values (γ) for Benzothiazole, Benzimidazole and Benzoxazole

Compound	λ_{\max} (nm) ^a	γ (esu)
	294.5 (2) 284.1 (2) 250.8 (1)	2.6×10^{-35} $\pm 3.4 \times 10^{-36}$
	281.1 (2) 274.3 (2) 245.6 (1)	2.0×10^{-35} $\pm 3.0 \times 10^{-36}$
	277.0 (2) 270.7 (2) 239.0 (1)	1.6×10^{-35} $\pm 3.2 \times 10^{-36}$

^a The number in parentheses refers to the relative intensities of the absorption peaks.

The positions of dominant absorption peaks in the UV-VIS spectra which were measured in THF solutions are listed in Table 2. The letters in parentheses refer to the intensities of the peaks. Generally these absorption transitions are either $n\pi^*$ or $\pi\pi^*$ type with the $n\pi^*$ transitions corresponding to lower energies but smaller oscillator strengths. Based on the description of molecular hyperpolarizabilities by the sum-over-states approach, a larger contribution to γ from the $\pi\pi^*$ transitions is expected than the contribution from the lower lying $n\pi^*$ transitions. However, the relative importance of those two types of transitions cannot be assessed with any confidence without the knowledge of all the terms entering the sum-over-states expression.

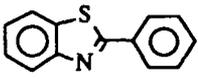
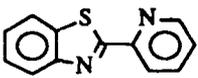
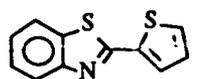
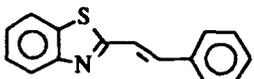
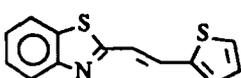
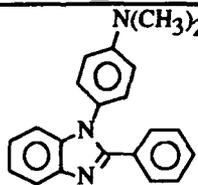
The values in Table 2 show the decrease in nonlinearity in the order benzothiazole, benzimidazole, and benzoxazole. This trend in order is also expected from the shifts in the positions of the corresponding absorption peaks. Qualitatively, this ordering of the absorption transitions and the nonlinearity for the three molecules can be explained as

follows. The heteroatoms donate p-electrons to the molecular π orbitals of the heteroatomic molecules. While the electronegativities of a sulfur and carbon atom are not very different, the electronegativity of the nitrogen atom is markedly larger than carbon and the electronegativity of the oxygen atom is even greater than nitrogen. As a consequence of these differences in electronegativity the π orbitals in sulfur-containing heteroaromatics are better delocalized than in molecules containing nitrogen or oxygen. In the case of sulfur an important factor may also be the presence of empty d orbitals that can contribute to the molecular π orbitals. The net effect of this contribution is a reduction in the energy of the $\pi\pi^*$ transition and thus a greater hyperpolarizability.

2.2.2. Molecules With Two Aromatic Units

Since benzothiazole has the highest γ value among the three molecules considered in Section 2.2.1, a logical progression to study the nonlinearity of more extended π -electron systems containing benzothiazole was undertaken. Compounds 1-3 (Table 3) contain linkages of benzothiazole with benzene, pyridine, and thiophene. In all three cases, the hyperpolarizability was strongly enhanced in comparison to the benzothiazole unit. The second order hyperpolarizability increased very fast with the extension of the π -electron system, and it was far from additive when additional aromatic units were attached which is exemplified in compounds 4-6. Although the observed differences in γ between compounds 1-3 were only slight, the highest hyperpolarizability and the smallest band gap was observed for the thiophene derivative of benzothiazole (3). One explanation for this difference may be the different degree of overlap of π -electron systems of benzothiazole with its respective aromatic link in compounds 1-3. Deviations from planarity in 1-3 will thus modify this overlap. The presence of lone electron pairs on nitrogen in the pyridine unit of 2 and the sulfur in the thiophene unit of 3 may also contribute to greater γ and lower band gaps in 2 and 3.

Table 3. Maximum UV-VIS Absorption Peaks (λ_{\max}) and Second-Order Hyperpolarizability Values (γ) for Molecules With Two Connecting Units

Compound	NLO Measurement Method	λ_{\max} (nm) ^a	γ (esu)
 1	THF	297.2	4.3×10^{-35} $\pm 5.7 \times 10^{-36}$
 2	THF	309.4	4.7×10^{-35} $\pm 4.8 \times 10^{-36}$
 3	THF	325.8	5.4×10^{-35} $\pm 1.1 \times 10^{-36}$
 4	THF	337.7	7.7×10^{-35} $\pm 1.8 \times 10^{-36}$
 5	THF	355.8	8.8×10^{-35} $\pm 1.5 \times 10^{-36}$
 6	THF	295.8 (2) 267.8 (1)	1.1×10^{-34} $\pm 3.4 \times 10^{-35}$

^a The number in parentheses refers to the relative intensities of the absorption peaks.

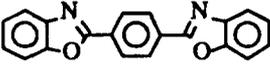
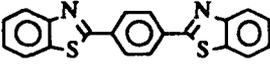
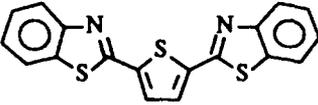
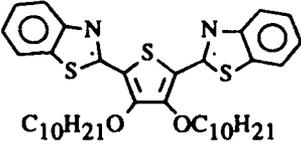
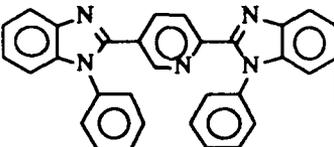
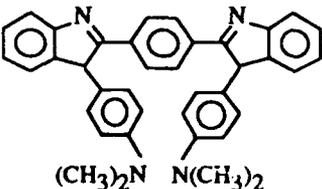
Compounds **4** and **5** involve the linkage of benzothiazole with benzene and thiophene through an ethylene bridge. Again, the enhanced π -electron conjugation is manifested by the increased values of γ and the decreased band gap. Obviously, these two effects can be expected to appear together, and in consequence, lead to limitations on the feasibility of building highly nonlinear molecules with a reasonable optical transparency range.

A very interesting result is observed for compound 6. Although the less nonlinear heterocyclic unit of benzimidazole is used in 6 instead of benzothiazole, the nonlinearity of this molecule is much higher than that of compound 1 while the transparency ranges of 1 and 6 were approximately the same. The enhancement of γ in 6 was due to the presence of the side group attached to the benzene ring of benzimidazole. An obvious reason for this enhancement is that compound 6 is a two-dimensional π -electron system unlike other systems represented in Table 3. Therefore, the orientationally averaged γ value should contain relatively high additional contributions, apart from γ_{zzzz} - that is, for example, γ_{xxxx} and γ_{xxzz} , if xz is taken as the molecular plane. In addition, the introduction of the pendant N,N-dimethylamino group, a strong electron donor, may also have a beneficial effect on the nonlinearity since its presence will modify the electron distribution in the molecule and possibly lead to a higher anharmonicity of the potential acting on the π -electrons. An added benefit of introducing such pendant groups was also an improvement in solubility of the molecule, which is important for the processing of any nonlinear optical materials built using fused ring heterocyclic structures. As was previously observed in the simple fused ring models of Section 2.2.1, the symmetric curves of the DFWM signals for model compounds 1-6 also indicated no one or two-photon absorbance.

2.2.3. More Complicated Combinations of Heterocyclic Molecules

The nonlinear optical properties of more complicated heteroaromatic molecules are given in Table 4. Because of the larger number of π -electrons which can take part in the conjugation (i.e., an increased conjugation length), the γ values of these molecules are markedly higher than the γ values for smaller π -electron systems considered in Table 3. As was observed in the previous two groups of model compounds, the symmetric DFWM signals for model compounds 7-12 indicated no one or two-photon absorbances, so the γ values are nonresonant values. The trend of hyperpolarizability changes observed for 7-12

Table 4. Maximum UV-VIS Absorption Peaks (λ_{\max}) and Second-Order Hyperpolarizability Values (γ) for Molecules With Three or More Connecting Aromatic Units

Compound	NLO Measurement Method	λ_{\max} (nm) ^a	γ (esu)
 7	film	357.6 (3) 339.5 (1) 325.0 (2)	9.0×10^{-35}
 8	film	367.0 (3) 352.0 (1) 337.0 (2)	1.9×10^{-34}
 9	THF	397.0 (3) 385.8 (1) 368.2 (2)	2.6×10^{-34} $\pm 1.2 \times 10^{-34}$
 10 $C_{10}H_{21}O$ $OC_{10}H_{21}$	THF	412.6 (3) 390.2 (1) 371.0 (2)	3.9×10^{-34} $\pm 2.8 \times 10^{-35}$
 11	THF	339.6	1.1×10^{-33} $\pm 2.4 \times 10^{-34}$
 12 $(CH_3)_2N$ $N(CH_3)_2$	film	325.2 (2) 268.0 (1)	2.2×10^{-33}

^a The number in parentheses refers to the relative intensities of the absorption peaks.

was again intuitively predictable. Compound **8** exhibited a higher hyperpolarizability than **7**. The lowering of the band gap energy of the electronic transitions in **8** also contributed to higher hyperpolarizability. Since **7** and **8** were approximately the same length, the

difference in γ resulted from the difference in electronic properties of their respective parent molecules, benzothiazole and benzoxazole. Qualitatively, the differences in γ between 7 and 8 were attributed to better conjugation in the benzothiazole derivative.

A cautious comparison between 8 and 9 was taken because 8 was investigated in solid film state while 9 was studied in THF solutions. As already discussed such comparisons lead to some differences because of an inadequacy of the assumption of the orientational averaging for γ in the solid state as well as a shift in the position of the electronic resonances. Nevertheless, the difference between 8 and 9 is at least qualitatively in agreement with previous observations of higher γ values in compounds with thiophene moieties adjacent to benzothiazole units. By substituting two thiophene hydrogens with alkoxy groups (compound 10), an improvement in both γ value and solubility in organic solvents was realized.

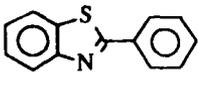
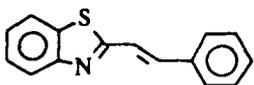
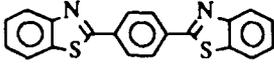
Finally, compounds 11 and 12 were not truly one-dimensional systems and both show greatly increased γ values. This increase of nonlinearity was not accomplished at the expense of reduced transmittance window, that is, a decrease in the band gap. Obviously the qualitative rule for one-dimensional systems, which relates the increase in γ to a decrease in the band gap as conjugation increases by either adding more π -electron units or improving the overlap of existing units, does not hold true for two-dimensional systems. The larger γ value of compound 12 versus 11 is believed to be contributed by the electron donating pendant N,N-dimethylamino groups, whose addition also enhanced the γ value of compound 6. Therefore, the approach of adding pendant groups to introduce two-dimensional π -electron delocalization appears to be highly promising for enhancing the nonresonant third-order optical nonlinearity while improving solubility.

2.2.4. Conclusion

The third-order optical nonlinearities of organic molecules was demonstrated as substantially improved if a judicious procedure of building a molecule from optimized units is performed. Generally, the third-order nonlinear optical properties of such systematically

constructed molecules have been interpreted in a qualitative way just by considering changes in the delocalization of π -electrons as additional units are added to a molecule or as heteroatoms are substituted for carbon atoms. Theoretical calculations on some of the listed compounds have been performed by Goldfarb et al. (Reference 22) using a semi-empirical method involving a modified neglect of differential overlap (MNDO) approximation with the Finite Field (FF) approach. Since this method utilizes a static field, the calculated γ values are molecular static hyperpolarizabilities which represent either the extrapolation to low frequency or a nonresonant case. The calculated γ values (Reference 22) as well as the experimental values from this study are listed in Table 5 and the structural conformation assumed for the theoretical calculation is specified.

Table 5. Experimentally Determined and Theoretically Calculated Second-Order Hyperpolarizabilities (γ) for Some Representative Benzothiazole Model Compounds

Compound	Experimental γ (esu)	Theoretical	
		Conformation	γ (esu)
 1	4.3×10^{-35}	staggered planar	6.2×10^{-35} 2.41×10^{-34}
 4	7.7×10^{-35}	trans-staggered trans-planar	2.19×10^{-34} 6.14×10^{-34}
 8	1.9×10^{-34}	planar	1.227×10^{-33}

Although this approach does not generally produce a quantitatively reliable computation of γ , a qualitative trend for a systematically varied structure is deduced. For example, when the theoretically computed values of Table 5 were compared with the experimental results of this study, the experimentally determined γ values for **1**, **4**, and **8** were smaller than the

theoretically calculated values, and the discrepancy increases with the molecular size. Besides the experimental errors in the measurement of γ value, the limitation of the approximation for the theoretical model may play an even more significant role in causing such a discrepancy in γ . However, both experimentally determined and calculated γ values show the same increasing trend as the molecules become larger.

Several issues should be addressed before attempting to derive any conclusion from such a systematic study. The first important issue is the reliability of the experimental data and the comparisons made between results obtained for various molecules. It was previously stated that meaningful comparisons are only made between orientationally averaged values of the hyperpolarizabilities. Solution measurements are, therefore, superior to solid state measurements. The molecular properties in both physical states, derived from measurements of a macroscopic quantity, $\chi^{(3)}$, were compared. Although the use of the simple Lorentz approximation for the local field factor is widespread, there is actually no sound justification for the use of this approximation. The approximation of an isotropic local field factor may break down in the example of an anisotropic solid, especially in very asymmetric materials such as quasi-one-dimensional oligomers or polymers. Thus, the reliability of any hyperpolarizability data derived from solution measurements would appear to be better.

But in the case of DFWM, a process described formally by a third-order susceptibility $(-\omega; \omega, -\omega, \omega)$ in which all interacting fields have the same frequency is encountered. The third-order nonlinear interaction may be viewed as a change in the susceptibility induced by interaction of two fields and generation of a nonlinear polarization by probing with a third field. In the degenerate case all fields have the same frequency. Therefore, an interaction of two fields leads to a change in the susceptibility which does not oscillate in time. The third field of frequency ω generates a nonlinear polarization at the same frequency. However, the appearance of a time-dependent term in the interaction of two optical fields leads to the inclusion of all low frequency material modes in the nonlinear

process producing the susceptibility change. In practice, the duration of laser pulses is the limitation for the frequencies involved. Nevertheless, even with picosecond or subpicosecond pulses it is expected that molecular motions having the characteristic frequencies of the order of 10^{-12} seconds may give a contribution to the observed nonlinearity.

In the case of liquids, the dominant process apart from the electronic nonlinearity, is the reorientation of anisotropic molecules in the optical field. Such reorientation depends on the anisotropy of the molecular polarizability tensor α_{ij} with its characteristic time constraints in picoseconds or even femtoseconds. In the case of solids the molecular motions are limited to small amplitude vibrations and translations, but their contribution should also be present. These uncertainties concerning the role of γ anisotropy and the contributions of reorientational (nuclear) nonlinear hyperpolarizability make the comparisons between results for various molecules rather difficult.

The second important issue to consider in this study is dispersion of γ . While from the technological point of view the relevant γ value is the susceptibility at the combination of frequencies to be used in an application, a comparison between properties of various molecules is more meaningful if the electronic hyperpolarizability is extrapolated to zero frequency. Otherwise, an enhancement of the hyperpolarizability, for example, by substituting a nitrogen in a heterocycle with a sulfur atom may be interpreted as a dispersion effect, that is, the result of a shift of electronic resonances to lower energies. In our case an attempt to extrapolate our experimental results to zero frequency to obtain "static" hyperpolarizabilities may not be useful because of the uncertainty regarding the contributions of various excited states to the total hyperpolarizability. As already mentioned the presence of both $n\pi^*$ and $\pi\pi^*$ excitations leads to a dispersion relation for γ which must include both types of excited states as well as the transitions between them. Therefore, at the present time we are limited to a comparison between the data taken at a single frequency.

Our qualitative comparisons lead to the following conclusions:

- i). Molecular hyperpolarizabilities in quasi-one-dimensional molecules increase very rapidly with the length of the conjugated π -electron system.
- ii). Inclusion of heteroatoms in the π -electron system may be beneficial for the nonlinearity because of either the role of additional p and/or d orbitals provided by the heteroatoms or the role of steric factors in the π -electron conjugation.
- iii). Sulfur containing fused ring aromatic linkages are more nonlinear than those containing nitrogen and/or oxygen.
- iv). A transition from one-dimensional π -electron conjugation to two-dimensional systems using imidazole N-linkages enhances third-order optical nonlinearity without reducing the band gap and at the same time improves the solubility of the compound.

SECTION 3. EXPERIMENTAL

3.1. Preparation of Model Compounds 1-5, 7-10

All solvents, commercially available, were distilled and stored over molecular sieves (Linde 4A) before use. All other reagents were used without further purification. Thin layer chromatography (TLC) was performed either on precoated plastic silica gel strips with UV-254 indicator (Beckmann Instruments, Inc., Westbury, NY) or on glass precoated KC18 reverse phase plates with UV-254 indicator (Whatman, Ltd.). Melting points were uncorrected. Electron impact mass spectra (E.I.M.S.) were performed on a Finnegan GC/MS/DS system model 4021. Infrared spectra were recorded on a Beckmann IR-33 using KBr films; values were reported in wavenumbers (cm^{-1}). Physical properties, elemental analyses, literature references and infrared spectral data for all model compounds are summarized in Table I.

Procedure A

A mixture of α -aminothiophenol (0.005 mol), the appropriate aromatic carboxylic acid (0.005 mol), PPSE (6.0 g) and α -dichlorobenzene (15 mL) was stirred at room temperature under nitrogen while tri-*n*-butylamine (TBA) (0.01 mol) was added dropwise. After the addition of base was completed the reaction mixture was heated at 85° C under nitrogen for 18 h. The temperature was then raised to 135°C for 18 h and finally to 165°C for 4 h. At the end of the final heating period the reaction mixture was allowed to cool to room temperature and poured into water (200 mL). This mixture was then extracted twice with methylene chloride (100 mL each) and separated. The combined methylene chloride extracts were washed with water (200 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the resulting oily solid was stirred with methanol (50 mL). The resulting solid was then purified by recrystallization from the appropriate solvent (Table 1).

Procedure B

A mixture of the appropriate aromatic dicarboxylic acid (0.005 mol), either α -aminophenol or α -aminothiophenol (0.01 mol), PPSE (12.0 g) and α -dichlorobenzene (30 mL) was stirred at room temperature under nitrogen. To this mixture TBA (0.02 mol) was

added dropwise and the temperature was raised to 85°C for 18 h. The temperature was then raised to 135°C for 18 h and finally to 165°C for 4 h. The reaction mixture was allowed to cool to room temperature and poured into methanol (500 mL). The resulting solid was filtered, air dried, and recrystallized from the appropriate solvent (Table 1).

Procedure C

2,5-Bis(benzothiazole-2-yl)thiophene (9)

A mixture of 2,5-thiophenedicarboxylic acid (1.01 g, 0.006 mol) and *o*-aminothiophenol (1.52 g, 0.012 mol) in polyphosphoric acid (15 g) was stirred and heated under nitrogen at 140°C for 2 h. The temperature of the reaction mixture was then raised to 155°C for 15 h. The dark-red solution was allowed to cool to approximately 60°C and poured into water (150 mL). The resulting mixture was neutralized to pH 8 with ammonium hydroxide. The solid was filtered, washed with water, and air dried to give a crude yellow product (1.85 g, 90%). Three recrystallizations from toluene afforded compound **9** (1.08 g, 47%): mp 241-242°C. This compound had a melting point that differed from the literature value (Reference 18) but gave satisfactory elemental and mass spectral analyses (Table 1).

Procedure D

3,4-Didecyloxy-2,5-diethylthiophene dicarboxylate

A mixture of 2,5-diethyl-3,4-dihydroxythiophene dicarboxylate (Reference 23) (52.1 g, 0.20 mol), 1-bromodecane (93.38 g, 0.42 mol), and potassium carbonate (30.04 g, 0.22 mol) in *N,N*-dimethylformamide (300 ml) was heated at 100° C under nitrogen for 20 h. The reaction mixture was allowed to cool to room temperature and the suspended potassium bromide salts were filtered from the solution over diatomaceous earth. The filtrate was divided into two portions and was poured into water (2500 mL each). The crude product was solidified upon stirring the aqueous solution for 30 min. The solid was

filtered, air dried, and recrystallized from methanol (5000 mL). The product was dried at room temperature under reduced pressure to afford colorless plates (80.65 g, 75%): mp 39-40°C.

Anal. calc'd for $C_{30}H_{52}O_6S$: C, 66.88; H, 9.73; S, 5.95. Found: C, 66.57; H, 9.39; S, 5.96.

FTIR (KBr): $\nu = 2920, 1725, 1550, 1490, 1285, 775 \text{ cm}^{-1}$.

E.I.M.S. [70 eV]: $m/z = 540 (M^+, 1), 204 (100)$.

3,4-Didecyloxy-2,5-thiophenedicarboxylic acid

In a modification of a reported procedure (Reference 24) a suspension of 3,4-didecyloxy-2,5-diethylthiophene dicarboxylate (50.0 g, 0.93 mol) in tetrahydrofuran (THF) (1500 mL) was slowly added to a cold (0-5°C), rapidly stirring slurry of potassium t-butoxide (62.5 g, 0.57 mol) and water (7.5 mL). The solution was allowed to warm to room temperature over a 24 h period. TLC on both a reverse phase plate (80:20 ethanol:water) and a silica gel strip (9:9:1 diethyl ether:hexane:acetic acid) indicated the absence of starting material. The potassium salts were filtered from the solution and washed with THF (250 mL) until TLC indicated the absence of trapped product. The solution was then reduced in volume to approximately 300 mL and poured into water (1500 mL). The crude diacid was precipitated after acidification with 37% hydrochloric acid (125 mL). The product was recrystallized first from toluene (800 mL) and finally from methanol (800 mL) to afford a white powder (44.28 g, 94%): mp 182-183°C.

Anal. calc'd for $C_{26}H_{44}O_6S$: C, 64.44; H, 9.15; S, 6.62. Found: C, 64.36; H, 8.61; S, 6.55.

FTIR (KBr): $\nu = 2920, 1680, 1655, 1298, 1200, 940, 775 \text{ cm}^{-1}$.

E.I.M.S. [70 eV]: $m/z = 484 (M^+, 0.44), 204 (100)$.

3,4-Didecyloxy-2,5-bis(benzothiazole-2-yl)thiophene (10)

To a mixture of 3,4-didecyloxy-2,5-thiophenedicarboxylic acid (2.42 g, 0.005 mol), *o*-aminothiophenol (1.37 g, 0.01 mol) and PPSE (12.0 g) in *o*-dichlorobenzene (30

mL) under nitrogen was dropwise added TBA (7.42 g, 0.04 mol) over a period of 20 min. The reaction mixture was slowly heated up to 85°C and maintained at 85°C for 18 h. The temperature of the reaction mixture was then raised to 135°C over a period of 6 h and maintained at that temperature for an additional 18 h. The reaction mixture was allowed to cool to room temperature and the *o*-dichlorobenzene was removed under reduced pressure. The resulting oily residue was stirred with 10% sodium bicarbonate (100 mL). The resulting solid was filtered, washed with water, and air dried. The crude product was purified by column chromatography on silica gel using 3:1 methylene chloride:hexane as the eluent. The second band was highly fluorescent and upon evaporation yielded a yellow-green solid. Recrystallization from absolute ethanol afforded yellow-green needles (1.77 g, 53%): mp 92-93°C (Table 1).

Anal. calc'd for C₃₈H₅₀N₂O₂S₃: C, 68.83; H, 7.60; N, 4.23. Found: C, 68.93; H, 7.36; N, 4.00.

FTIR (KBr): $\nu = 2925, 2850, 1515, 1320, 1050, 755, 725 \text{ cm}^{-1}$.

E.I.M.S. [70 eV]: $m/z = 662 (M^+, 2), 43 (100)$.

3.2. Preparation of Model Compounds 6, 11, 12

Infrared (IR) spectra were recorded on a Nicolet 5DX spectrometer. Elemental analyses were done at Midwest Microlab, Indianapolis, IN and at the Department of Chemistry, Wright State University. Proton NMR spectra were carried out on a Varian EM 360A NMR and ¹³C NMR spectra were performed on a Bruker AC100 (internal standard, TMS). Mass spectrometric analyses were done on Finnigan MAT (INCOS 50) and Finnigan 4021 mass spectrometers.

Procedure E

N-[4-(N,N-Dimethylamino)phenyl]-2-nitroaniline

To a solution of 1-fluoro-2-nitrobenzene (4 g, 0.028 mol) in THF (25 mL) was added a 5% mol-equivalent excess of N,N-dimethyl-1,4-phenylenediamine (4.045 g, 0.03 mol). The mixture was refluxed for 15 h under a nitrogen atmosphere, cooled, poured into

cold water and stirred for 15 min. The crude product was decolorized and recrystallized from ethanol:water (70:30). A second recrystallization afforded reddish-brown crystals (2.91 g, 40%): mp 123.5-125°C.

Anal. calc'd for $C_{14}H_{15}N_3O_2$: C, 65.37; H, 5.88; N, 16.33. Found: C, 65.87; H, 6.01; N, 16.42.

FTIR (KBr): $\nu = 3373$ (NH), 2895 (CH_3), 1616 and 1504 (aromatic ring), 1566 and 1348 cm^{-1} (NO_2).

1H -NMR ($CDCl_3$): $\delta = 9.3$ (s, 1 H, amine NH), 8.1 (d, 1 H, proton on C_3), 7.4-6.45 (m, 7 H, aromatic CH), 2.9 ppm (s, 6 H, CH_3).

^{13}C -NMR ($CDCl_3$): $\delta = 149.1, 145.04, 135.48, 132.04, 127.05, 126.65, 126.37, 116.14, 115.04, 113.12$ and 40.54 ppm.

MS: $m/z = 257$ (M^+ , 100).

N-[4-(N,N-Dimethylamino)phenyl]-1,2-diaminobenzene

To an oxygen-free ethanol:water mixture (90:10, 60 mL) was added N-[4-(N,N-dimethylamino)phenyl]-2-nitroniline (2.00 g, 0.08 mol) and sodium sulfide nonahydrate (6.78 g). The mixture was refluxed for 10 h under an inert atmosphere. The major part of the alcohol was evaporated under reduced pressure and the residue diluted with oxygen-free water (50 mL). The precipitate was collected and washed with oxygen-free water. The crude product was dissolved in oxygen free ethanol, decolorized, and precipitated with water to yield a white precipitate (1.28 g, 72%): mp 83-88°C.

Anal. calc'd for $C_{14}H_{17}N_3$: C, 73.98; H, 7.54; N, 18.49. Found: C, 74.20; H, 7.46; N, 18.57.

FTIR (KBr): $\nu = 3429$ and 3339 (NH_2), 1606, 1518 and 1440 (aromatic ring), 2895 cm^{-1} (CH_3).

1H -NMR (CF_3COOD): $\delta = 11$ (br s, 3 H, CF_3COOH by exchange with amine protons), 6.9-7.8 (m, 8 H, aromatic CH), 3.5 ppm (s, 6 H, CH_3).

MS: $m/z = 227$ (M^+ , 100).

N-[4-(N,N-Dimethylamino)phenyl]-N'-benzoyl-1,2-diaminobenzene

Into a degassed mixture of N-methylpyrrolidone (25 mL) and triethylamine (0.53 g, 0.005 mol) was dissolved N-[4-(N,N-dimethylamino)phenyl]-1,2-diaminobenzene (1.0 g, 0.004 mol). Benzoyl chloride (0.74 g, 0.005 mol) was added over a period of 15 min at room temperature. This mixture was stirred for 1 h at room temperature under a nitrogen atmosphere. The mixture was then poured into water containing sodium bicarbonate and filtered to yield the crude product (1.28 g, 89%). Recrystallization from acetone and hexane gave pure lemon-yellow crystals: mp 145.5-147°C.

Anal. calc'd for C₂₁H₂₁N₃O: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.49; H, 6.39; N, 12.70.

FTIR (KBr): $\nu = 3296$ (NH), 2895 (aliphatic CH); 1637 (C=O), 1603, 1525 and 1454 cm⁻¹ (aromatic ring).

¹H-NMR (CDCl₃): $\delta = 8.4$ ppm (s, 1 H, amide NH), 8.1-6.7 (m, 14 H, aromatic CH), 5.5 (s, 1 H, amine NH), 2.8 ppm (s, 6 H, CH₃).

¹³C-NMR (CDCl₃): $\delta = 165.78$ (C=O), 146.67, 136.36, 134.79, 131.65, 130.39 (C), 128.59, 127.10, 125.58, 123.03, 122.68, 121.49, 119.97, 114.54 (CH), 41.45 ppm (CH₃).

MS: m/z = 331 (M⁺, 35), 182 (100).

1-[4-(N,N-Dimethylamino)phenyl]-2-phenylbenzimidazole (6)

N-[4-(N,N-Dimethylamino)phenyl]-N'-benzoyl-1,2-diaminobenzene (4.4 g, 0.013 mol) was heated at 160°C for 8 h under a nitrogen atmosphere. The crude product was scraped out of the flask and recrystallized from an ethanol:water mixture to yield white fibrous crystals of product (2.76 g, 66%): mp 158-159°C (Table 1).

Anal. calc'd for C₂₁H₁₉N₃: C, 80.48; H, 6.11; N, 13.41. Found: C, 80.67; H, 6.05; N, 13.38.

FTIR (KBr): $\nu = 2895$ (CH₃), 1608, 1525 and 1474 cm⁻¹ (aromatic CH).

¹H-NMR (CDCl₃): $\delta = 8-6.7$ (m, 13 H, aromatic CH), 2.9 ppm (s, 6 H, CH₃).

^{13}C -NMR (CDCl_3): $\delta = 152.59, 150.23, 142.91, 138.03, 130.42, 129.40, 129.16, 128.02, 125.41, 125.08, 122.95, 122.60, 119.63, 112.64, 110.70, 40.41$ ppm (CH_3).

MS: $m/z = 313$ (M^+ , 100).

Procedure F

2,5-Di(N-phenylbenzimidazole-2-yl)pyridine (11)

Freshly prepared pyridine-2,5-dicarbonyl chloride (Reference 25) (1.36 g, 0.007 mol) was added to a solution of N-phenyl-1,2-phenylenediamine (2.47 g, 0.013 mol) in degassed N-methylpyrrolidone (20 mL). The solution was warmed at 80°C for 15 h. The dark-purple solution was poured onto cracked ice (75 g), filtered, and the crude wet solid recrystallized from ethanol:water to give purple crystals (2.1 g, 68%): mp $231\text{-}236^\circ\text{C}$. The product was dissolved in ethanol (20 mL), decolorized and reprecipitated with water. An additional recrystallization from ethanol:water afforded a pale-yellow microcrystalline solid (1.4 g, 45%): mp $238\text{-}240^\circ\text{C}$ (Table 1).

Anal. calc'd for $\text{C}_{31}\text{H}_{21}\text{N}_5$: C, 80.33; H, 4.57; N, 15.11. Found: C, 80.52; H, 4.69; N, 15.06.

FTIR (KBr): $\nu = 3054$ (aromatic CH), 1595 and 1499 cm^{-1} (aromatic ring).

^1H -NMR (CDCl_3): 7.9-7.2 (broad m, aromatic CH).

MS: $m/z = 462$ (M^+ , 100).

Procedure G

N,N'-Di-(2-[4-(N,N-dimethylamino)anilino])terephthalamide

N-[4-(N,N-Dimethylamino)phenyl]-1,2-diaminobenzene (1.0 g, 0.004 mol) was dissolved in a degassed solution of N-methylpyrrolidone (15 mL) and triethylamine (0.445 g, 0.004 mol). To this solution was added terephthaloyl chloride (0.446 g, 0.002 mol) over a period of 15 min at room temperature. This mixture was allowed to stir for 1 h at room temperature under a nitrogen atmosphere. The mixture was poured into water

containing sodium bicarbonate and filtered to yield the crude product (1.4 g, 54%).

Recrystallization from N,N-dimethylformamide and acetone gave golden-yellow crystals: mp 256-257°C (by raising temperature of the mp apparatus to 250°C before inserting the sample).

Anal. calc'd for $C_{36}H_{36}N_6O_2$: C, 73.95; H, 6.21; N, 14.37. Found: C, 73.65; H, 6.29; N, 14.36.

FTIR (KBr): $\nu = 3374$ and 3259 (NH), 2895 (aliphatic CH), 1645 (C=O), 1603 , 1518 and 1446 cm^{-1} (aromatic ring).

$^1\text{H-NMR}$ (CF_3COOD): $\delta = 11.8$ (s, 4 H, CF_3COOH by exchange with amine protons), $8.15\text{-}7.35$ (m, 20 H, aromatic CH), 3.5 ppm (s, 12 H, CH_3).

MS: $m/z = 584$ (M^+ , 4), 182 (100).

1,4-Di-(1-[4-(N,N-dimethylamino)phenyl]benzimidazole-2-yl)benzene

(12) A solution of N,N'-Di-(2-[4-(N,N-dimethylamino)anilino])terephthalamide (2.0 g, 0.003 mol) in N-methylpyrrolidone (5 mL) was heated under nitrogen at 190°C for 16 h. The mixture was poured into water, filtered and washed with acetone to yield a white solid (1.37 g, 73%): mp: $> 320^\circ\text{C}$ (Table 1).

Anal. calc'd for $C_{36}H_{32}N_6$: C, 78.81; H, 5.88; N, 15.32. Found: C, 79.15; H, 5.80; N, 15.36

FTIR (KBr): $\nu = 2889$ (aliphatic CH), 1606 , 1526 and 1454 cm^{-1} (aromatic ring).

$^1\text{H-NMR}$ (CF_3COOD): $\delta = 8.15\text{-}7.5$ (m, 20 H, aromatic CH), 3.6 ppm (s, 12 H, CH_3).

MS: $m/z = 548$ (M^+ , 66), 44 (100).

3.3. Preparation of Thin Films

For those compounds that were not sufficiently soluble in THF, the DFWM measurements were performed on thin solid films. Two methods of preparation were utilized: vacuum deposition and quenching of the melt. The vacuum deposition was performed at deposition rates between 30 and 50 Angstroms/sec in a vacuum chamber

where the vacuum was kept at 10^{-6} to 10^{-5} Torr. Microscope glass slides were used as substrates. The deposition rate and the final thickness of the film were estimated using a quartz crystal film thickness monitor (FTM4). In some cases the thickness was also calibrated by dissolving the film from a given area in a known volume of a solvent and determining the concentration using UV-VIS absorption spectra of the solution. Alternatively, the thicknesses were measured with a profilometer (Model α -4).

Acceptable optical quality films by vacuum evaporation were obtained only for those compounds with large molecular weights. For low molecular weight substances the films obtained exhibited microcrystalline structure and excessive light scattering which prohibited any optical measurements. In those cases thin films were prepared by fast quenching of the melt under nitrogen on microscopic slides. This procedure often gave films with reasonably good quality areas of a few square millimeters which were then used for measurements. The nonuniformity of the films, unknown orientation of the crystals and a relatively large error in the determination of the film thickness all contribute to a large uncertainty in the results for γ obtained on this type of sample.

SECTION 4. REFERENCES

1. *Nonlinear Optical and Electroactive Polymers* ; P. N. Prasad and D. R. Ulrich, eds.; Plenum Press, New York, 1988.
2. *Nonlinear Optical Properties of Polymers* ; A. J. Heeger, J. Orenstein and D. R. Ulrich, eds.; Materials Research Society Symposium Proceedings, Pittsburgh, 1987; Vol. 109.
3. M. T. Zhao, B. P. Singh and P. N. Prasad, *J. Chem. Phys.* **1988** 89, 5535.
4. M. T. Zhao, M. Samoc, B. P. Singh and P. N. Prasad, *J. Phys. Chem.* **1989** 93, 7916.
5. M. T. Zhao, E. Perrin and P. N. Prasad, unpublished results.
6. S. Ghosal, M. Samoc, P. N. Prasad, and J. J. Tufariello, *J. Phys. Chem.* **1990** 94 (7), 2847.
7. I. Kminek, J. Klimovic and P. N. Prasad, unpublished results.
8. P. Prasad, N. Perrin and M. Samoc, *J. Chem. Phys.* **1989** 91, 2360.
9. J. M. Aizpurua and C. Palomo, *Bull. Chim Soc. Fr.* **1984** 3-4 (2), 142.
10. K. Yamamoto and H. Watanabe, *Bull. Chem. Soc. Jpn.* **1982**, 1225.
11. C. Rai and J. Braunwarth, *J. Org. Chem.* **1961** 26, 3434.
12. A. Ozuka, Y. Uno, H. Horiuchi and H. Suzuki, *Synthesis* **1984** (2), 145.
13. A. Addison, T. Nageswara Rao and C. G. Wahlgren, *J. Heterocyclic Chem.* **1983** 20 (6), 1481.
14. V. Cohen, *J. Heterocyclic Chem.* **1979** 16 (1), 13.
15. G. Kaupp, E. Grundken and D. Matthies, *Chem. Ber.* **1986** 119, 3109.
16. W. Reid and S. Hinsching, *Liebigs Ann. Chem.* **1956** 608, 47.
17. W. Moyer, *J. Polym. Sci. A3* **1965**, 2107.
18. P. Liechti, A. Siegrist, M. Duennenburger, E. Maeder, Ger. Pat. 1,282,021 (Cl. CO6d, D 061), 7 Nov. 1968.

19. Y. R. Shen, *The Principle of Nonlinear Optics*; Wiley Interscience: New York, 1984.
20. *Optical Phase Conjugation*; R. A. Fisher, ed.; Academic Press: New York, 1983.
21. H. J. Eichler, P. Gunter, and D. W. Pohl, *Laser-Induced Dynamic Gratings*; Springer-Verlag: Berlin, 1986.
22. I. J. Goldfarb and J. Medrano in *Nonlinear Optical Effects in Organic Polymers*, J. Messier, F. Kajzar, P. Prasad and D. R. Ulrich, eds.; Kluwer Academic Publishers: Dordrecht, 1989; p. 93.
23. V. N. Gogte, L. G. Shah, L. B. D. Tilak, K. N. Gadekar and M. B. Sahasrabudhe, *Tetrahedron* **1967** *23*, 2437.
24. P. G. Gassman and W. N. Schenk, *J. Org. Chem.* **1977** *42* (5), 918.
25. S. D. Lazarus and I. C. Twilley, Fr. Patent 1,462,569 (Cl. C 08g), 16 Dec. 1966; CA *67*: P64886j.