

AD-A271 067



REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

2

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 this 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 Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

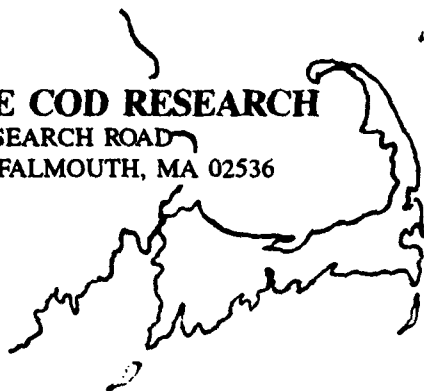
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 20 Sep 93	3. REPORT TYPE AND DATES COVERED FINAL REPORT 15 Dec 93-14 Aug 93
4. TITLE AND SUBTITLE Complex and Stereoregular Nonlinear Optical Materials			5. FUNDING NUMBERS 63218C 1602/01
6. AUTHOR(S) Dr Brian G. Dixon			AFOSR-TR- 93 07 57
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Cape Code Research, Inc P O Box 600 Buzzards Bay, MA 02532			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC 110 DUNCAN AVENUE SUITE B115 BOLLING AFB DC 20332-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER R49620-93-C-0006
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) This Phase I research program resulted in the synthesis and identification of a previously unknown set of aromatic phosphonic acid compounds, which possessed interesting thermal properties. There are very few phosphonate compounds reported that are liquid crystalline in nature. However, the non-linear optical properties of these compounds were determined to be unremarkable. Very probably, this is due to a relatively small dipole between the phosphonate moiety and a distal cyano group.			
14. SUBJECT TERMS non-linear optics, phosphonate			15. NUMBER OF PAGES
			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

93-24265



CAPE COD RESEARCH

19 RESEARCH ROAD
EAST FALMOUTH, MA 02536



TELEPHONE (508) 540-4400

FAX (508) 540-4428

**COMPLEX & STEREOREGULAR
NONLINEAR OPTICAL MATERIALS**

Final Report

September 7, 1993

Contractor: Cape Cod Research, Inc.
19 Research Road
East Falmouth, MA 02536

Principal Investigator: Dr. Brian G. Dixon

Contract Number: F49620-93-C-0006

Contract Dollar Amount: \$59,942

Contract Award: Competitive

Sponsor: Dr. Charles Y-C Lee (202) 767-4960
AFOSR
Directorate of Chemistry & Materials Science
Building 410
Bolling AFB DC 20332-6448

EXECUTIVE SUMMARY

This Phase I research program resulted in the synthesis and identification of a previously unknown set of aromatic phosphonic acid compounds, which possessed interesting thermal properties. There are very few phosphonate compounds have been reported that are liquid crystalline in nature. However, the non-linear optical properties of these compounds were determined to be unremarkable. Very probably, this is due to a relatively small dipole between the phosphonate moiety and a distal cyano group. More specifically, the research yielded the following results: (1) A previously unknown set of phosphono-substituted biphenyl compounds was synthesized, and characterized. (2) It was established that this new set of compounds possessed liquid crystalline properties. (3) Corona poling of the new compounds in polymer films was carried out to align the liquid crystalline materials, in order to improve their non-linear optical properties. (4) The synthesized phosphonates did not exhibit non-linear optical properties.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

TABLE OF CONTENTS

	PAGE
1.0 STATEMENT OF THE OPPORTUNITY	4
2.0 TECHNICAL APPROACH & PHASE I SUMMARY	5
2.1 Technical Approach	5
2.2 Technical Objectives	6
3.0 PHASE I RESEARCH CARRIED OUT	7
3.1 Phosphonatobiphenyl Syntheses	7
3.2 Liquid Crystallinity - Thermal Properties	10
3.3 Nonlinear Optical Results	15
3.4 Experimental	17
3.5 Analytical	20
4.0 RESEARCH RESULTS & ASSESSMENTS	23
5.0 CONCLUSIONS & RECOMMENDATIONS	24
6.0 POTENTIAL APPLICATIONS	24
7.0 REFERENCES	24

1.0 STATEMENT OF THE OPPORTUNITY

This Phase I SBIR project was carried out in response to Topic SDIO92-011 under the heading of *Optical Computing and Optical Signal* and involved research concerning innovative organic-inorganic hybrid materials that possess superior nonlinear optical properties.

It is widely recognized that materials possessing large and fast nonlinear optical (NLO) susceptibilities have great potential for use in the emerging photonics industry.¹⁻⁸ In fact, materials (for example LiNbO_3) which possess useful second order nonlinearities, $\beta^{(2)}$, are already being applied to optical switching and frequency mixing applications. It is also clear that if the potential of NLO materials is to be realized, significant advancements in the magnitude of the observed nonlinearity will be required. A second area requiring progress is NLO materials processing.

Much of the NLO research carried out to date has focused upon organic materials, and there are very good reasons why this is so. Compared to inorganic crystalline materials, like LiNbO_3 , organic materials offer the distinct advantages of large susceptibilities, high laser damage thresholds, faster response times, and a versatility of molecular modifications. It would also seem clear that the key to obtaining a large second order hyperpolarizability, β , is to synthesize materials with specific stereochemistries. In essence the problem distills down to one of stereochemical control during the synthetic process. A number of interesting and partially successful attempts to achieve this goal have been carried out, including the use of liquid crystalline solvents to prepare organic NLO materials, the use of orientational fields, Langmuir-Blodgett films, and others. The use of templates for the stereochemical induction of NLO materials is a research area that is just beginning to be explored.

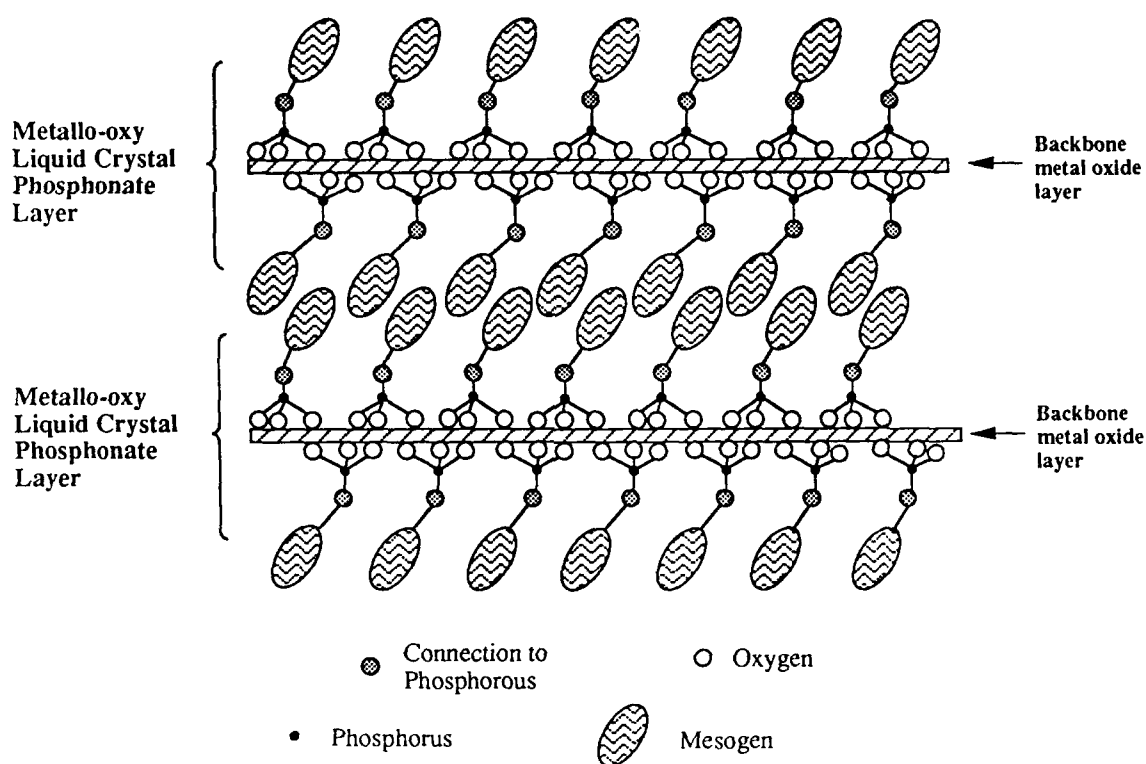
The study of inorganic-organic hybrid materials as template-NLO materials is an area that is in its infancy, but it is also an area that has great potential. The primary objective of this Phase I research program was to demonstrate the feasibility of preparing organic-inorganic hybrid materials that possess interesting non-linear optical properties. More specifically, this Phase I SBIR program investigated the

feasibility of preparing lamellar liquid crystalline-phosphonate metal oxide composites with superior nonlinear optical properties.

2.0 TECHNICAL APPROACH & SUMMARY OF THE PHASE I WORK

2.1 Underlying Basis of the Technical Approach

The technical approach was to use the known high structural order of intercalating metal oxides as templates for synthesizing inorganic-organic hybrid liquid crystalline nonlinear optical materials. Basically the intercalating metal oxide served as a crystalline framework which forced the liquid crystalline component into a very highly organized and defect free state. The basic concept is shown graphically by the following artwork:

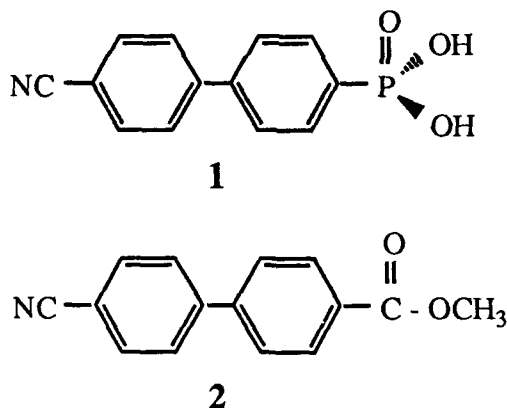


The liquid crystalline portion of this complex molecule is closely related, chemically, to materials that are known to have useful and interesting NLO properties. What had not been heretofore investigated was making this type of hybrid organic-inorganic species. In fact, the vast majority of research to date has focused upon

organic materials, and very little work had been done upon hybrid inorganic-organic materials. The proposed liquid crystalline-phosphonate metal oxide composites were previously unknown.

There were two fundamental questions which had to be answered. First, could complex and intermixed organic-inorganic composites be readily synthesized? Second, did they have useful NLO properties, and how did they compare with the NLO properties of simple liquid crystalline materials? The answer to the first question is yes. Although the specific intermixed materials to be synthesized had not previously been prepared, this research has demonstrated that the proposed layered inorganic-organic complexes are accessible.

Unfortunately, the answer to the second question appears to be no, although the chemical similarity between the basic liquid crystalline phosphonate moiety to be used in this research, structure 1, and the known liquid crystalline species, 2, is apparent.



2.2 Specific Technical Objectives

The primary objective of the Phase I research program was to demonstrate the feasibility of preparing lamellar liquid crystalline-phosphonate metal oxide composites with superior nonlinear optical properties. In order to demonstrate the feasibility of the concept, the Phase I research focused upon answering the following fundamental questions:

- * Can the previously unknown liquid crystalline phosphonate monomer, 1, be readily synthesized?
- * Does the phosphonate monomer 1 form an intercalating lamellar composite within a metal oxide structure?
- * What are the physical and liquid crystalline properties of the novel materials?
- * What are the optical properties of liquid crystal 1 and the final composite, and how do they compare with established nonlinear optical materials?

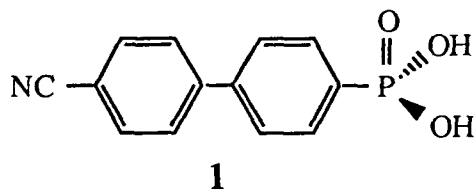
Answers to all of these questions have been obtained during the Phase I program. The results are described in Section 3.0, which follows.

3.0 PHASE I RESEARCH CARRIED OUT

The Phase I research was split into two three fundamental parts. The first part dealt with the synthesis and characterization of phosphonate 1, and its derivatives. Section 3.2 reports on the liquid crystalline properties of the synthesized materials, while Section 3.3 describes the non-linear optical experiments, and results. Sections 3.4 and 3.5 detail the experimental and analytical procedures used throughout the program.

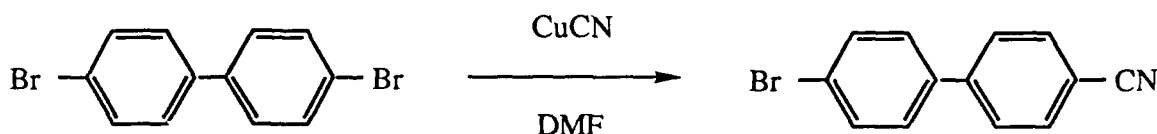
3.1 Synthesis of 4-Cyano-4'-Phosphonato Biphenyls

A couple of different synthetic routes to the desired phosphonato compounds were evaluated during the feasibility test program. As described in the original proposal the structural similarities between 1 and known liquid crystals suggested that 1 might be liquid crystalline as well.

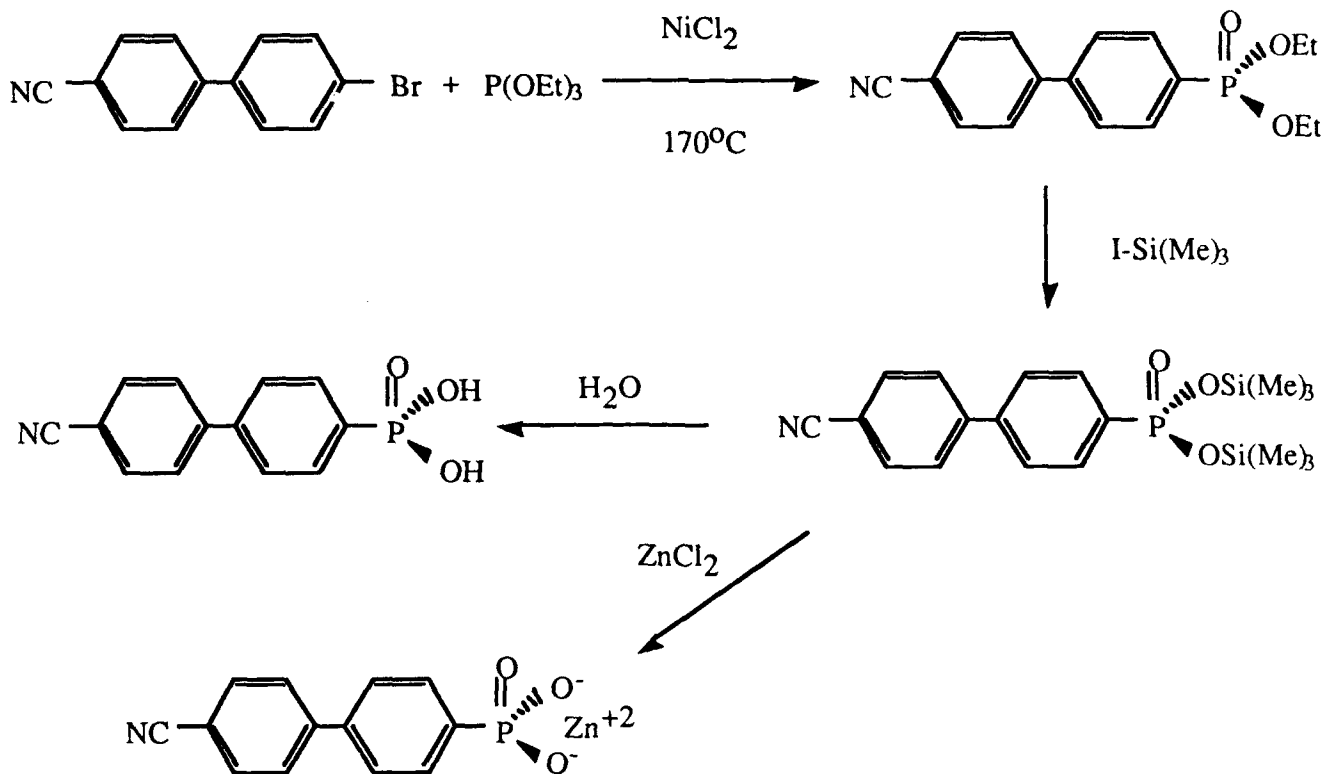


Both routes to 1 began with 1,4-dibromobiphenyl, a low cost starting material. One route went through a sequence of conversion to the Grignard reagent, followed by a sequential conversion to first the corresponding carboxylic acid, then the amide, and finally to the desired nitrile. This route was abandoned for a number of reasons. A four step synthesis from the dibromo compound to the bromo-cyano compound was prohibitive. In addition, the yields were poor. An alternative route took the dibromobiphenyl directly to the bromocyanobiphenyl in one step.

The synthetic route is shown below, and involved simply taking 4,4'-dibromobiphenyl directly to the bromocyanobiphenyl in one step. 4,4'-dibromobiphenyl was reacted, in dimethylformamide, with copper cyanide at reflux. Separation of the products was accomplished with a combination of recrystallization, column chromatography, and/or sublimation.



Compound 1 results directly from the reaction of the 4-bromo-4'-cyanobiphenyl in an Arbuzov type of reaction as shown in the first step in the scheme below. Although in general aromatic compounds do not undergo the Arbuzov reaction at all, the presence of a catalytic amount of nickel (II) chloride facilitates the transformation.



The reaction conditions are relatively harsh, however, and require that the nickel (II) chloride be pre-dried, and that the reaction be run neat. A number of experiments were run in which solvents were used, however, these reactions simply did not go to completion.

The diester product was converted into the corresponding trimethylsilyl phosphonate ester by reaction with iodotrimethyl silane, which in turn, is easily converted to the phosphonic acid by hydrolysis with water to yield the desired product 1. The synthesis of the metal ion salt derivatives of 1 was carried out by simply doing the hydrolysis step with aqueous solutions of the desired salt, shown above for the example of zinc. Once again standard recrystallization and/or column chromatography procedures were used to purify the products.

3.2 Liquid Crystallinity & Thermal Properties

As hoped, the new phosphonate compounds were found to be liquid crystalline materials. It was also found that the various phosphonate compounds gave the same thermal scans, suggesting that the observed thermal properties were due to the substituted biphenyl groups and were virtually independent of the P-O-X moiety. Differential Scanning Calorimetry (DSC, run on a Perkin Elmer Delta Series DSC7, see Section 3.5 for the procedural details) measurements showed multiple transitions, as expected for liquid crystals. Figures 1-6 demonstrate results which are representative of the experimental program.

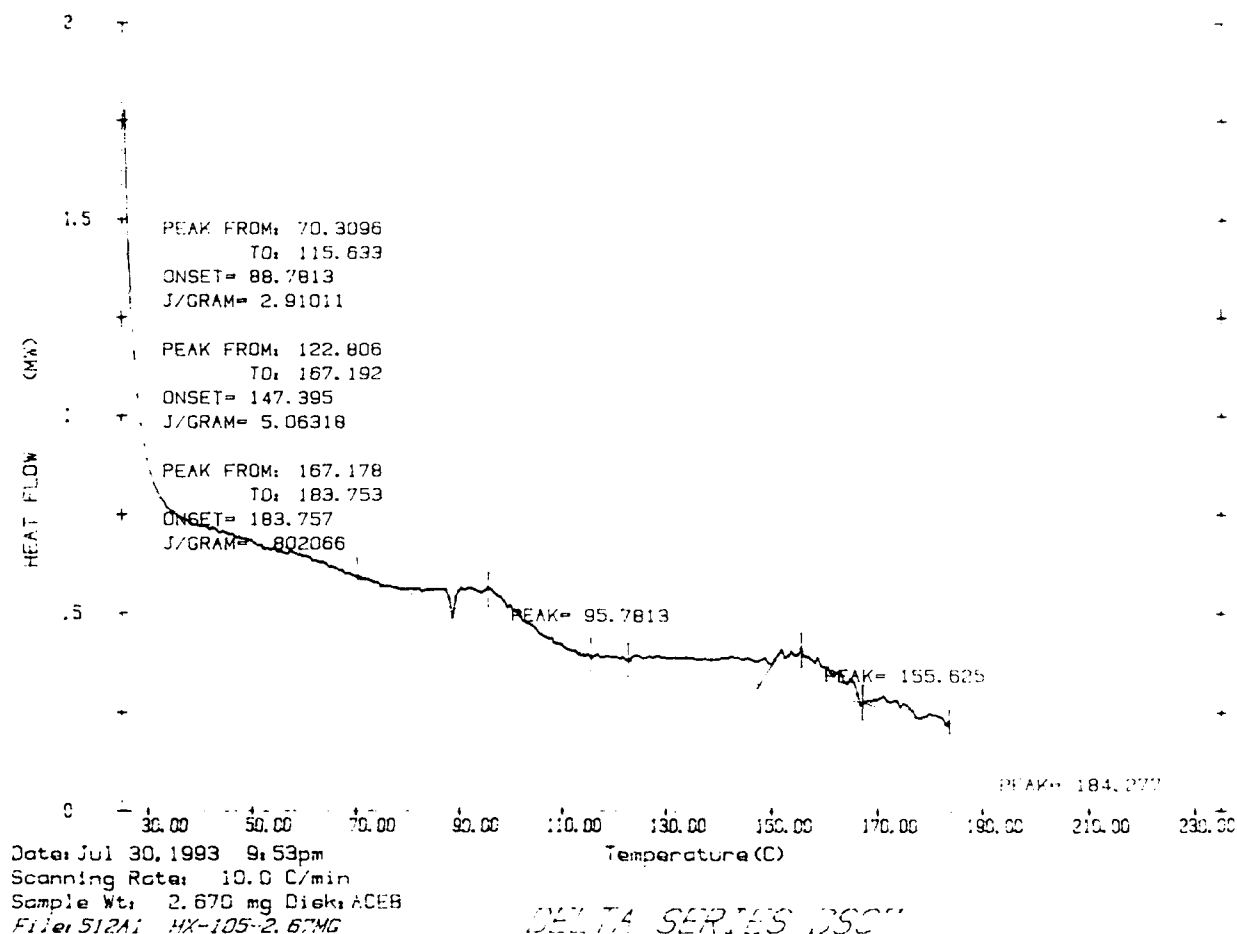


Figure 1: DSC Scan of 4-cyano-4'-diethylphosphonate biphenyl - Heating

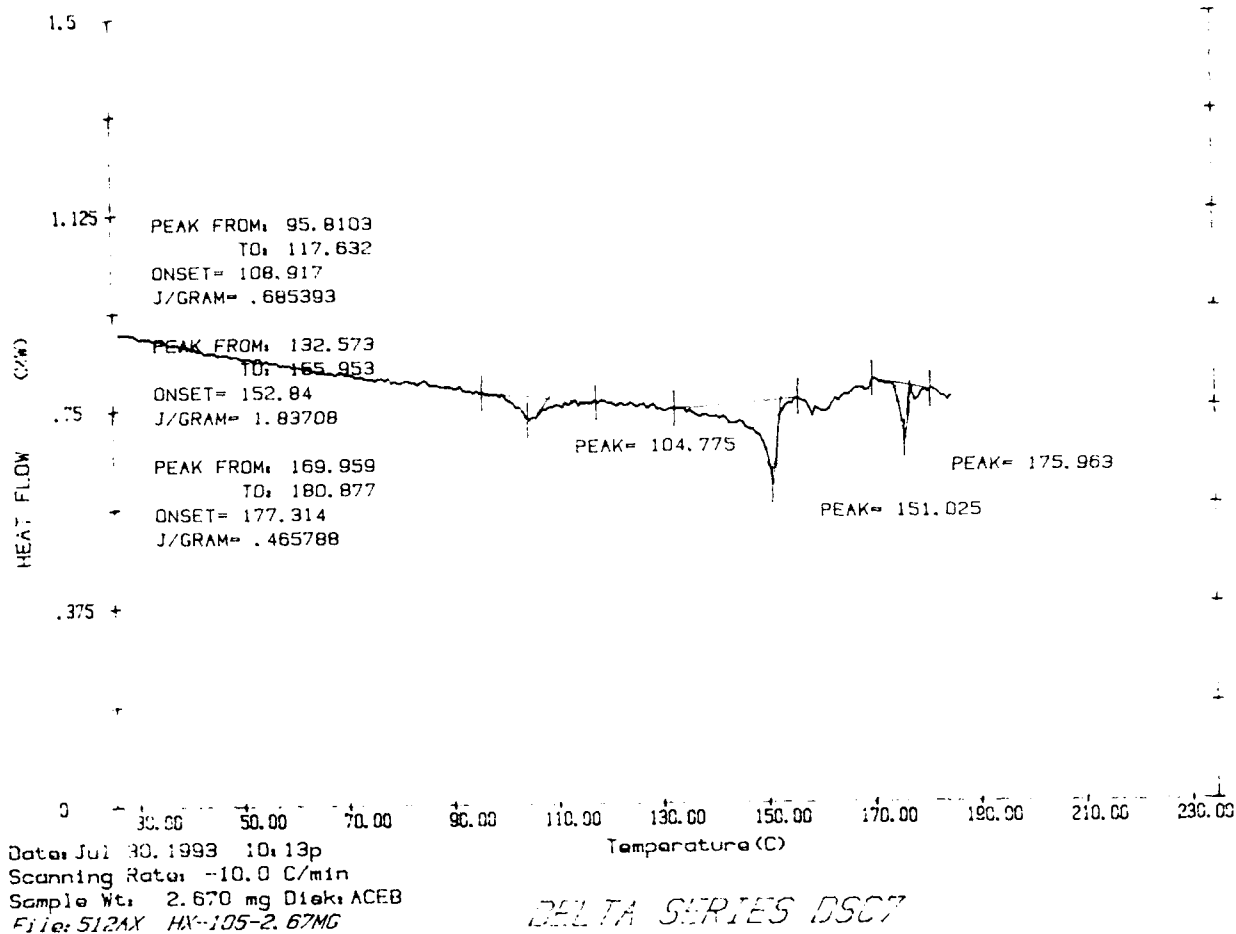


Figure 2: DSC Scan of 4-cyano-4'-diethylphosphonate biphenyl - Cooling

Figures 1 and 2 are the heating and cooling curves for ester compound, 4-cyano-4'-diethylphosphonate biphenyl, respectively. Figures 3 and 4 are the corresponding curves for the phosphonic acid, compound 1. Figures 5 and 6 are the results for the zinc salt. The three sets of figures are very similar in that they show a series of small thermal transitions, which typical of liquid crystalline behavior. An examination of the cooling curves shows three transitions between 106-110, 148-153, and 170-180°C.

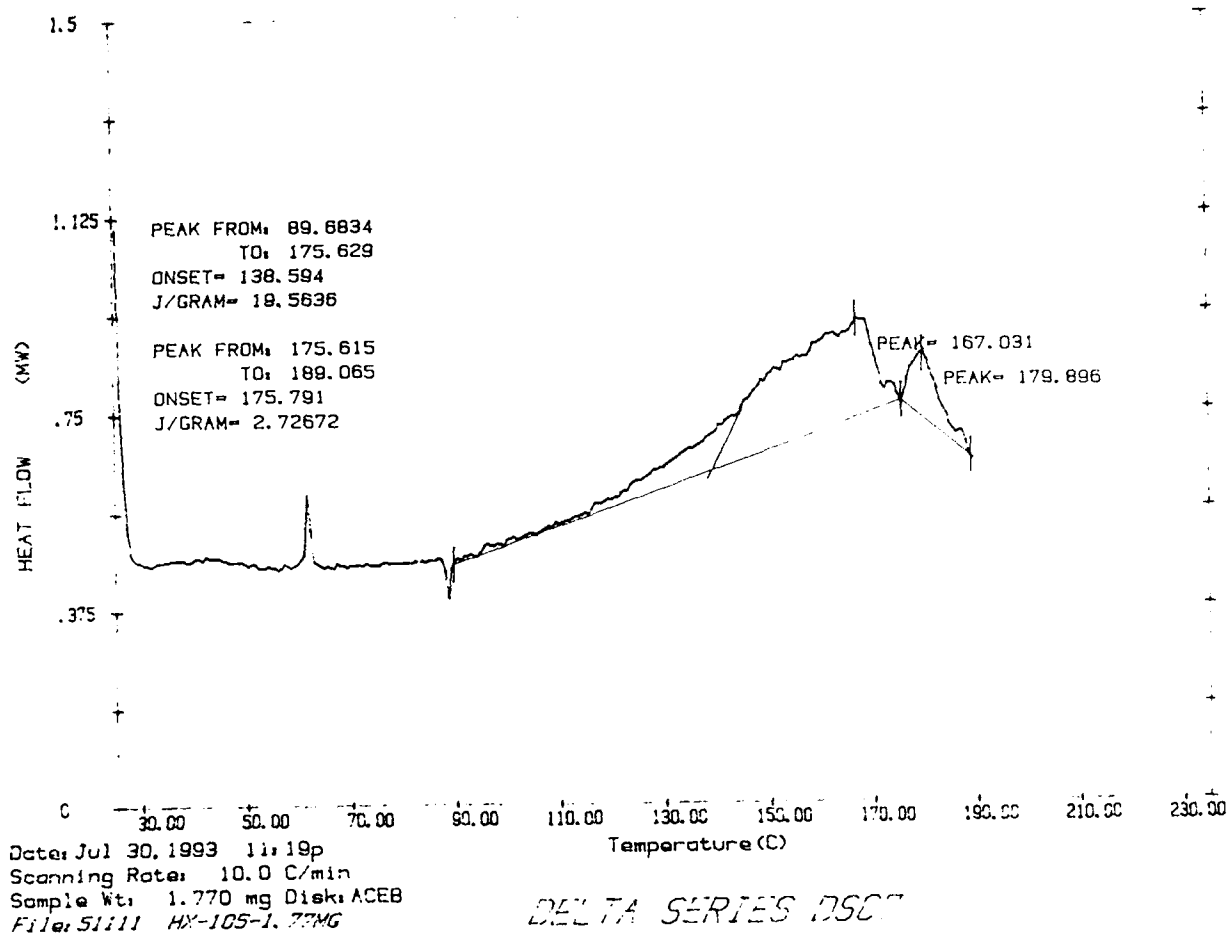


Figure 3: DSC Scan of 4-cyano-4'-phosphonic acid biphenyl - Heating

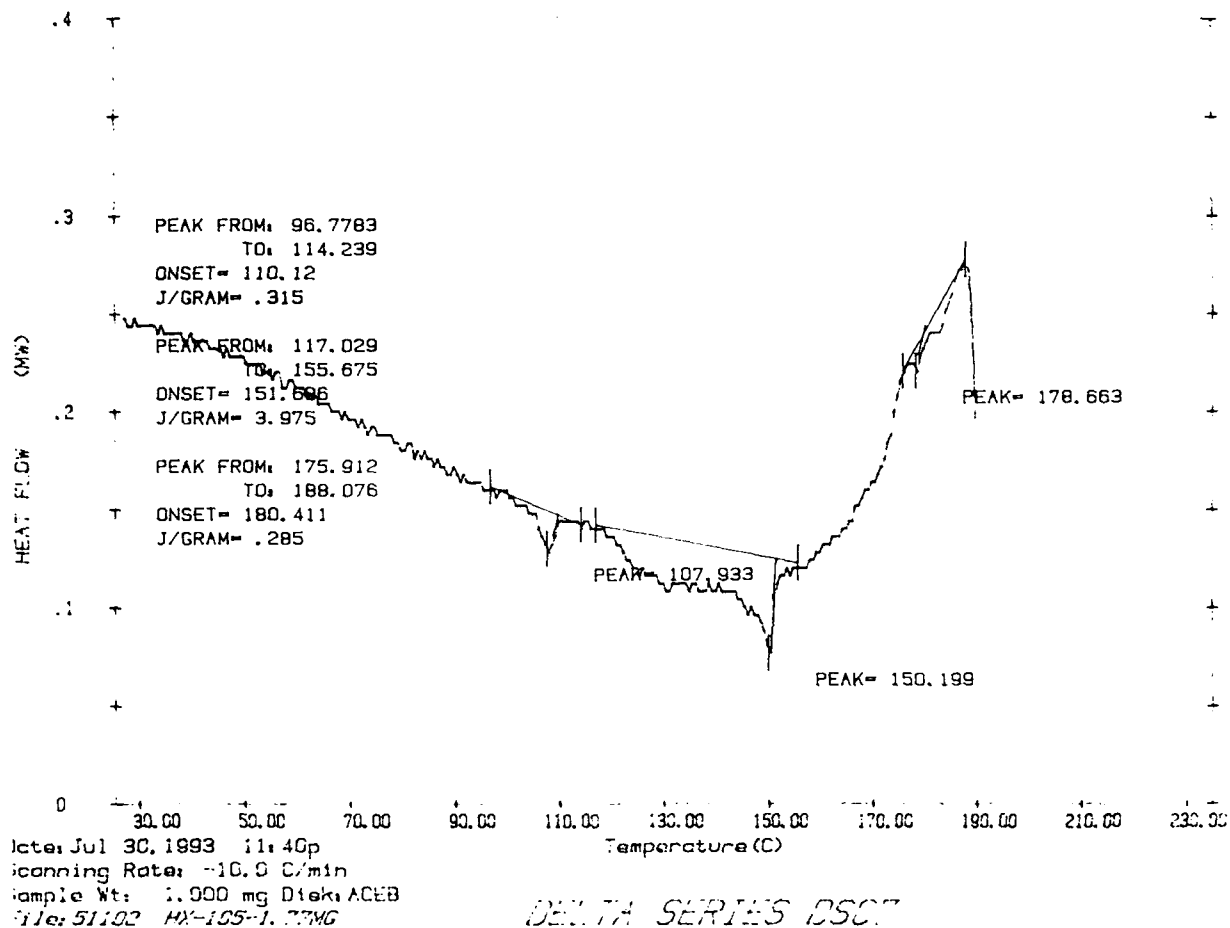


Figure 4: DSC Scan of 4-cyano-4'-phosphonic acid biphenyl - Cooling

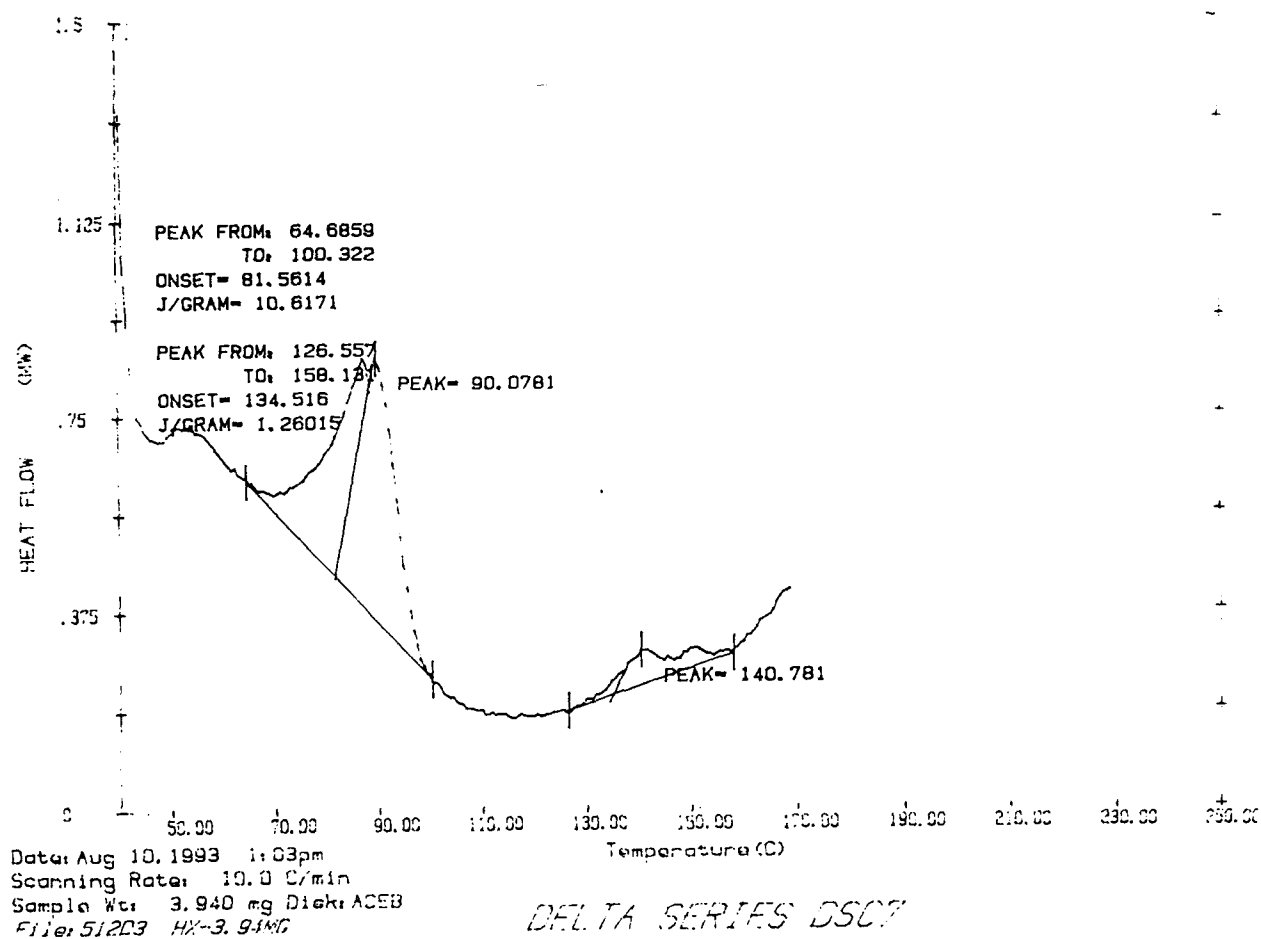


Figure 5: DSC Scan of 4-cyano-4'-phosphonic acid biphenyl, zinc salt - Heating

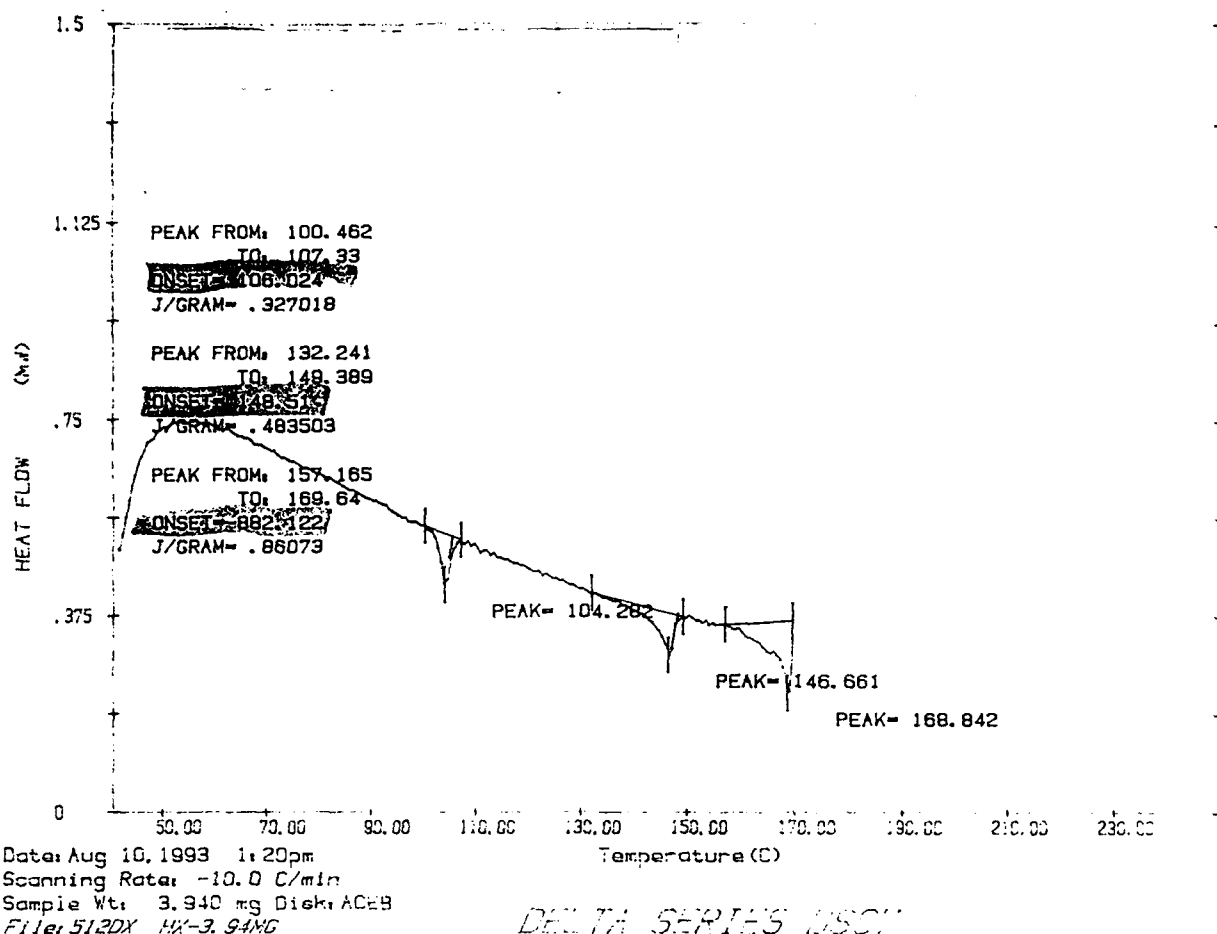


Figure 6: DSC Scan of 4-cyano-4'-phosphonic acid biphenyl, zinc salt - Cooling

The corresponding heating curves also indicate liquid crystalline activity, and as expected, the peaks are shifted significantly from those of the cooling curves.

The associated energies of phase transition were between about 0.3 Joules/gram and 20 Joules/gram. These values are typical for liquid crystalline transitions.

3.3 Nonlinear Optical Measurements & Results

SHG is a special case of frequency mixing which occurs when light waves of frequency ω passing through an array of molecules interact with them in such a way as to produce coherent light waves at 2ω . Nonlinear optical (NLO) effects occur at the molecular level in the dopants due to a deviation from a harmonic electronic potential energy. Typical dopants have a conjugated π -electron system with an electron donor and electron acceptor on either end, creating a large molecular

hyperpolarizability, β , along the transition dipole axis. Second-order NLO properties, including SHG, are described by the second-order macroscopic susceptibility, $\chi^{(2)}$, tensor in the relationship for the bulk material polarization, P :

$$P = \chi^{(1)} \cdot E(\omega) + \chi^{(2)} : E(\omega)E(\omega) + \chi^{(3)} : E(\omega)E(\omega)E(\omega) + \dots \quad (1)$$

where $E(\omega)$ is the optical field incident on the sample, and the susceptibility tensors $\chi^{(n)}$ measure the macroscopic compliance of the electrons. Since the second-order polarization is proportional to the square of the optical field, SHG is zero in a centrosymmetric system. Thus, to induce SHG, NLO dopants must be oriented noncentrosymmetrically in the polymer matrix; this is typically achieved by electric field poling.

Under normal poling conditions $\mu E_z^* f_z^*$ is small compared to kT , where μ is the dipole moment of the dopant, E_z^* is the applied dc-poling-field, f_z^* is a local field factor, k is Boltzmann's constant and T is absolute temperature)

$$\chi^{(2)} \sim N E_z^0 [\mu \beta / 5kT + \gamma] \quad (2)$$

where N is the number density of chromophores, β is the molecular second-order nonlinear hyperpolarizability and γ is one-fifth of the molecular third-order nonlinear hyperpolarizability. The first term in brackets in equation (2) is due to orientation of the NLO chromophores while the second term, γ , is due to electric-field-induced third-order effects which appear instantaneously ($<10^{-12}$ sec) upon application of the dc-field, and disappear instantaneously upon its removal. The relative contribution of γ to the overall values of $\chi^{(2)}$ depends on the chromophore used, not on the polymer in which it is doped.

During SHG experiments, the SHG intensity, $I(2\omega)$, is measured. It is proportional to the square of $\chi^{(2)}$. Thus, in order to increase the steady-state SHG signal, several strategies may be employed. The number (or molar) concentration of the dopants in the polymer may be increased, the dc-field may be increased, the temperature may be decreased or the quantity $\mu\beta$ may be increased by use of a different dopant.

As measured relative to our quartz reference, the variously prepared biphenyl phosphonates, including the diethyl ester and the free acid, showed no SHG intensity, either with the electrical field applied or immediately after its removal, beyond the background noise of the photomultiplier. For the conditions tested (3 wt.% dopant, etc), the value of $\chi^{(2)}$ achievable in these samples is approximately a factor of 200 or more times smaller than that achievable with Disperse Red 1 (also at 3 wt.%).

3.4 Experimental Procedures

All chemicals were purchased from the Aldrich Chemical Co., Milwaukee, WI.

Synthesis of 4-bromo-4'cyanobiphenyl

4,4'-dibromobiphenyl (3.5g, 10.2mmole) and copper (I) cyanide (0.98g, 10.2mmole) were dissolved in 120mL of dimethylformamide (DMF), and refluxed for 24 hours. A stock solution of 200g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 50mL HCl(concentrated), and 300mL H_2O was prepared. The latter solution was added to the cooled DMF reaction solution, and the total was heated to 65°C for twenty minutes. This solution was then extracted with successive 200mL aliquots of toluene. The combined toluene extracts were washed successively with 300mL 10% HCl, 150mL water, 300mL 5% NaOH, 300mL water (twice), and then dried over MgSO_4 . The toluene was removed *in vacuo* leaving a yellow solid. The melting point of the crude solid was determined to be 150-152°C. FTIR analysis showed a definitive absorption, due to the -CN moiety, at 2227 cm^{-1} . The IR of this product is shown in Figure 7. Purification of the crude product was performed by recrystallization from dichloromethane or chloroform, or column chromatography.

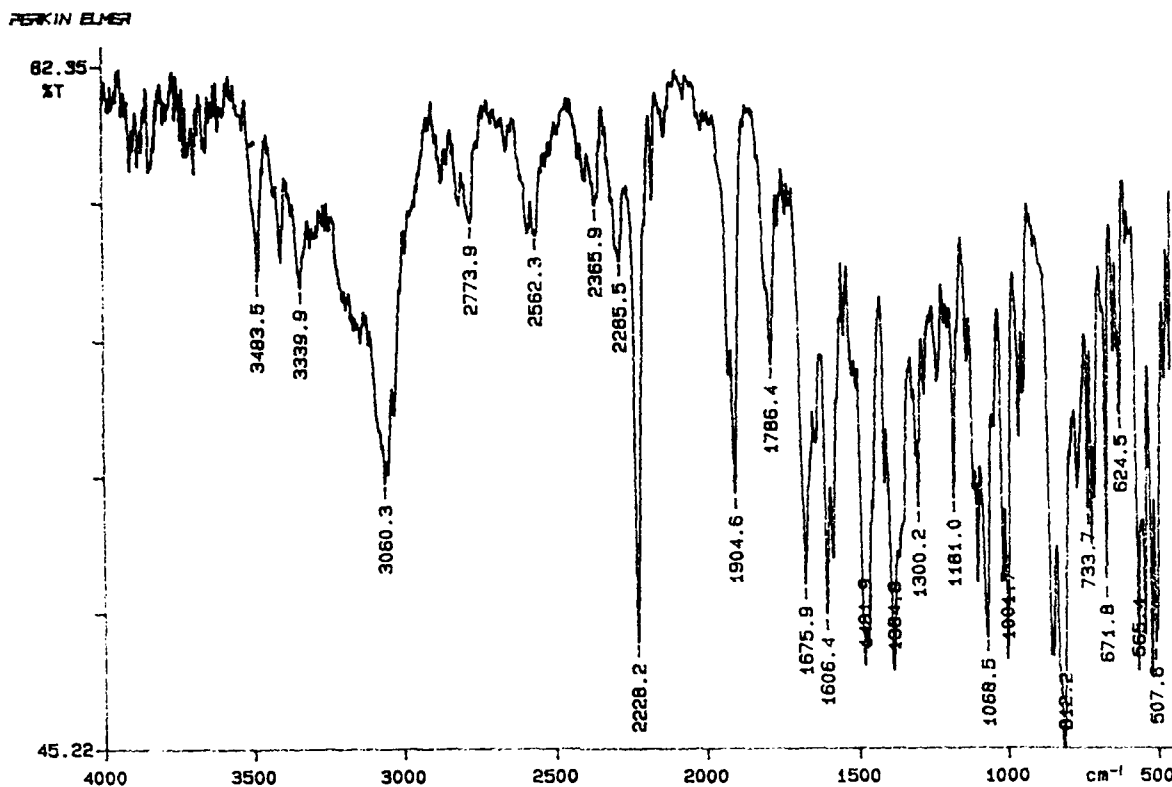


Figure 7: FTIR of 4-bromo-4'cyano biphenyl

Synthesis of 4-cyano-4'-diethylphosphonatobiphenyl

Nickel chloride was dried for 24hrs at 150°C. 4-bromo-4'-cyanobiphenyl (2g, 7.75mmole) and NiCl_2 (0.05g, 0.2mmole), were placed in a three neck round bottom flask and purged with N_2 . The mixture was then heated, under N_2 , to a bath temperature of 170°C, at which point the biphenyl compound was liquified. Triethyl phosphite (1.33g, 8.0mmole) was then added dropwise very slowly with stirring. The reaction was observed to have an incubation period of ≈ 30 seconds, and the reaction was quite exothermic.

After the phosphite addition was completed, the mixture was kept at the same temperature for thirty minutes. The crude product was purified by recrystallization from chloroform. Definitive IR (see Figure 8) absorptions were: 2227 cm^{-1} (-CN), 1248 cm^{-1} (-P=O), 966-1024 cm^{-1} (-P-O-).

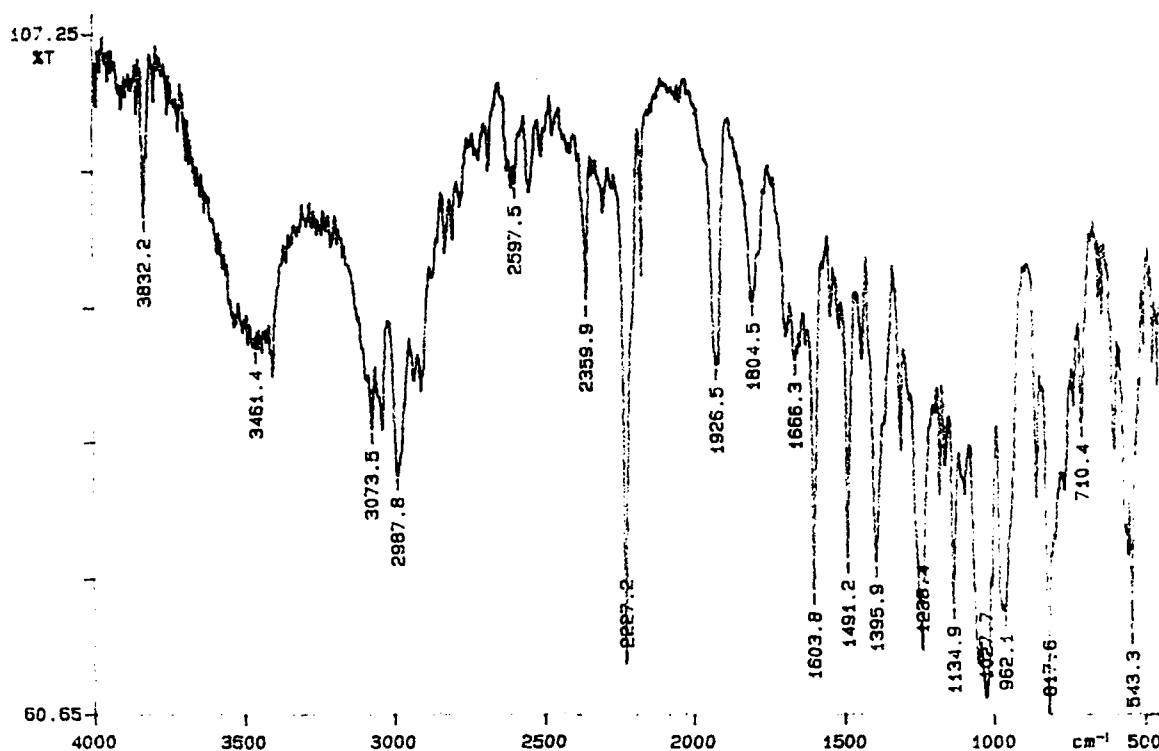


Figure 8: FTIR of 4-cyano-4'-diethylphosphonatobiphenyl

Synthesis of 4-cyano-4'-phosphonic acid biphenyl & the Metal Ion Salts

The reaction procedure was carried out under an inert atmosphere. 4-cyano-4'-diethylphosphonatobiphenyl (0.5g, 1.59mmole) was dissolved into 20mL CCl₄ (pre-distilled from P₂O₅). Iodotrimethylsilane (1.28g, 6.34mmole) was slowly added to the CCl₄ solution, with stirring. After 30 minutes, the reaction mixture was heated to drive off the volatiles. 4 mL of H₂O was then added resulting in a change from an orange to a yellow color. The solution was stirred for an hour, and the liquids removed *in vacuo*. The yellow residue was recrystallized from dichloromethane/heptane. The IR spectrum, Figure 9, gave the expected somewhat broad absorption at $\approx 2900\text{--}3050\text{cm}^{-1}$ typical of phosphonic acids, as well as the CN absorption at 2227cm^{-1} .

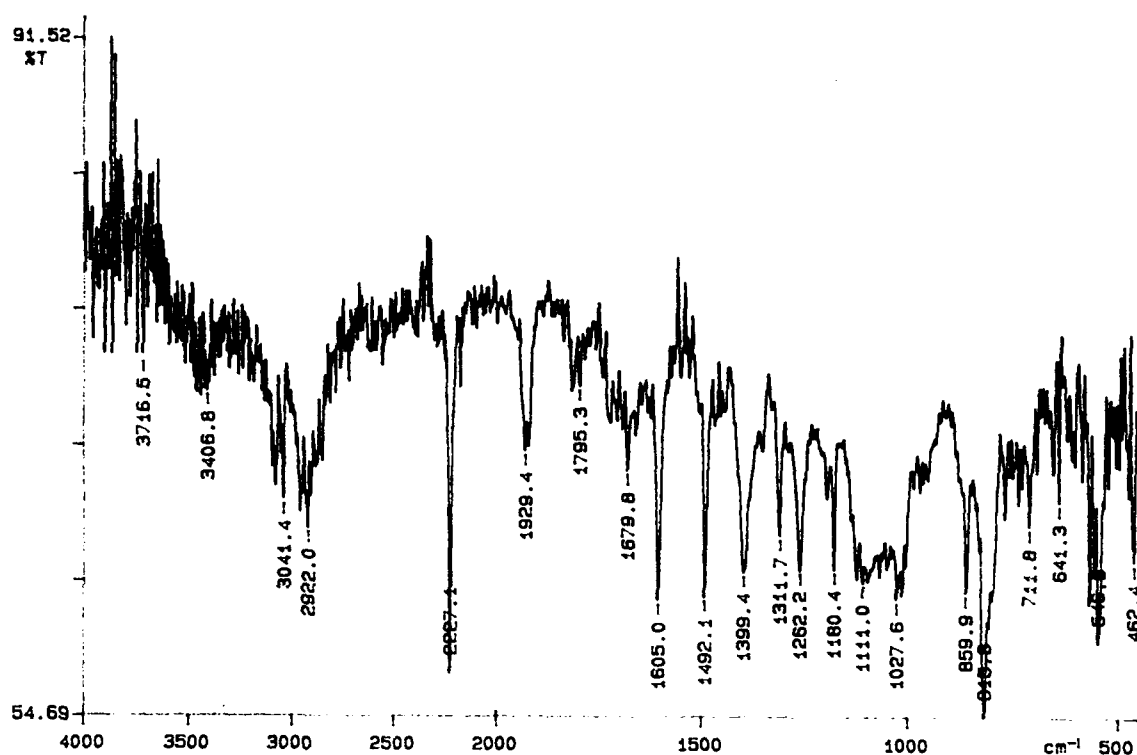


Figure 9: FTIR of 4-cyano-4'-phosphonic acid biphenyl

Mg²⁺, Zn²⁺ and Fe³⁺ phosphonic acid salts were prepared as described immediately above, with one exception. The water added to the CCl₄ solution contained a ten-fold molar excess of the appropriate metal ion salt, either the chloride or sulfate salt. This addition resulted in the precipitation of the phosphonic acid salt as a yellow or off-white solid. FTIR analysis of the products were similar to that of the simple acid.

3.5 Analytical & Testing

Infrared Analyses

The progress of the various reactions described, as well as all liquid product characterizations, were performed using conventional infrared analysis between polished KBr plates or liquid cells. Solid samples were characterized by Diffuse Reflectance using Fourier Transform Spectroscopy (DRIFTS), with a Perkin Elmer

Model 1600 FTIR equipped with MIR, Diffuse Reflectance and Fixed Angle Specular attachments. DRIFTS is an excellent technique for samples which are in a powder form. The technique involves dispersing the sample as a 3-5% mixture in spectroscopic grade KBr. When radiation impinges on the sample, the scattered radiation contains absorption information characteristic of the sample. This technique has the advantage of rapid sample preparation and high sensitivity. For purposes of this Phase I research approximately 256 scans were taken on each sample and averaged to insure that a high signal to noise ratio was obtained, resulting in smooth, well resolved spectra.

Latent Heats

Differential Scanning Calorimetry (DSC) analyses were carried out using a Perkin-Elmer model Delta Series DSC7 at a scanning rate of 10 or 20°C/min. All heating and cooling curves were normalized to a sample weight of 1mg. DSC data analysis was accomplished on a Perkin-Elmer model 3700 Data Station equipped with a Perkin-Elmer TAC 7/3 Instrument Controller and a Perkin-Elmer Graphics Plotter 2.

Corona Poling & Nonlinear Optical Measurements

PMMA (Scientific Polymer Products) was used as received. Disperse Red 1 (Aldrich) was recrystallized using toluene. (Structure of Disperse Red 1 is given in Figure 10.) Other dopants provided to us were used as received. Polymer + 3 wt.% dopant was dissolved in spectroscopic grade chloroform and spin coated onto a quartz substrate which was patterned with planar chrome electrodes using standard photolithographic techniques. The gap between the two electrodes was 800 μm . The films were dried below the glass transition temperature, T_g , of the polymer ($\sim 100^\circ\text{C}$) for 24 hrs and above T_g for 12 hrs under vacuum. The final film thickness was 0.85 μm . Films were poled using either 1200 or 2400 volts across the 800 μm gap resulting in an electric field of 15 or 30 kV/cm. Steady-state SHG intensities were obtained by poling the samples above T_g (where steady-state conditions are reached in a matter of seconds) and then cooling to 35°C. Measurements are reported at 35°C.

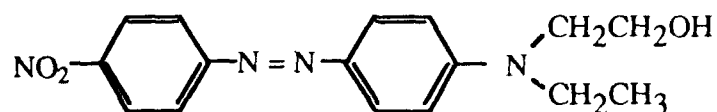


Figure 10: Structure of Red Disperse 1

Figure 11 shows a schematic of the SHG measurement apparatus. The laser light is generated by a q-switched Nd:YAG laser at 1.064 μm . The beam is p-polarized and split so that a y-cut quartz reference, used for monitoring laser power, and the sample are measured simultaneously. A photomultiplier and integrator collect and analyze the emergent SHG light (at 532nm), and the optical signal is ratioed against the quartz reference in order to eliminate any issue concerning fluctuations in laser power.

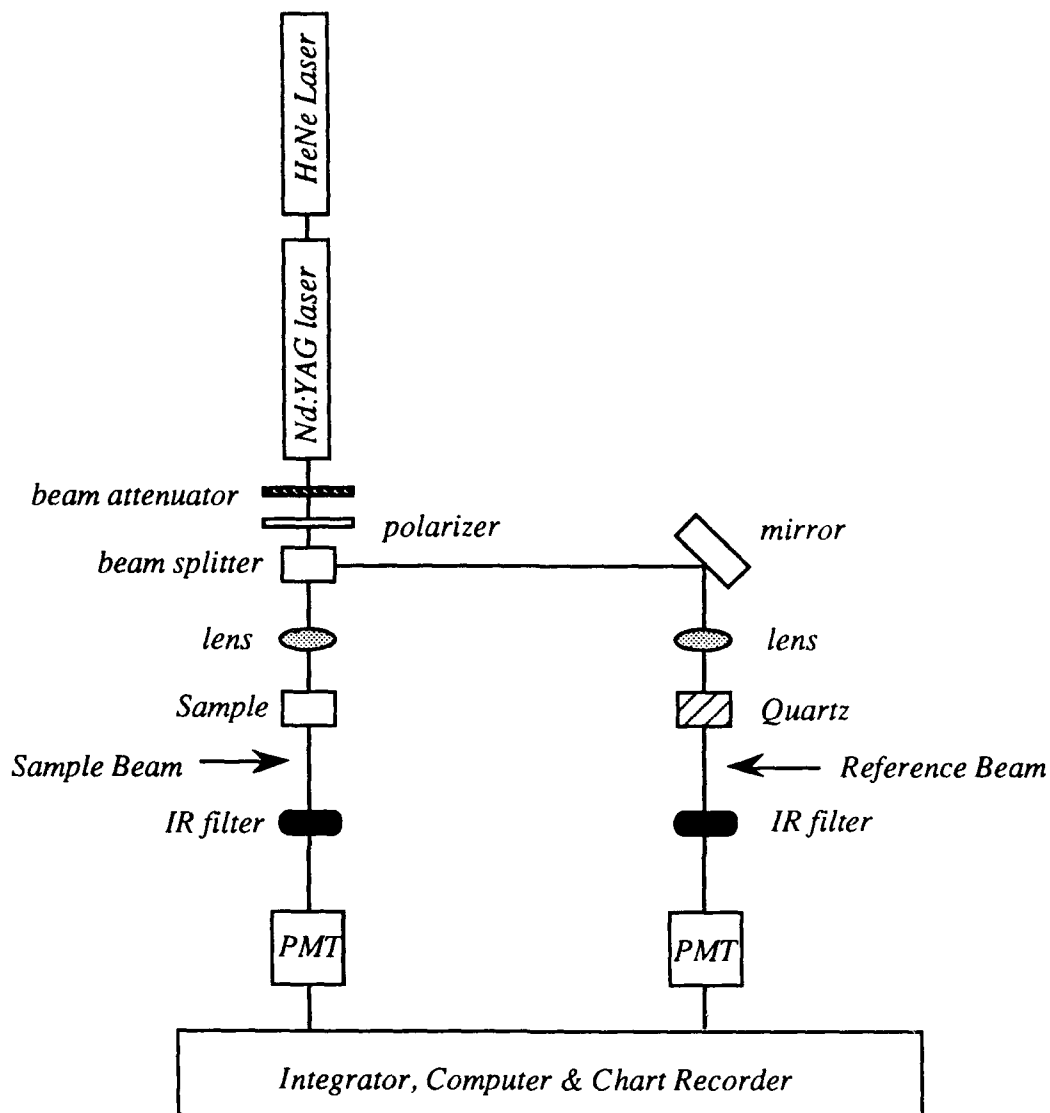


Figure 11: Laser System used to Make the SHG Measurements

4.0 RESEARCH RESULTS & ASSESSMENTS

The Phase I research has resulted in the synthesis and identification of a previously unknown set of aromatic phosphonic acid compounds, which possessed interesting thermal properties. More specifically, the research yielded the following results:

- * A previously unknown set of phosphono-substituted biphenyl compounds was synthesized, and characterized.

* It was established that this new set of compounds possessed liquid crystalline properties.

* Corona poling of the new compounds in polymer films was carried out to align the liquid crystalline materials, in order to improve their non-linear optical properties.

* The synthesized phosphonates did not possess non-linear optical properties.

5.0 CONCLUSIONS & RECOMMENDATIONS

The Phase I research resulted in the synthesis and characterization of a previously unknown, and interesting set of aromatic phosphonic acid compounds that possess liquid crystalline properties. There are very liquid crystals that have been reported that are liquid crystalline in nature. However, the non-linear optical properties of these compounds were determined to be unremarkable. Very probably, this is due to a relatively small dipole between the phosphonate moiety and the cyano group. Based upon these results a Phase II program is not warranted, and therefore is not recommended. Nevertheless, interesting ideas and research work suggest themselves. Some of these ideas will undoubtedly be pursued in the future.

6.0 POTENTIAL APPLICATIONS

There is a great potential, both commercially and within the Federal Government, for high performance nonlinear optical materials. Potential applications include, but are not limited to, switches, modulators, guided wave devices, oscillators and harmonic generators. However, recent years have witnessed a plateau in the improvement of these materials.

7.0 REFERENCES

1. Heeger, A.J.; Orenstein, J.; Ulrich, D.R.; *Nonlinear Optical Properties of Polymers*, Materials Research Society; Pittsburgh, PA, Symposium Series # 109 1988.
2. Chiang, L.Y.; Chaikin, P.M.; Cowan, D.O.; *Advanced Organic Solid State Materials*, Materials Research Society; Pittsburgh, PA, Symposium Series # 173 1990.

3. Williams, D.J.; *Angewante Chemie Int. Ed.*; 23 690 1984.
4. Chen, M. et al.; *Macromolecules*; 24 5421 1991.
5. Yu, L.; Dalton, L.R.; *J. Amer. Chem. Soc.* 111 8699 1989.
6. Koide, N.; et al.; *Mol. Cryst. Liq. Cryst.*; 198 323 1991.
7. Kanis, D.R.; Ratner, M.A.; Marks, T.J.; *J. Amer. Chem. Soc.* 112 8203 1990.
8. Green, M.L.H.; Qin, J.; O'Hare, D.; Bunting, H.E.; *Pure & Applied Chem.* 61 817 1989.