Design and synthesis of new nonlinear optical chromophores incorporating diphenylphosphino groups and their incorporation into electroactive dendrimers
by Luis Gustavo Madrigal

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
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Abstract:
The replacement of first row elements by second row elements (e.g. S for O) in electron donating groups in conjugated organic materials has been shown to produce an enhancement of the nonlinear response. Amino functionalities have been utilized as strong donors in the design of molecules for both second and third order NLO applications. In the present work N (Nitrogen) has been replaced by P (Phosphorus) in various chromophore functionalities. A series of bis-(diphenylphosphino) diphenyl polyenes with up to five double bonds, a bis-(diphenylphosphino)-PPV dimer, and a diphenylphosphino DANS equivalent have been synthesized. In addition, the first generations (G0) of two types of dendrimers were made by a divergent approach. The first type is a series of three arm dendrimers with stilbene type units. The second type is a series of three arm dendrimers with PPV type units.

These new molecules were compared to the N equivalents in several characteristics such as absorption, organic light emitting diodes (OLED), nonlinear optical properties, two-photon absorption, and reverse saturable absorption.

It was found out that diphenylphosphino substituents behave as weak electron-withdrawing groups despite the lone pair of electrons. Compared to N, the lone pair of electrons of P participates weakly in the conjugation of 71-systems, which results in a blue shift in λ

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of a dissertation submitted by

Luis Madrigal

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies,

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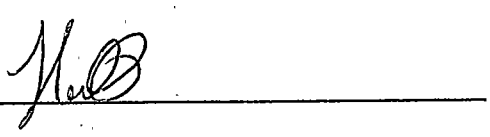
Signature 

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TABLE OF CONTENTS

Page

LIST OF TABLES....vii

LIST OF FIGURES....ix

LIST OF SCHEMES....xii

LIST OF ABBREVIATIONS....xv

ABSTRACT....xvi

1. INTRODUCTION....1

2. HISTORICAL SECTION....4

STRUCTURE-PROPERTY RELATIONSHIP FOR THIRD-ORDER NON-LINEAR OPTICAL ACTIVITY....4
Donor-Acceptor Strengths....5
Styrene Derivatives: The Efficacy of Vinyl Extension....8
The Length of Various π Systems....9
Planarity....12
Extreme Bond Alternation....13
Heteropentacyclic Derivatives: Minimization of Aromaticity....15

SYNTHESIS OF SUBSTITUTED DIPHENYLPOLYENES....18

SYNTHETIC IINCORPORATION OF DIPHENYLAMINO AND DIPHENYLPHOSPHINO GROUPS....32
Diphenylamino Groups....33
Dendrimers Containing Diphenyl Amino Units....37
Diphenylphosphino Substitutions....39
Dendrimers Containing Diphenylphosphino Groups....44

AROMATIC AMINES AS HOLE-TRANSPORT MATERIALS IN ORGANIC LIGHT-EMMITING DIODES....45

ORGANIC MATERIALS FOR REVERSE SATURABLE AND TWO-PHOTON ABSORPTION OPTICAL LIMITING....54
Reverse Saturable Absorption....55
Two-photon Absorption....59

3. RATIONALE FOR PROPOSED RESEARCH....64

NLO ENHANCEMENT BY SECOND ROW ELEMENTS....64
Synthesis of Diphenylphosphinopolyenes....65
Synthesis of Bis-(Diphenylphosphino)-PPV Dimer (176)
4-Diphenylphosphino-4'-Nitrostilbene (177)....66
Dendrimer Design and Synthesis....67

4. RESULTS AND DISCUSSION....70

SYNTHSIS OF p-(DIPHENYLPHOSPHINO-BORANE) BENZALDEHYDE 180....70
Synthesis of Diphenylphosphinoborane Witig Salt....71
Synthesis of Diphenylphosphinopolyenes....72
Synthesis of Dendrimer Cores....78
Synthesis of G0 Dendrimers with Stilbene Arms....80
Synthesis of Witig Salts to make G0 Dendrimers with PPV Dimer Arms....83
Syntehsis of Stilbene Type G0 Dendriemrs....85

UV-VIS SPECTRA OF DIPHENYLPHOSPHINOPOLYENES AND DENDRIMERS....87

STUDY OF CHROMOPHORES AND DENDRIMERS FOR ORGANCI LIGHT-EMITTING DIODES (OLEDs)....112

NON-LINEAR OPTICAL PROPERTIES OF DIPHENYLPHOSPHINO-POLYENES AND DENDRIMERS....115

OPTICAL LIMITING STUDIES AND PHOTO-INDUCED ABSORPTION STUDIES OF DENDRIMERS....118
Two-Photon Absorption Experiments....118
Photo-Induced Absoption (PIA) Experiments....123

5. CONCLUSIONS....132

6. EXPERIMENTAL SECTION....134

GENERAL....134
Synthetic Procedures....135

REFERENCES....169

LIST OF TABLES

Table Page

1. NLO results on monosubstituted benzenes and stilbenes (units in esu).....5
2. NLO results on para-disubstituted benzenes (units in esu).....7
3. NLO results on 4,4'-disubstituted stilbenes (units in esu).....7
4. NLO results on 4- and β -substituted styrenes (units in esu).....8
5. NLO results on 4-donor, β -acceptor-substituted α-phenylpolyene oligomers(units in esu).....9
6. NLO results on disubstituted α,ω-diphenylpolyene oligomers (units in esu).....10
7. Second hyperpolarizabilities for disubstituted diphenyl polyenes.....10
8. NLO results on 4-4'-disubstituted biphenyls and fluorenes (units in esu) 12
9. NLO results on α,ω-dinitropolyphenyl oligomers (units in esu) 13
10. NLO results on 4-4'-substituted diphenylacetylenes (units in esu).....13
11. NLO results on 4-4'-disubstituted α,ω-diphenylpolyyne oligomers (units in esu).....14
12. NLO comparison of effect of aromatic vs. heteroaromatic structure on μβ and γ.....16
13. Thermal data for amino groups with methyl and phenyl susbtituents.....33
14. λ_{max} of bis-substituted-diphenylpolyenes.....87
15. λ_{max} of unsymmetrical compounds.....88
16. λ_{max} of molecular equivalents of PPV.....88
17. λ_{max} for G0 dendrimers with stilbene arms.....88
18. λ_{max} for G0 dendrimers with PPV arms.....89
19. IR C=O stretch of aromatic aldehydes.....94
20. λ_{max} for stilbene derivatives..... 95
21. Thermal properties of chromophores used for OLED studies.....112

22. γ values for diphenylphosphino and diphenylamino polyenes determined at 1907 and 1312 nm.....116

23. Incident energy point where TPA is observed.....118

LIST OF FIGURES

Figure Page

1. Design and materials used in the construction of first OLED 45

2. Starburst molecules for use as the HTL in OLEDs 48

3. TDAB and methyl derivatives m-MTDAB and p-MTDAD for HTLs in OLEDs...49

4. Starburst p-DPA-TDBA for use as HTL in OLEDs.....50

5. Molecules with an ET unit (Oxadiazole group) and an HT unit (Triphenylamine group).....50

6. Effect on Tg by asymmetric substitutions 51

7. Molecules for HTL materials with the two nitrogen atoms identically substituted 52

8. Tgs for asymmetric substituted biphenyl derivates 53

9. Optical limiter based on nonlinear optical (NLO) materials 54

10. Energy level diagram for RSA 55

11. Diphenyl polyenes **161** and dithienyl polyenes **162** that form stable bipolaron-like dications upon oxidation with $SbCl_5$ 56

12. Formation of polaron radical-cation and bipolaron-dication of 1,8-bis(2'-thienyl)octa-1,3,5,7-tetraene (**341**).....56

13. Doping of 1,10-Bis(2'-thienyl)-1,3,5,7,9-decapentaene with $SbCl_5$ 57

14. Material used for a typical RSA optical limiter.....58

15. Optical limiting for **167**, C_{60}, and a C_{60}/**167** combination 59

16. Energy level diagram for TPA 60

17. Enhanced two-photon cross section in two molecular systems (Reinhart et al).....61

18. Two-photon cross sections for Chromophores with a D-A-D (**172**) pattern and a A-D-A pattern (**173**) (Mader and Perry et al.).....62

19. PPV derivatives with enhanced two-photon cross sections (Spangler et al.)..... 62

20. Model dendrimer for TPA applications 63

21. Change in γ by substitution of a sulfur atom by oxygen.....64

22. Diphenylphosphino equivalents of both PPV and DANS.....67

23. G0 dendrimers derived from stilbene units with P and N substitutions 68

24. G0 dendrimers derived from PPV units with N and P substitutions.....69

25. Resonance structures of p-diphenylphosphinobenzaldehyde.....93

26. Absorption spectra for neutral 4,4'-bis-(diphenylphosphino)-stilbene (**190**).....97

27. Absorption spectra for neutral 4',4"-bis-(diphenylphosphino)-1,4-diphenyl-1,3-butadiene (**191**).....98

28. Absorption spectra for neutral 4'-4"-bis-(diphenylphosphino)-(1,6-diphenyl)-1,3,5-hexatriene (**192**).....99

29. Absorption spectra for neutral 4'-4"-bis-(diphenyl phosphino)-1,8-diphenyl)-1,3,5,7-octatriene (**193**).....100

30. Absorption spectra for neutral 4'-4"-bis(diphenylphosphino)-1,10-diphenyl -1,3,5,7,9-decapenteane (**194**) 101

31. Absorption spectra for neutral 1,4-bis-[6'-diphenylphosphino] distyryl benzene (**176**) 102

32. Absorption spectra for neutral 4-diphenylphosphino-4-nitro stilbene (**177**) 103

33. Absorption spectra for neutral and doped 4-diphenylphosphino -4'-diphenylamino stilbene (**198**) 104

34. Absorption spectra for neutral tris-(4'-diphenylphosphino-4-stilbenyl) phosphine G0 dendrimer (**201**) 105

35. Absorption spectra for neutral and doped tris-(4'diphenylamino-4-stilbenyl) phosphine G0 dendrimer (**203**) 106

36. Absorption spectra for neutral and doped tris-(4'-diphenyl phosphino-4-stilbenyl) amine G0 dendrimer (378) 107

37. Absorption spectra for neutral and doped [4'-(4"-diphenylphosphino-β-styryl]amine G0 dendrimer (**216**) 108

38. Absorption spectra for neutral and doped [4'-(4"-diphenylamino-β-styryl) -4-stilbenyl] phosphine G0 dendrimer (217).....109

39. EPR spectrum of 4-diphenylphosphino-4'-diphenylamino stilbene (**198**).....110

40. Solvatochromic behavior of 4'4"-bis-diphenylphosphino)-1,6-diphenyl-1,3,5 hexatriene.....111

41. Solvatochromic behavior of 4',4"-bis-(diphenylamino)-1,6-diphenyl-1,3,5-hexatriene.....111

42. Structures of bis(diphenylphosphino)- and bis(diphenylamino)-E-stilbene oligomers and model dendrimers based on these repeat units.....112

43. PL emission spectra of oligomers **99** and **198** in a) $CHCl_3$ and b) vapor-deposited films.....114

44. PL emission spectra of dendrimers **114** and **204** in a) $CHCl_3$ and b) vapor-deposited films.....114

45. a) Current density/voltage plots, and b) optical power/current density plots for OLEDS made of dendrimers **114** and **204** as HTL materials.....115

46. Structure of dendrimers used for TPA studies.....118

47. Transmission %/incident energy plots for two photon absorbers at 722 nm.....120

48. Transmission %/incident energy plots for two photon absorbers at 760 nm.....121

49. Transmission %/incident energy plots for two photon absorbers at 830 nm.....122

50. G0 stilbene dendrimers used for optical limiting experiments.....124

51. G0 PPV dendrimers used for optical limiting experiments.....125

52. Photoinduced absorption of G0 dendrimer **203**.....126

53. Photoinduced absorption of G0 dendrimer **204**.....127

54. Photoinduced absorption of G0 dendrimer **114**.....128

55. Photoinduced absorption of G0 dendrimer **217**.....130

56. Photoinduced absorption of G0 dendrimer **218**.....131

LIST OF SCHEMES

Scheme Page

1. Synthesis of diphenylpolyenes by Perkin condensation....18
2. Synthesis of 4',4"-bis(p-methoxy)diphenylbutadiene **(11)** by a double Stobbe condensation....19
3. Synthesis of diarylbutadiene by Wittig condensation (Method A)....20
4. Synthesis of Diarylbutadiene by Wittig condensation (Method B)....20
5. Synthesis of 1,4-Bis(4'-arylbutadienyl)benzenes....21
6. The HEW method for polyenes synthesis....22
7. HEW synthesis of 1,10-Diphenyl-1,3,5,7,9-decapentaene **(26)**....22
8. Synthesis of Diphenyl-octatetraene **(35)** by the Wittig method....23
9. Bis-Wittig salts for the synthesis of diphenylhexatrienes....24
10. Bis-Wittig salt of $(nBu)_3P$ used in the synthesis of 1,4-di-nitro-diphenyl-hexatrienes....24
11. 1,10-diphenyldecapentaene synthesis by reaction of cyclooctatetraene with aldehydes....25
12. Synthesis of diphenyl polyenes by the catalysed reaction of Nickel(1,5-cyclooctaene) with aldehydes and 1,3 diolefins....25
13. Synthesis of diphenylhexatriene **(37)** by transfer catalysis....26
14. Synthesis of 1,8-diphenyl-1,3,5,7-octatetraene **(54)** by the catalytic action of $FeCl_2$ in the Meerwein reaction....27
15. Palladium catalized arylation for the synthesis of 4',4"-dinitro-1,4-diphenyl-1,3-butadiene **(59)**....27
16. Synthesis of an asymmetric diaryltriene....28
17. Aldehyde extension reactions....29
18. Aldehyde extension with 1-cyanoethanephosphanate....30

19. Synthesis of Bis-Wittig salts **39** and **77**.....31

20. General Procedure for Diphenylpolyene synthesis.....31

21. Synthesis of 4-diphenylamino-4'-nitrostilbene (**92**).....34

22. Vilsmeier-Haack formylation of triphenylamine (**94**).....34

23. Synthesis of intermediates **96**, **97**, and **98**.....35

24. Synthesis of the polyenes **99** and **100** 36

25. Bis-(diphenylamino) diphenylpolyene synthesis with 3 to 8 double bonds..... .36

26. Synthesis of 1,4-bis-(4'-diphenylamino-β-styryl)benzene.. 37

27. Divergent synthesis of a the first generation 3-arm dendrimer **114**.....38

28. Synthesis of core molecule **116** 39

29. Synthesis of compound **119** 40

30. Synthesis of (p-vinylphenyl)diphenylphosphine 40

31. Synthesis of bis-(diphenylphosphino) stilbene **122** 41

32. Synthesis of compound **126** ..... .41

33. Synthesis pf p-diphenylphosphino-benzaldehyde **130** 42

34. Synthesis of aldehyde **130**.....43

35. Synthesis of phosphinoboranes 43

36. Synthesis of a dendrimer surface functionalized with diphenylphosphino 44

37. Synthesis of bis-(diphenylphosphino)diphenylpolyenes 66

38. Synthesis of p-(diphenylphosphino-borane) benzaldehyde.....70

39. Synthesis of Wittig salt 183.....71

40. Synthesis of 4,4'-bis-(diphenylphosphinoborane)-E-stilbene. Method A.....72

41. Synthesis of 4,4'-bis-(diphenylphosphinoborane)-E-stilbene. Method B.....72

42. Synthesis of 4"-(diphenylphosphinoborane) cinnamaldehyde.....73

43. Synthesis of 4',4"-bis-(diphenylphosphinoborane)-1,4-diphenyl-1,3-butadiene.....73

44. Synthesis of diphenylphosphinopolyenes with three and four double bonds.....74

45. Synthesis of 4'-4"-bis-(diphenylphosphinoborane)-1,10-diphenyl-1,3,5,7-decapentaene.....74

46. Diphenylphosphinopolyene deprotection.....75

47. Synthesis of 1,4-bis-[4'-diphenylphosphino-β-distyryl] benzene.....76

48. Synthesis of 4-diphenylphosphino-4'-nitro stilbene.....77

49. Synthesis of 4-diphenylphosphinoborane-4'-diphenylamino stilbene.....77

50. Synthesis of 4,4',4"-tri formyl triphenyl phosphino.....78

51. Synthesis of 4,4',4"-tri-formyl triphenyl amine.....79

52. Synthesis of tris-(4'-diphenylphosphino-4-stilbenyl) triphenylphosphino G-0 dendrimer.....80

53. Synthesis of tris-(4'-diphenylphosphino-4-stilbenyl) triphenylamino G-0 Dendrimer.....81

54. Synthesis of tris-(4'-diphenylamino-4-stilbenyl) triphenylphosphino G0 dendrimer.....82

55. Synthesis of 4-diphenylphosphinoborane-4'-stilbenylmethyl tributyl phosphonium bromide.....83

56. Synthesis of 4'-diphenylamino-4-stilbenylmethyl tributylphosphonium Bromide.....84

57. Synthesis of tris-[4'-(4"-diphenylphosphino-β-styryl)-4-stilbenyl] triphenylamino G0 dendrimer.....85

58. Synthesis of tris-[4'-(4"-diphenylamino-β-styryl)-4-stilbenyl] triphenylphosphino G0 dendrimer.....86

LIST OF ABBREVIATIONS

NLO : nonlinear optical optical

DANS: p-diphenylamino-p'-nitrostilbene

G0: generation zero of a dendrimer.

PPV: p-phenylene vinylene

OLED: organic light emmiting diode.

EFISH: electric field induced second harmonic generation

THG: third harmonic generation

E-O: electro optics

Tg: glass transition temperature

ITO: indium tin oxide

HTL: hole transport layer

ETL: electron transport layer

EL: electroluminescence

RSA: reverse saturable absorption

TPA: two-photon absorption

ISC: intersystem crossing

TS: possible transient state

EWG: electron withdrawing group

EDG: electron donating group

PIA: photo induced absorption

ABSTRACT

The replacement of first row elements by second row elements (e.g. S for O) in electron donating groups in conjugated organic materials has been shown to produce an enhancement of the nonlinear response. Amino functionalities have been utilized as strong donors in the design of molecules for both second and third order NLO applications. In the present work N (Nitrogen) has been replaced by P (Phosphorus) in various chromophore functionalities. A series of bis-(diphenylphosphino) diphenyl polyenes with up to five double bonds, a bis-(diphenylphosphino)-PPV dimer, and a diphenylphosphino DANS equivalent have been synthesized. In addition, the first generations (G0) of two types of dendrimers were made by a divergent approach. The first type is a series of three arm dendrimers with stilbene type units. The second type is a series of three arm dendrimers with PPV type units.

These new molecules were compared to the N equivalents in several characteristics such as absorption, organic light emitting diodes (OLED), nonlinear optical properties, two-photon absorption, and reverse saturable absorption.

It was found out that diphenylphosphino substituents behave as weak electron-withdrawing groups despite the lone pair of electrons. Compared to N, the lone pair of electrons of P participates weakly in the conjugation of π-systems, which results in a blue shift in λ_{max}.

INTRODUCTION

The synthesis of polyacetylene (**1**) by Shirakawa[1] in the 1970s permitted the study of the chemistry, physics and applications of conducting polymers. This has resulted in an increasing interest in electroactive materials that has given us a better understanding of the formation and stabilization of the charge states and the nature of the insulator-metallic transition upon chemical or electrochemical doping. It is currently accepted that polymers like polyacetylene are dominated by polaronic (radical-cations or radical-anions) or solitonic species, while polymers such as polythiophene (**2**) and poly[p-phenylenevinylene] (**3**) are dominated by bipolaronic species (di-ions) in the conducting state. The insulator-conductor transitions due to an oxidative doping have been linked to the appearance of new midgap states, which seem to be characteristic of π-conjugated polymers in general. It has been demonstrated that electroactive polymers also have unique optical properties.[2] For this reason, the nature of charge-state formation and stabilization in extended π-systems and the relationship of the electron delocalization and polarization to electronic and/or photonic properties is an ongoing area of study.

Several research groups have shown that electroactive polymers and oligomers possess enhanced nonlinear optical properties. The NLO properties rise from an interaction of an electric field E of light with matter that can be described on the molecular level by equation 1,

$$P = \alpha E + \beta E E + \gamma E E E + \ldots \quad \text{eq. (1)}$$

where P is the induced polarizability by the electric field, α is the linear polarizability, and β and γ are the first and second order hyperpolarizability respectively.[3] The nonlinear response is generally very weak and it is only possible to observe in some NLO materials when strong electromagnetic fields are used, as the one obtained with a coherent laser beam causing a polarization response in the π-electron cloud of conjugated organic molecules. This polarization response is intensity-dependent and thus non-linear. In a practical sense, this interaction produces a temporary change in the material optical properties, such as index of absorption or refraction, which are present as long as the electric field is present.

In bulk materials, like polymer films, the non-linear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$ are third and fourth order tensors respectively, that relate all components of the polarization vector (P) to all components of the electric field vector (E) as described by equation 2:

$$P(E) = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \ldots \quad \text{Eq. (2)}$$

Nonlinear optical properties can be assessed by a variety of techniques, which probe the NLO response of a system. Two common ways of doing this is by Third Harmonic Generation (THG) and Electric Field Induced Second Harmonic generation (EFISH) measurements. THG[3] is a process that describes production of the third harmonic of the incident laser frequency and is related to the magnitude of the third order hyperpolarizability. EFISH[3] is a technique where a strong dc electric field is applied to a sample, causing the molecules to orient the dipole moment with the interacting applied field. EFISH has contributions form both $\chi^{(2)}$ and $\chi^{(3)}$; however, for centrosymmetric structures or structures with zero second-order nonlinearity, the EFISH generation are derived form the third order nonlinearity.

Results of studies on γ, the third order hyperpolarizability, show that it increases with increasing conjugation length.[4] However, this conjugation can be limited to an effective conjugation length that is less than the formula conjugation length due to steric or conformational effects that may cause twisting out of planarity and a loss of orbital overlap.[5] It has been postulated that γ enhancement may be possible by the incorporation of polaronic and bipolaronic charge states in conjugated π-systems. This prediction has been supported by more refined calculations, and such enhancement has been experimentally verified for both small molecules in solution and polymers.[6,7] The solubility of dibutyl-substituted dithienylpolyenes series has allowed the determination for the first time of length-dependence on bipolaronic species studies. Nonlinear optical studies of the oxidative doping of these series have confirmed the prediction of γ enhancement by bipolaron formation. These materials are among the most nonlinear small molecules yet studied (γ values approaching 10^{-30} esu). Since the polarizability of a π–conjugated system is related to the extent of π–electron delocalization in the system, the possibility of coupling bipolaronic enhancement of $\chi^{(3)}$ with three-dimensional charge delocalization in dendritic macromolecules promises to be a seminal approach to the design of new NLO materials, and may allow third-order NLO macromolecules to compete for the first time with electric-field poled second-order polymers in a variety of applications. These materials can then be used in a variety of photonic applications such as eye protection via reverse saturable absorption or two photon absorption, in optical wave-guiding, third harmonic generation for nonlinear optical (NLO) applications, for electrochromic thin films for high contrast electrochromic applications, and finally in organic light-emitting diodes (OLEDs).

HISTORICAL SECTION

Structure-Property Relationship for Third-Order Non-linear Optical Activity

Over the past 10 years there have been tremendous efforts to synthesize organic molecules with high third-order optical non-linearity[8,10]. These synthetic efforts have been focused in finding the right structure-property relationships that correspond to molecules with an enhanced NLO response. From these studies it has been found that the second hyperpolarizability is proportional to the extent of electron delocalization in molecules containing π-electron systems[11]. In an attempt to model and predict the consequences of increasing conjugation, several researchers have made use of a power relation of the form[12,13],

$$\gamma \alpha N^a$$

where N is the number of repeat units, like double bonds, carbon atoms, or length of the molecule. Beratan et al.[13], using a Huckel approach, have shown that γ increases rapidly for polyenes as conjugation increases to 10-15 repeat units, and then more slowly up to 40 repeat units. Based on ab initio calculations for a series of polyenes up to $C_{22}H_{24}$, Hurst and coworkers[14] found that γ was proportional to chain length with power dependence of 4.0; however, this dependence levels off as N increases. Garito and coworkers[15] calculated a power law dependence of γ on chain length in the order of 4.6 ± 0.2. They suggest that only conjugation sequences of intermediate length (100 Å) are needed in order to obtain large values of $\chi^{(3)}$. Also, Prasad[16] has measured γ for a series of polythiophene oligomers by degenerate fourwave mixing (DFWM) in solution and found a power law dependence for γ of 4. He also concluded that γ levels off with increasing N. In addition, from $\chi^{(3)}$ measurements on poly (3-dodecylthiophene) he

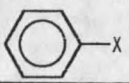
found that the effective conjugation, for NLO purposes, did not extend much beyond 10 repeat units, and that similar measurements for poly (p-phenylene) showed a leveling off of $\chi^{(3)}$ at the terphenyl level (N=3). All this suggests that it may not be necessary to synthesize a chain with very long number of repeat units in order to produce high third-order nonlinearity[17].

Cheng et al.[18], in an attempt to understand what structural parameters most affect γ, made extensive measurements on benzene, styrene, and stilbene derivatives. Tables 1, 2, and 3 show the results from that study.[18] These studies were focused on experimental measurements on molecules where the following parameters were systematically changed to correlate their influence on the nonlinear properties.

Donor-Acceptor Strengths

Table 1 shows the result of the studies on molecular hyperpolarizability on

Table 1: NLO results on monosubstituted benzenes and stilbenes (units in esu)



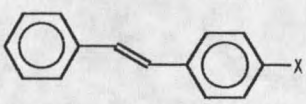
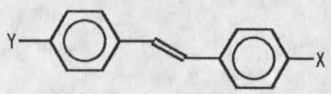
X	$\gamma^{EFISH} \times 10^{-36}$	$\gamma^{THG} \times 10^{-36}$	$\gamma^{EFISH}/\gamma^{THG}$	$\alpha \times 10^{-23}$	$\beta \times 10^{-30}$
OMe	3.8	4.8	0.79	1.4	<0.2
SMe	5.9	7.2	0.82	1.7	1.1
NH_2	7.8	8.1	1.70	2.4	1.3
NMe_2	14.1	8.1	1.70	1.7	1.1
Julodiamine	16.7	7.8	2.14	2.4	1.3
SO_2F	6.7	4	1.7	1.5	0.3
CN	10.3	4.3	2.4	1.3	0.36
COH	14.8	5.3	2.8	1.3	0.80
$COCF_3$	25.0	5.3	4.7	1.7	1.3
NO	30.0	6.8	4.4	1.4	1.7
NO_2	40.8	5.7	7.2	1.4	1.9
$C_2H(CN)_2$	82.3	12	6.9	2.0	3.1
					
NH_2	104	31	3.4	2.8	7.4
NMe_2	167	64	2.6	3.3	10
NO_2	276	61	4.5	2.9	11

Table 2: NLO results on para-disubstituted benzene (units in esu)

Y	X	$\alpha \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
OMe	CN	1.7	1.9	4
SMe	CN	2.0	2.8	9
NH_2	CN	1.6	3.1	6
NMe_2	CN	2.1	5.0	10
OMe	CHO	1.7	2.2	8
SMe	CHO	1.9	2.6	13
NH_2	CHO	1.6	3.1	6
NMe_2	CHO	2.0	6.3	18
Me	CHO	1.6	1.7	7
OPh	CHO	2.6	1.2	9
OMe	NO_2	1.5	5.1	10
SMe	NO_2	1.9	6.1	17
NH_2	NO_2	1.7	9.2	15
NMe_2	NO_2	2.2	12	28
CN	NO_2	1.7	0.6	7
CHO	NO_2	1.7	0.2	7
NH_2	CHO	1.6	3.1	6
NMe_2	CHO	2.0	6.3	18
Julolidine	$CHC(CN)_2$	3.0	44	

Table 3: NLO results on para-disubstituted benzene (units in esu)



Y	X	$\alpha \times 10^{-23}$	$\beta \times 10^{-30}$	$\gamma \times 10^{-36}$
HOHexO	SO_2C5H_{11}	6.0	10	68
OMe	SO_2C6F_{13}	4.8	14	93
OMe	$COCF_3$	3.9	16.4	83
OH	CN	3.2	13	52
OMe	CN	3.4	19	54
N(Me)2	CN	3.9	36	125
H	NO_2	2.9	11	61
Me	NO_2	3.5	15	77
Br	NO_2	3.8	14	98
OH	NO_2	3.3	17	104
OPh	NO_2	4.2	18	80
OMe	NO_2	3.4	28	79
SMe	NO_2	3.9	26	113
NH2	NO_2	3.2	40	147
N(Me)2	NO_2	3.4	73	225
Julolidine	NO_2	4.5	96	
COOMe	NO_2	3.8	4.0	46

monosubstituted benzene and stilbene derivatives.[18] In the case of benzene, the most striking observation is that, except in N,N-dimethylaniline and julolidine, all donors groups are found to be ineffective in inducing charge and polarization asymmetry. This is seen in the small values for β and γ. Examination of the second order nonlinear property (γ^{EFISH} and γ^{THG} values) in Table 1 show that for monosubstituted benzenes, both values change in parallel, indicating a limited dipole contribution to EFISH signal. This is partly due to the small dipole moments. The situation is the same for halogen derivatives. The ineffectiveness of donors in inducing asymmetry may be attributed to two factors. Apart from the dimethylamino group and the bridged structure in julolidine, the connecting atom in all the donors, including the amino, is sp^3 hybridized. Due to the tetrahedral geometry, there is not an efficient overlap between the lone pair containing donor and the π orbitals of the benzene ring. Besides, these donor substitutions only result in minimal extension of the overall conjugation[19]. On the other hand, electron withdrawing groups are found to be more effective. Their efficiencies increase in the order of SO_2CH_3, SO_2F, CN, CHO, $COCF_3$, NO, NO_2, and $CHC(CN)_2$. The reason for the effectiveness of the accepting groups may be the proper hybridizations and longer extensions of the benzene conjugation.

It is also interesting to investigate the cooperative effects of donor and acceptor groups by studying para-disubstituted benzene and 4,4'-disubstituted stilbene. Tables 2 and 3 show the results on these systems performed by Cheng et al[18]. In all cases there is a significant increase of β and γ compared to the monosubstituted fragments. This is the well-recognized enhancement resulting form the charge transfer (CT) interactions between donor and acceptor groups[20]. Charge transfer interactions between susbtituents can be seen as resonance structures that connect charge-neutral and charge-separated states with alternating single and double bonds.