

AD-A281 350



REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 6/14/94	3. REPORT TYPE AND DATES COVERED Annual Report 5/1/93-4/30/94		
4. TITLE AND SUBTITLE Systematic Optimization of Second Order Nonlinear Optical Materials		5. FUNDING NUMBERS F49620-93-1-0314 63218C 1601/06		
6. AUTHOR(S) Seth Marder		8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR- 94 0410		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) California Institute of Technology 1201 East California Blvd., Mail Stop 213-6 Pasadena, CA 91125				
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr Charles Y-C Lee Ms. Patricia Bell AFOSR/PKA - Bolling Air Force Base 110 Duncan Avenue, Suite B115 Washington, DC 20332-0001		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release Distribution in unclassified		DTIC ELECTE JUL 11 1994 12b. DISTRIBUTION CODE S F D		
13. ABSTRACT (Maximum 200 words) We have developed a new compounds with a thiophene bridge and an acceptors that gain aromaticity, such as 3-phenyl-5-isoxazolone, diphenylthiobarbituric acid. These compounds have a large second-order nonlinearity roughly tens time that of the common dye Disperse-Red 1) and good thermal stability and are therefore a promising candidates for electro-optic poled polymer applications.				
DTIC QUALITY INSPECTED 2				
14. SUBJECT TERMS		15. NUMBER OF PAGES 22		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT	

1. ANNUAL TECHNICAL REPORT

Approved for public release;
distribution unlimited.

a) A comprehensive list of objectives of the research effort.

The objectives of this work are to 1) develop a fundamental understanding of the chemistry that will lead to thermally, electrochemically and photochemically stable second-order nonlinear optical materials and 2) to develop advanced electrooptic and photonic materials for enhanced performance of optoelectronic interconnects and optical computing systems.

Accession For		
NTIS	CRA&I	<input checked="" type="checkbox"/>
DTIC	TAB	<input type="checkbox"/>
Unannounced		<input type="checkbox"/>
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and/or Special	
A-1		

94-20942



23PA

94 7 8 051

b) Status of the research effort: Enhanced Second-Order Optical Nonlinearities in Extended Thiophene Containing Compounds

Part I Dicyanovinyl and phenylisoxazolone compounds

1.1. INTRODUCTION

In an attempt to understand and optimize second-order optical nonlinearities of organic molecules, our group has correlated the first hyperpolarizability (β) with a molecular parameter, bond length alternation (BLA), defined as the difference in length between adjacent carbon-carbon bonds in a conjugated chain.¹⁻³ Theoretical calculations⁴ predict that β is maximized when $|\text{BLA}|$ is ~ 0.04 Å. We believe, however, that it will be difficult to obtain this value of $|\text{BLA}|$ needed to maximize β with conventional chromophores that have strongly aromatic ground-state structures, e.g. those containing stilbene bridges. Thus, for molecules containing multiple phenyl groups, the aromatic stabilization in the neutral canonical resonance form will hinder charge-separation and consequently lead to large values of $|\text{BLA}|$ and in most cases, diminished nonlinearities. Much larger nonlinearities can often be achieved for a given donor-acceptor combination when the conjugated bridge between the donor and acceptor possesses reduced aromatic stabilization energy in the neutral form, e.g. a polyene chain or a heterocycle.⁵⁻¹⁰ For example, Jen *et al.* have synthesized and characterized several thiophene containing compounds with a range of acceptors including nitro, dicyanovinyl and tricyanovinyl.⁶⁻¹⁰ Their results indicate that thiophene compounds have much larger nonlinearities than the analogous phenyl containing chromophores. Alternatively, large nonlinearities can be achieved if one can utilize a functionality that can gain aromaticity upon charge separation. One such group is the acceptor functionality, 3-phenyl-5-isoxazolone (Figure 1.1). In particular, Marder *et al.* have found that compounds containing this acceptor can have unprecedented nonlinearities.⁵ The 3-phenyl-5-isoxazolone compounds with the largest nonlinearities also contain extended polyene chains, which, although they are very polarizable, compromise the high temperature stability of the materials required for many poled polymer applications.^{11,12}

When the 3-phenyl-5-isoxazolone acceptor is connected to a phenyl or thiophene ring by a single methine bridge, steric interactions prohibit the acceptor and bridge rings from being coplanar. As a result, there is a reduction in the overlap between the π -electron systems of the bridge and acceptor, which would reduce the molecular polarizability and could therefore lead to diminished β . We therefore synthesized new thiophene containing compounds with zero or one vinyl group between the thiophene and 3-phenyl-5-isoxazolone acceptor, to determine whether the extra double bond would lead to a significant enhancement of β . For comparison, we also synthesized analogous compounds containing the dicyanovinyl acceptor, in which both the shorter and longer compounds are expected to be planar. Finally, we compared the stabilities of these longer compounds with those of the shorter ones and measured the electro-optic coefficients of host-guest poled poly(methyl methacrylate) (PMMA) polymer systems containing these chromophores.

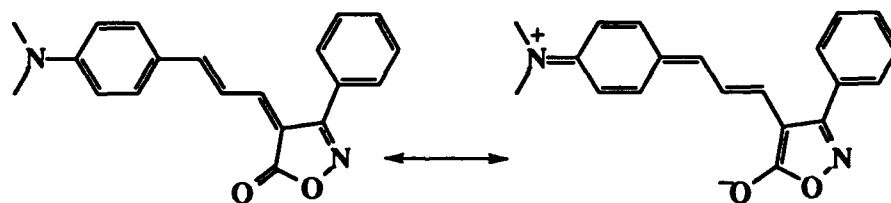


Figure 1.1: Limiting resonance structures of a 3-phenyl-5-isoxazolone acceptor substituted polyene. The charge-separated form on the right has lost the aromatic stabilization of the phenyl ring but has gained aromatic stabilization in the isoxazolone acceptor.

1.2. EXPERIMENTAL

1.2.1 Synthesis

Scheme 1 illustrates the syntheses of the thiophene chromophores with dicyanovinyl and 3-phenyl-5-isoxazolone acceptors. These compounds were purified by chromatography on silica

and recrystallized from dichloromethane by cooling and adding hexanes. The compounds were characterized by electronic absorption and ^1H nuclear magnetic resonance (NMR) spectroscopy, as well as elemental analysis.

1.2.2 Nonlinear optical characterization

The $\mu\beta$ values, where μ is the molecular dipole moment, were measured in chloroform solution by the electric field induced second harmonic generation (EFISH) experiment, using $1.907\ \mu\text{m}$ fundamental radiation. Full details of this experiment are given elsewhere.¹³ Non-resonant electro-optic (r_{33}) coefficients of poled films of a PMMA host matrix loaded with 1 or 2 mole % of chromophore were obtained by a thin film modulated ellipsometry technique, using a $1.3\ \mu\text{m}$ laser diode source.¹⁴⁻¹⁶ Spin-coating a filtered ($0.2\ \mu\text{m}$ pore size) chlorobenzene solution of dye and PMMA onto a glass slide produced $1\ \mu\text{m}$ thick films, as determined by a surface profiling instrument. This $1\ \mu\text{m}$ thickness was achieved by using 7 ml of solvent to 0.5 g of PMMA and 1 mmol of dye (for 2 mole % loading) and spinning at a rate of 800 rpm for 2 minutes. For guest-host systems the loading level was limited by the solubility of the chromophore in the PMMA/chlorobenzene film-casting solution. The center of the slide was coated with a strip (7 mm wide) of transparent indium tin oxide (ITO), that acted as one electrode for poling. The films were baked, above the glass transition temperature (T_g), for three hours under vacuum, at $120\ ^\circ\text{C}$, to remove residual solvent. The upper electrode was formed by evaporating a strip of aluminum ($\sim 100\ \text{nm}$ thick) in a direction perpendicular to the ITO electrode. Thus, an active square area of ITO, polymer film, aluminum was formed in the center of the glass substrate. Thin wire contacts were attached to the upper and lower electrodes using silver paste. Anisotropy was induced in the samples by applying a DC voltage (100 V) across the film, while the specimen was held above T_g for two minutes. With the field still applied, the sample was then allowed to cool to room temperature.

A schematic of the experimental set-up is shown in Figure 1.2. The laser beam is passed through a polarizer with its polarization vector maintained at 45° , so that the parallel (p-wave) and

perpendicular (s-wave) components of the optical field are equal. At an incidence angle θ , the beam propagates through the glass substrate, the ITO and the polymer film and is reflected from the aluminum electrode. The reflected beam then passes through a variable phase-retarder and an analyzer crossed with respect to the polarizer, and is then detected by a germanium photodiode. When a modulating voltage at 300 Hz is applied across the electrodes, the electro-optic effect causes an anisotropic change in the refractive index of the polymer matrix which alters the path length and phase angle between the s- and p-waves. This change in phase angle is converted to intensity modulation of the beam by the analyzer. The phase-retarder biases the output light intensity at half the intensity point, I_c . Using the approximation that $r_{33} = 3r_{31}$, where 1 and 3 represent directions parallel and perpendicular to the film, respectively, and assuming that the ordinary and extraordinary refractive indices, n_o and n_e , are equivalent and that there are no multiple reflections, then the electro-optic coefficient can be obtained as

$$r_{33} = \frac{3\lambda L (n - \sin^2 \theta)^{1/2}}{4\pi V_m n^2 \sin^2 \theta} \quad (1)$$

where λ is the wavelength of the incident light, I_m is the half intensity of the modulating signal, and V_m is the magnitude of the modulating voltage.

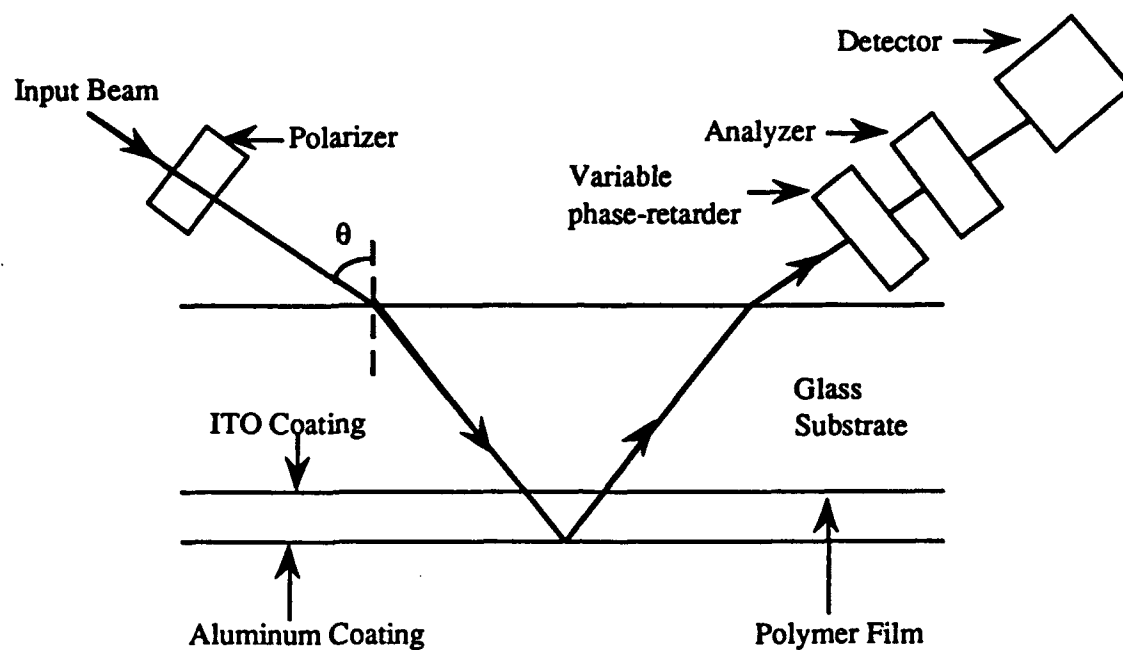


Figure 1.2: Experimental set-up for the electro-optic measurement.

1.2.3 Thermal stability tests

The samples used for thermal stability tests were identical to those used for electro-optic studies with the exception that the glass substrate had no ITO coating and the upper aluminum electrode was not deposited. The optical absorbance of the film was determined, the sample was baked at a specific temperature for 3 hours in air, and the absorbance re-measured. The degradation of the chromophore was determined by the ratio absorbance at the absorption maximum (λ_{\max}) before and after baking.

1.3. RESULTS

The optical absorption maximum in dioxane, the scalar product of μ and β , $\mu\beta$, as determined by EFISH, the zero frequency form of $\mu\beta$, ($\mu\beta(0)$) corrected for dispersion using a

two-state model¹⁷, and r_{33} normalized to 2 mole % loading for thiophene containing compounds are shown in Table 1.1.

Table 1.1: EFISH and electro-optic data for compounds 6 - 9.

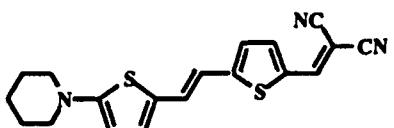
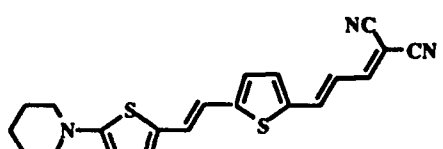
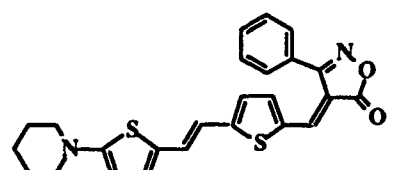
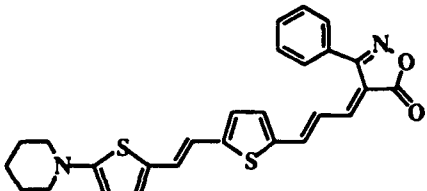
Compound	λ_{\max} (nm)	$\mu\beta/10^{-48}$ (esu)	$\mu\beta(0)/10^{-48}$ (esu)	loading (mol%)	r_{33} (pmV ⁻¹)
6 	590	1900	1060	2.0	2.7
7 	608	2910	1550	2.0	3.3
8 	626	2460	1250	2.0	4.9
9 	648	4130	1970	1.0	5.3

Table 1.2 shows the percentage of chromophore remaining after baking at temperatures of 150, 170 and 190 °C.

Table 1.2: Percentage of initial absorbance retained at λ_{\max} after heating for 3 hours for compounds 6 - 9.

Compound	150 (°C)	170 (°C)	190 (°C)
6	96	68	67
7	96	75	65
8	94	43	45
9	100	63	30

1.4. DISCUSSION

The first hyperpolarizabilities of **6** - **9**, when compared to the prototypical nonlinear optical chromophore, 4-N,N-dimethylamino-4'-nitrostilbene (DANS), where $\mu\beta = 470 \times 10^{-30}$ esu,¹⁸ are all fairly large. The phenyl containing compound analogous to **6** has a $\mu\beta$ of 1100×10^{-30} esu, which is around half that of the thiophene compound.⁸ Thus, this enhanced nonlinearity is not only derived from the stronger acceptors and extended conjugation, but also from replacing the phenyl rings with thiophenes. As shown by both the EFISH and electro-optic data, the chromophores containing the 3-phenyl-5-isoxazolone acceptors, **8** and **9**, have greater nonlinearity than their dicyanovinyl counterparts **6** and **7**. We believe this enhanced nonlinearity is due to the 3-phenyl-5-isoxazolone acceptor gaining aromaticity when going to the charge-separated form, leading to a more optimal degree of ground-state polarization and BLA.

Adding an extra double bond between the thiophene group and the acceptor is also seen to enhance the $\mu\beta$ and r_{33} values for both the dicyanovinyl and 3-phenyl-5-isoxazolone compounds. As can be seen in Table 2, the addition of an extra bond does not appear to significantly reduce the thermal stability of the chromophores.

1.5. CONCLUSIONS

We have shown that both the $\mu\beta$ and r_{33} values for the 3-phenyl-5-isoxazolone acceptor compounds are greater than for their analogous dicyanovinyl counterparts and we believe that this is due to the 3-phenyl-5-isoxazolone gaining aromaticity when in the charge-separated form. As expected, increasing the length of the molecule, by adding an extra double bond between the thiophene and the acceptor increases the nonlinearity, but does not lead to decreased thermal stability even though this extra conjugation is derived from a polyene chain (3 carbon atoms long) which are typically believed to be thermally unstable. We conclude that one can generate increased nonlinearities by incorporating moieties which gain aromaticity in going from the neutral

to charge separated form and that short polyene-like chains within a molecule do not seem to appreciably decrease the thermal stability

1.6. REFERENCES

1. S.R. Marder, D.N. Beratan and L.-T. Cheng, *Science* **252**, 103 (1991).
2. B.G. Tiemann, S.R. Marder and L.-T. Cheng, *J. Chem. Soc., Chem. Commun.* 735 (1992).
3. S.R. Marder, C.B. Gorman, L.-T. Cheng and B.G. Tiemann, *Proc. SPIE* **1775**, 19 (1992).
4. S.R. Marder, and C.B. Gorman, *Proc. Nat. Acad. Sci.* **90**, 11297 (1993).
5. S.R. Marder, L.-T. Cheng, B.G. Tiemann, A.C. Friedli, M. Blanchard-Desce, J.W. Perry and J. Skindhøj, *Science* **263**, 511 (1994).
6. C.W Dirk, H.E. Katz, M.L. Schilling and L.A. King, *Chem. Mater.*, **2**, 700 (1990).
7. A.K-Y. Jen, V.P. Rao, K.Y. Wong and K.J. Drost, *J. Chem. Soc., Chem. Commun.*, 90 (1993).
8. V.P Rao, A.K-Y. Jen, K.Y. Wong, K.J. Drost and R.M. Minnini, *Proc. SPIE* **1774**, 32 (1992).
9. V.P Rao, A.K-Y. Jen, K.Y. Wong and K.J. Drost, *Tetrahedron Lett.* 1747 (1993).
10. A.K-Y. Jen, K.Y. Wong, V.P Rao, K.J. Drost and R.M. Minnini, *Mater. Res. Symp. Proc.* **247**, 59 (1992).
11. P.N. Prasad and D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York (1991).
12. *Nonlinear Optical Properties of Polymers*, edited by A.J. Heeger, A.J. Orenstein, D.R. Ulrich (Mater. Res. Soc. Proc. **109**, Pittsburgh, PA (1987).
13. L.-T. Cheng, W. Tam, S.H. Stevenson, G.R. Meredith, G. Rikken and S.R. Marder, *J. Phys. Chem.* **95**(26), 10631 (1991).
14. K.D. Singer, S.L. Lalama, J.E. Sohn and R.D. Small in *Nonlinear Optical Properties of Organic Molecules and Crystals I*, edited by D.S. Chemla and J. Zyss (Academic Press Inc. 1987) p. 437.
15. C.C. Teng and H.T. Man, *Appl. Phys. Lett.* **56**, 1734 (1989).
16. J.S. Schildkraudt, *Appl. Optics*, **29**(19), 2839 (1990).
17. J.L. Oudar and H.E. Le Person, *Opt. Commun.* **66**, 2664 (1977).
18. L.-T. Cheng, W. Tam, S.H. Stevenson, G.R. Meredith, G. Rikken and S.R. Marder, *J. Phys. Chem.* **95**, 10631 (1991).

Part II: Synthesis of Diarylthiobarbituric acid Chromophores with Enhanced Second-order Optical Nonlinearities and Thermal Stability

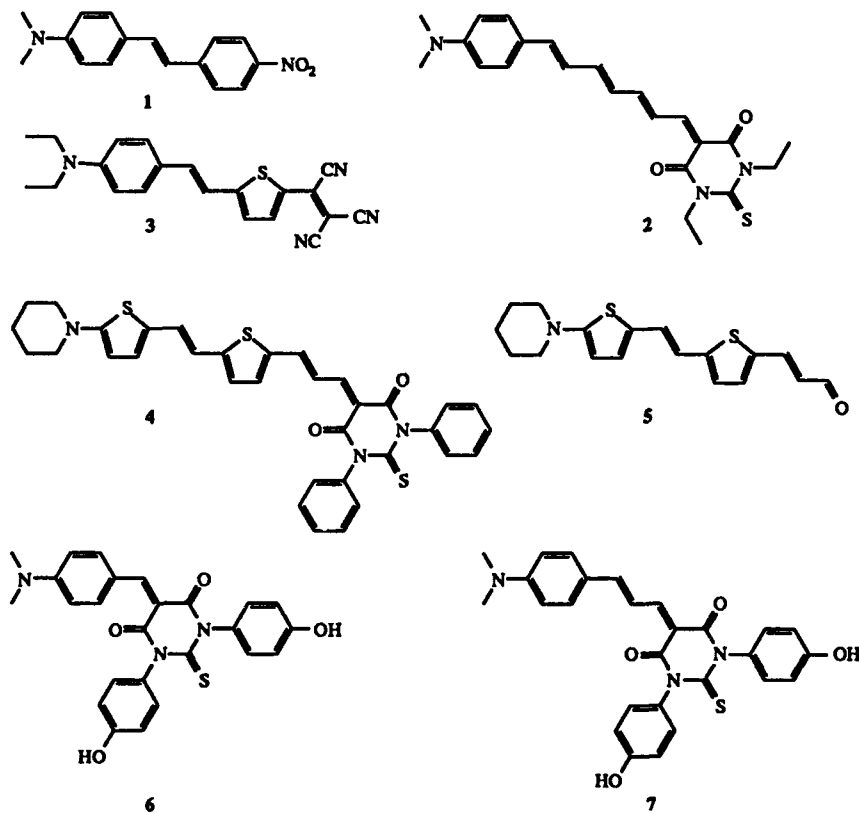
2.1 INTRODUCTION

There is substantial effort being devoted to developing organic poled polymers for electro-optic applications.¹ If this technology is to compete with inorganic crystalline materials, it is necessary to: (i) incorporate a high density of chromophores with large optical nonlinearities into a polymer; (ii) achieve a high degree of alignment of these chromophores and; (iii) lock in this alignment for long periods (years) even at elevated temperatures (at least 80 °C).² In poled polymer systems, the alignment is locked in place either by using host polymers with high glass transition temperatures,³ at least 125-150 °C above the anticipated operating temperature, or by cross linking the chromophore polymer -composite.⁴ In either case, it is necessary to develop highly nonlinear chromophores that are thermally robust at temperatures in excess of 200 °C and, preferably, that are covalently attachable to polymers. Recently, theoretical⁵ and experimental⁶ studies suggest that chromophores with strongly aromatic ground states such as 4-N,N-dimethylamino-4'-nitrostilbene, **1**, (Scheme 2.1) will tend to have only moderate nonlinearities. Thus, for **1**, the dot product of the dipole moment and the first hyperpolarizability, $\mu\beta$, which is the relevant parameter for poled polymer applications, is 480×10^{-48} esu.⁷ It has been shown that by reducing the ground-state aromaticity by either replacing the phenyl-groups with heterocyclic rings that lose less aromatic stabilization energy upon charge separation,^{6a-c} or by using extended conjugated π -systems that incorporate acceptors such as 3-phenyl-5-isoxazolone^{6d} and diethylthiobarbituric acid,^{6a} very large nonlinearities can be achieved. In the case of the diethylthiobarbituric acid chromophores such as **2**, (Scheme) for which $\mu\beta = 9800 \times 10^{-48}$ esu,^{6d} the polyene chain of this chromophore does not have the requisite thermal stability to be poled at temperatures in excess of 200 °C.⁸ In contrast, many of the heterocyclic chromophores, including **3** (Scheme) exhibit excellent thermal stability well in excess of 200 °C.^{3b} In addition,

Moylan *et al.*⁹ and we¹⁰ have found that replacement of the ethyl groups in diethylthiobarbituric acids with aryl group leads to chromophores with excellent thermal stability.

2.2 RESULTS AND DISCUSSION

Motivated to develop thermally robust and highly nonlinear chromophores, and building upon the observations described above, we set out to synthesize chromophore **3** (Scheme 2.1). It was our hope that replacement of: (i) the phenyl groups and extended polyene fragment in **2**, with the thiophene-vinyl-thiophene bridge in **4** and; (ii) the ethyl groups on the thiobarbituric acid with phenyl groups, would significantly improve the thermal stability without sacrificing the nonlinearity. In order to minimize steric interactions between the diphenylthiobarbituric acid and thiophene rings that could preclude their coplanarity, a vinyl group was incorporated between the thiophene bridge and the diphenylthiobarbituric acid ring.



Scheme 2.1

Compound 4 was prepared by reaction of 5,¹¹ (Scheme 2.1) with diphenylthiobarbituric acid in acetic anhydride. Chromatography of the crude 4 material on silica gel eluting with dichloromethane and hexane (1:1) gave a blue solid on evaporation to dryness. After recrystallization from dichloromethane compound 4 was isolated in 24% yield and was characterized by ¹H nuclear magnetic resonance (NMR), ultraviolet visible and mass spectroscopies.¹² Electric field induced second harmonic generation⁷ experiments on 4, performed at two different laboratories, at 1.907 μm in chloroform (Dupont) and in dichloromethane (EniChem America), were in good agreement, both giving μβ products of 8600 x 10⁻⁴⁸ esu. In both of these solvents, the absorption maximum for 4 was at 710 nm and thus the correcting these values for dispersive enhancement using the two-level correction,¹² gave zero a frequency value, μβ(0), of 3300 x 10⁻⁴⁸ esu, which is approaching an order of magnitude greater than for 1 (μβ(0) of 370 x 10⁻⁴⁸ esu). Thermal stability studies on 4 dissolved in poly(methyl methacrylate), PMMA, in which the absorption spectra were monitored before and after heating a sample for 30 minutes, showed less than 10% change (at the absorption maximum) at temperatures up to 210 °C. Furthermore, when 4 was poled as a host-guest system in PMMA at 0.5 mole% and 1 MVcm⁻¹ poling field, the resulting polymer had a electro-optic coefficient, r₃₃, of 2.6 pmV⁻¹ measured at 1.3 μm, consistent with the large molecular nonlinearity. Chromophore solubility prohibited incorporating concentrations greater than 1 mole% of this chromophore in PMMA. Since covalent attachment of chromophores to polymers via one or more bonds, in general, allows for incorporation of higher concentrations of chromophores, and leads to improved temporal stability, we decided to synthesize a functionalized diarylthiobarbituric acid. Thus, reaction of di(4-acetoxyphenyl)thiourea^{13a} with malonic acid and acetyl chloride gave, after deprotection of the hydroxy group in aqueous base, and acidic work-up, crude di(4-hydroxyphenyl)thiobarbituric acid.^{13b} This crude material reacted cleanly with 4-N,N-dimethylaminobenzaldehyde or 4-N,N-dimethylaminocinnamaldehyde in tetrahydrofuran, THF, to give 6 and 7 (Scheme) respectively as microcrystalline precipitates, which after filtration were

isolated in analytically pure form. These compounds demonstrate that functionalized diarylthiobarbituric acid chromophores suitable for covalent attachment to polymers can be synthesized.

In summary, the compounds reported here demonstrate that it is possible to design chromophores that simultaneously exhibit large nonlinearity and good thermal stability. Furthermore, with the synthesis of di(4-hydroxyphenyl)thiobarbituric acid, we believe that it should be possible to covalently incorporate, these and other rather nonlinear chromophores into poled polymers at high concentrations. Experiments to test this hypothesis are in progress.

2.3 EXPERIMENTAL

Reaction procedure for 4.

A solution of 5 (0.4 g, 1.22 mmol) in acetic anhydride (30 ml) was added to a solution of 1,3 diphenyl thiobarbituric acid (0.54g, 1.82 mmol) in acetic anhydride (5 ml). The resulting solution immediately turned green/blue and was refluxed for 15 minutes. The acetic anhydride was removed by adding water to the solution and extracting the product three time with dichloromethane. The combined dichloromethane extracts were washed twice with water and dried over magnesium sulfate. The solution was filtered and solvent removed under reduced pressure. Yield 0.173 g (24%).

Characterizing data for 4: ^1H NMR (CD_2Cl_2) δ 8.27 (dd, $J = 14.0, 12.7$ Hz, 1H), 8.20 (d, $J = 12.7$ Hz, 1H), 7.61 (d, $J = 14.1$ Hz, 1H), 7.45 (m, 6H), 7.35 (d, $J = 4.1$ Hz, 1H), 7.27 (m, 4H), 7.12 (d, $J = 15.3$ Hz, 1H), 6.96 (d, $J = 4.1$ Hz, 1H), 6.88 (d, $J = 4.1$ Hz, 1H), 6.59 (d, $J = 15.4$ Hz, 1H), 5.96 (d, $J = 4.2$ Hz, 1H), 3.24 (t, $J = 5.6$ Hz, 4H), 1.70 (m, 4H), 1.62 (m, 2H). High resolution MS calcd for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_2\text{S}_3$: 607. 1428. Found: 607.1422.

Reaction procedure for 3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid.

1. 3,5-bis-(4-acetoxyphenyl)-thiourea.

4-aminophenol (100g, 0.916 mol) and thiophosgene (35 ml, 0.458 mol) were added alternately and in portions to 1 L of deionized water while it was being cooled in an ice bath. The reaction vessel was shaken vigorously for several minutes after each addition of reactant. A brown oil formed quickly with evolution of heat. After stirring ~15-20 minutes, solid sodium carbonate (65g, 0.47 mol) was added in small portions with vigorous shaking between additions. Care must be taken during this process since there is significant gas evolution. After most of the sodium carbonate had been added, a white crystalline solid appeared, as well as small amount of dark material. The dark solid slowly disappeared upon further shaking. The viscous slurry was allowed to stand for 4 hours at which time all of the solid had become white. While the reaction vessel was cooled in an ice bath, sodium hydroxide pellets (55g, 1.4 mol) were added in portions to give dissolution of the white solid to a murky purple solution with evolution of heat. When the reaction solution was cool, it was transferred to a 4 L beaker. Acetic anhydride (116 ml, 1.4 mol) was added slowly to the reaction solution while the reaction solution was being stirred vigorously with a thick glass rod. White solid appears immediately when the acetic anhydride comes in contact with the reaction solution. The reaction mixture quickly becomes a viscous slurry. After all traces of the purple solution had disappeared from the mixture, the mixture was suction filtered over paper and allowed to dry.

2. 3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid.

Finely powdered, crude 3,5-bis-(4-acetoxyphenyl)-thiourea (40.9 g, 0.119 mol) and malonic acid (12.3 g, 0.119 mol) were added to a 1L round bottom flask and the flask shaken thoroughly. Acetyl chloride (19 ml, 0.238 mol) was added and again the mixture was shaken and stirred thoroughly. The flask was then connected to an ethanol bubbler and the reaction was heated in a water bath (100°C) for 5.5 hours. Gas was evolved and the dirty gray mixture became a viscous yellow mass. The reaction mixture was allowed to cool and sit overnight. The mixture was partitioned between 30 ml of dichloromethane and saturated sodium bicarbonate solution. The dichloromethane solution was washed with the sodium bicarbonate solution until addition of

concentrated hydrochloric acid to small portions of the sodium bicarbonate solution gave no pale yellow solid. The combined aqueous sodium bicarbonate portions were washed once with dichloromethane. The final volume of aqueous sodium bicarbonate solution was 1 liter. To this solution was added sodium hydroxide pellets (23.9 g, 0.597 mol) which dissolved. The solution was allowed to react over night. The next day, dilute hydrochloric acid was added to the pale yellow reaction solution to precipitate a pale yellow solid. The crude product was suction filtered and allowed to dry and used for the synthesis of 6 and 7 without further purification. Yield, 18.5g (47.4%).

Reaction procedure for 6.

Crude 3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid (0.500g, 1.52 mmol) 4-Dimethylaminobenzaldehyde (0.227g, 1.52 mmol) were separately dissolved in ~10 ml and ~4 ml of tetrahydrofuran respectively. With rapid stirring, the 4-dimethylaminobenzaldehyde solution was added to the thiobarbituric acid solution to give an immediate red-orange color. After sitting for 10 minutes, a red-orange solid was precipitated, which was filtered over a medium glass frit under positive pressure and then dried in air. Yield, 0.500g (71.5%).

Characterizing data for 6: ^1H NMR (d_6 -DMSO) δ 9.65 (s, 1H), 8.38 (d, $J = 9.4$ Hz, 2H), 8.24 (s, 1H), 7.03 (d, $J = 8.7$ Hz, 2H), 7.01 (d, $J = 8.7$ Hz, 2H), 6.77 (overlapping doublets, 6H) 3.12 (s, 6H). Anal Calcd for $\text{C}_{25}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: C, 65.35; H, 4.61. Found: C, 65.28; H, 4.64. MS calcd for $\text{C}_{25}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: 459.52. Found: 459.

Reaction procedure for 7.

3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid (0.500g, 1.52 mmol) and 4-Dimethylaminocinnamaldehyde (0.267g, 1.52 mmol) were each separately dissolved in ~10 ml tetrahydrofuran. With rapid stirring, the 4-dimethylaminocinnamaldehyde solution was added to the thiobarbituric acid solution to give an immediate purple color. After sitting for ten minutes, a

purple solid was precipitated, which was filtered over a medium glass frit under positive pressure and dried in air. Yield, 0.476g (64.4%).

Characterizing data for 7: ^1H NMR (d_6 -DMSO) δ 8.26 (dd, $J = 14.7, 12.5$ Hz, 1H), 8.10 (d, $J = 12.4$ Hz, 1H), 7.77 (d, $J = 14.7$ Hz, 1H), 7.59 (d, $J = 9.1$ Hz, 2H), 7.01 (overlapping doublets, 4H), 6.77 (overlapping doublets, 6H), 3.07 (s, 6H). Anal Calcd for $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_4\text{S}$: C, 66.79; H, 4.77. Found: C, 66.70; H, 4.78. MS calcd for $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_4\text{S}$: 485.56. Found: 485.

2.4 REFERENCES

- (1) (a) Prasad, P.N.; Williams D.J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991; pp 152-160.
- (2) Lytel, R.; Lipscomb, G.F.; Ticknor, A.J.; Mohlmann, G.R. *Proc. SPIE*, 1993, 2025, 14-19.
- (3) (a) Wu, J.; Valley, J.F.; Ermer, S.; Binkley E.S.; Kenney J.T.; Lipscomb, G.F.; Lytel, R. *Appl. Phys. Lett.*, 1991, 58, 225-227. (b) Wong, K. Y.; Jen, A. K.-Y. *J. Appl. Phys.* in press.
- (4) (a) Xu, C.; Wu, B.; Dalton, L. R.; Shi, Y.; Ranon, P. M.; Steier, W. H. *Macromolecules* 1992, 25, 6714-6715. (b) Xu, C.; Wu, B.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Macromolecules* 1992, 25, 6716-6718. (c) Ranon, P.M.; Shi, Y.; Steier, W.H.; Xu, C.; Wu, B.; Dalton, L. *Appl. Phys. Lett.*, 1993, 58, 2605-2607.
- (5) Gorman, C.B.; Marder, S.R. *Proc Nat. Acad. Sci.* 1993, 90, 11297-11301.
- (6) (a) Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater.* 1990, 2, 700-705. (b) Jen, A.K-Y.; Rao, V.P.; Wong, K.Y.; Drost, K.J. *J. Chem. Soc., Chem. Commun.*, 1993, 90-92. (c) Rao, V.P.; Jen, A.K-Y.; Wong, K.Y.; Drost *Tetrahedron Lett.* 1993, 1747-1750. (d) Marder, S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Blanchard-Desce, M.; Perry, J.W.; Skindhøj, J. *Science*, 1994, 263, 511-514.

- (7) Cheng, L-T.; Tam, W.; Stevenson, S.H.; Meredith, G.R. , Rikken, G; Marder, S.R., *J. Phys. Chem.* 1991, 95(26), 10631- 10643.
- (8) Skindhøj, J. Gilmour, S; Marder, S.R.; Perry J.W., unpublished observations.
- (9) Moylan, C.R.; Tweig, R.J.; Lee, V.Y.; Swanson, S.A.; Betterton, K.M.; Miller, R.D. *J. Am. Chem. Soc.* 1993, 115, 12599-12600.
- (10) Cheng, L.-T. A.; Tam. W *US patent* no. 454272218, issued December 21, 1993.
- (11) Gilmour, S; Marder, S.R.; Perry J.W.; Cheng, L.-K., *Adv. Mater.*, submitted.
- (12) Oudar, J.L. *J. Chem. Phys.* 1977, 67, 446-457.
- (13) (a)Dyson, G. M.; George, J. H.; *J. Chem. Soc.*, 1923, 125, 1702. (b) Das, P. K.; Behera, G. B.; Sahay, A. K.; Mishra, B. K., *Ind. J. Chem. B* 1985, 24, 437.

c) Cumulative list of publications (With acknowledgment of funds from AFOSR grant):

1. Marder S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. "*Large First Hyperpolarizabilities in Push-Pull Polyenes by Tuning Bond Length Alternation and Aromaticity.*" *Science*, **263** 511 (1994).
2. Gilmour, S; Jen, A.; Marder, S. R.; Niessink, A. J.; Perry, J. W.; Skindhøj, J.; Cai, M. "*Second-order Nonlinear Optical Properties of Thiophene Containing Chromophores with Extended Conjugation .*" in *Materials Research Society Symposium Proceedings Vol. 328*, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 485
3. Gilmour, S; Marder, S.R.; Perry, J. W.; Cheng, L.-T. "*Large Second-Order Optical Nonlinearities and Enhanced Thermal Stabilities in Extended Thiophene Containing Compounds.*" *Adv. Mater*, in press.
4. Gilmour, S; Montgomery, R. A. Marder, S.R.; Cheng, L.-T. Jen, A. K.-Y.; Cai, Y.M.; Perry, J. W.; Dalton, L. R. "*Synthesis of Diarylthiobarbituric Acid Chromophore with Enhance Second-Order Optical Nonlinearities and Thermal Stability.*" *Chem. Mater.* submitted.

d) List of Professional personnel associated with the research efforts:

Postdoctoral fellows who were supported either directly by salary or support for laboratory expenses are:

Dennis Ng

Rafeal Ortiz

Chin-Ti Chen

Peter Bedworth

Sandra Gilmour (National Research Council Resident Research Associate, no salary support, laboratory expenses only)

Christopher Gorman (Jet Propulsion Laboratory Postdoctoral Fellowship, no salary support, laboratory expenses only)

In addition, several people of are not directly receiving funding from this grant but are performing work in a collaborative manner, include

Dr. Joseph Perry (Jet Propulsion Laboratory)

Dr. Grant Bourhill (Jet Propulsion Laboratory)

Dr. Fabienne Meyers (Visiting Scientist from the University of Mons, Belgium)

Dr. Alex Jen (EniChem)

Dr Bob Twieg (IBM)

Dr. Bob Montgomery (Visiting Scientist from USC)

Professor Larry Dalton

e. Interactions:

i) Papers presented at scientific conferences:

1. Marder, S.R. "*Relationships Between Linear and Nonlinear Polarizabilities and Bond Length Alternation in Organic Molecules.*" Presented at the Canadian Chemical Society National Meeting, Sherbrooke, Quebec (Canada), May 30-June 4, 1993. (Invited Lecture).
2. Bourhill, G.H.; Brédas, J.L.; Cheng, L.-T.; Friedli, A.C.; Gorman, C. B.; Marder, S.R.; Meyers, F.; Perry, J.W.; Pierce, B.M.; Skindhøj, J.; Tiemann, B.G. "*Optimizing the First and Second Hyperpolarizabilities of Organic Dyes*" Presented at, Optical Society of America Topical Meeting: Organic Thin Films for Photonic Applications, Toronto, Canada, October 6-8, 1993. (Invited Lecture).
3. Marder, S.R. "*Attempts to Understand Relationships Between Chemical Structure and the Second- and Third-Order Optical Nonlinearities of Organic Molecules and Materials.*" Presented The First NSF-Sponsored Materials Chemistry Workshop, Albuquerque, NM, October 21-24, 1993.
4. Marder, S.R. ; Tiemann, B.G.; Perry, J.W.; Bourhill, G.H.; Gorman, C.B.; Friedli, A.C.; Cheng, L.-T.; Meyers, F.; Brédas, J.L.; Pierce, B.M. "*Structure Property Relationships for Second- and Third-Order Nonlinear Optics.*" Presented at Materials Research Society National Meeting, Boston, November 29 - December 3, 1993.(Invited Lecture).
5. Cheng, L.-T. Friedli, A.C.; Gilmour, S.; Gorman, C. B.; Marder, S. R.; Perry, J.W.; Perry, K. J.; Skindhøj, J.; Tiemann, B. G., Yang, E. "*The Effect of Bond Length Alternation on The Molecular Hyperpolarizabilities of Polymethine Dyes*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, (France) January 9-13, 1994.
6. Bourhill, G.H.; Cheng, L.-T.; Gorman, C. B.; Marder, S.R.; Perry, J.W.; Tiemann, B.G. "*Hyperpolarizabilities of Conjugated Donor-Acceptor Molecules with Varying Degree of Charge-Transfer in the Ground-State.*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, (France), January 9-13, 1994.
7. Marder, S.R. "*A Chemists View of the Science and Technology of Organic Nonlinear Optical Materials.*" Presented at the American Chemical Society National Meeting, San Diego, CA, March 13-18, 1994.(Invited Lecture).
8. Marder, S. R. "*Designing Highly Nonlinear Organic Dyes* " Presented at the Fourth Iketani Conference, The International Conference on Optical Nonlinear Organic Materials and Applications, Kona, HI May 17-20, 1994. (Invited Lecture).

Upcoming Invited Lectures:

1. Marder, S. R. "*The Relationship Between Ground-State Polarization and Molecular Polarizability and Hyperpolarizabilities of Organic Dyes* " To be presented at the Gordon Conference on Electronic Properties of the Organic Solid State, Andover, NH, July 24-29, 1994. (Invited Lecture).

2. Marder, S. R. " *Simple Model for Nonlinear Polarization in Organic Dyes* " To be presented at the Fifth Annual Symposium of the NSF Center for Photo-induced Charge Transfer, Rochester, NY August 1-3, 1994. (Invited Lecture).
3. Marder, S. R. " *Nonlinear Optical Properties of Organic Dyes* " To be presented at the Gordon Conference Electron Donor-Acceptor Interactions, Salve Regina, RI, August 14-19, 1994. (Invited Lecture)
4. Marder, S. R. " *Optimizing Molecular Hyperpolarizabilities in Linear Conjugated Organic Molecules* " To be presented at joint American Chemical Society, Optical Society of America Topical Meeting: Organic Thin Films for Photonic Applications, Washington DC, August 22-26, 1994. (Invited Lecture).
5. Marder, S. R. " *Nonlinear Optical Materials Design Criteria* " To be presented at American Chemical Society National Meeting, Anaheim, CA, April, 1995. (Invited Lecture).
6. Marder, S. R. " *Rational Design of Nonlinear Optical Materials* " To be presented at The Royal Society of Chemistry's Second International Meeting on Materials Chemistry, Kent, England, July, 18-21, 1995. (Plenary Lecture)

ii) none

f. none

g. none